

ELECTRONIC SUPPLEMENTARY INFORMATION

**Spatial variation in the atmospheric deposition of perfluoroalkyl acids: source elucidation through analysis of homologue and isomer patterns**

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### *Chemicals and standards*

Water was purified with a Milli-Q water purification system (Millipore). Methanol (MeOH, LiChrosolv grade), ammonium acetate (ProAnalysis) and formic acid (98% ACS, Reag. Ph Eur) was supplied by Merck. Ammonium formate (>99%, for HPLC) was purchased from Fluka. A 25% ammonium hydroxide (NH<sub>4</sub>OH) solution was purchased from Sigma-Aldrich. Characterized isomeric mixtures of PFOA and PFOS (TPFOA and TPFOS), native standards of linear substances and isotopically labeled internal standards were purchased from Wellington Laboratories dissolved in methanol. The isotope-labelled standards were certified to contain <0.5% of their native analogues.

### *Sample extraction and clean up*

The samples were then cleaned up on Oasis Weak-anion exchange (WAX) SPE cartridges (6 cm<sup>3</sup>, 150 mg, 30 μm) using a previously published method<sup>1</sup>. The cartridges were preconditioned with 4.5 mL 0.3% NH<sub>4</sub>OH in MeOH and activated with 4.5 mL 0.1 M formic acid in Milli-Q water. After sample loading, the cartridges were washed with 5 mL 20% MeOH in 0.1 M formic acid followed by 2 mL 0.3% NH<sub>4</sub>OH in Milli-Q water, before eluting the samples with 3 mL 0.3% NH<sub>4</sub>OH in MeOH.

### *Instrumental analysis and quantification*

Extracts were injected onto an Ascentis Express F5 PFP Column (2.7 μm, 10 cm × 2.1 mm, Sigma–Aldrich) equipped with an Ascentis Express F5 PFP guard column (2.7 μm, 5.0 mm × 2.1 mm), both maintained at 30 °C. An Accucore C18 (2.6 μm, 50 mm × 2.1 mm, Thermo Scientific) was placed upstream of the injector to separate PFAS originating from the LC pump from those injected onto the analytical column. The mobile phases consisted of A) 20 mM ammonium formate and 20 mM formic acid in Milli-Q water and B) 100% MeOH. The flow was set to 0.3 mL/min. Solvent blank injections were performed to monitor sample carry over. Instrumental drift was monitored by injecting a calibration standard after every 10 injections. The mass spectrometer was operated in negative electrospray ionization mode, using settings described below.

All analytes had authentic stable isotope labeled internal standard (IS) except perfluorobutane sulfonic acid (PFBS), perfluorodecane sulfonic acid (PFDS), perfluorotridecanoic acid (PFTriDA) and perfluorotetradecanoic acid (PFTeDA), for which quantification was performed using <sup>18</sup>O<sub>2</sub>-PFHxS, <sup>13</sup>C<sub>4</sub>-PFOS and <sup>13</sup>C<sub>4</sub>-PFDoDA (PFTriDA and PFTeDA) respectively. <sup>13</sup>C<sub>8</sub>-PFOA and <sup>13</sup>C<sub>8</sub>-PFOS were used as volumetric standards in the calculation of total method recovery of the internal standard. A linear relationship ( $R^2 > 0.97$ ) between signal and concentration was observed for all homologues in a seven-point external standard calibration curve (1/X weighted linear regression) with concentrations ranging from 0.02 to 10 pg μL<sup>-1</sup>. In the presence of blank contamination, limits of detection (LODs) and quantification (LOQs) were defined as the arithmetic mean plus the standard deviation of the analyte signal in the procedural blanks multiplied by 3 and 10 respectively. In the absence of blank contamination, a target analyte was considered detected when its peak area exceeded a signal-to-noise ratio (S/N) above 3. Quantification of analytes was only conducted when two criteria were satisfied: 1) the peak signal exceeded a S/N of 10 and 2) its concentration was within the linear range of the calibration curve.

For individual PFOA and PFOS isomers we use the nomenclature suggested by Benskin et al.<sup>2</sup>: linear perfluorooctanoic acid (n-PFOA), perfluoro-4-methylheptanoic acid (4-PFOA), perfluoro-5-methylheptanoic acid (5-PFOA), perfluoro-6-methylheptanoic acid (6-PFOA), linear perfluorooctane sulfonic acid (n-PFOS), perfluoro-1-methylheptane sulfonic acid (1-PFOS), perfluoro-2-methylheptane sulfonic acid (2-PFOS), perfluoro-3-methylheptane sulfonic acid (3-PFOS), perfluoro-4-methylheptane sulfonic acid (4-PFOS), perfluoro-5-methylheptane sulfonic acid (5-PFOS), perfluoro-6-methylheptane sulfonic acid (6-PFOS). Perfluoro-3-methylheptanoic acid (3-PFOA) is not reported in this study, as this substance could only be detected in injections of TPFOA above 2200 pg on column. As the sensitivity for this substance was low and its contribution to ECF PFOA is only 3%,

it was not observed in any sample. Furthermore, dimethyl-isomers of PFOA and PFOS were not included in the study as these contributed with <0.2 % to ECF PFOA and PFOS.

#### *Mass spectrometer settings*

Spray voltage: 3500 V  
Sheath Gas: 45  
Aux Gas: 2  
Sweep Gas: 0.5  
Ion Transfer Tube Temp: 350 °C  
Vaporizer Temp: 450 °C  
Cycle Time: 0.05 seconds  
Q1 Resolution (FWHM): 0.7  
Q3 Resolution (FWHM): 0.7  
Collision gas: 2 mTorr  
Chrome Filter: 3 seconds

#### *Ion analysis*

Concentrations of major ions were determined by chemically suppressed ion chromatography (IC; Dionex ICS-2000) using CG16/CS16 (cations) and AG11/AS11 columns (anions). A Dionex ATC-1 column was used before the injection valve to trap carbonates and other ionic contaminants. The injection volume was 25  $\mu$ L. The analytical detection limits, defined as a S/N of 2, were 0.01, 0.02, 0.01, 0.01, 0.03, 0.01, 0.01, and 0.03  $\mu$ Eq/L for  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , respectively. Analysis of both internal and external reference samples<sup>3</sup> showed that systematic errors were less than 2%.

#### *Quality assurance*

We performed a spike-recovery test on a pooled Stockholm rainwater sample divided into nine 0.9 L samples. Three of these were spiked to 9 ng/L with a mix of native linear PFAAs (PFAC-MXB from Wellington Laboratories), while another three of the rain samples were spiked 8 ng/L with technical standards of PFOS and PFOA (TPFOS and TPFOA from Wellington Laboratories). The samples were filtered, extracted and analyzed in the same manner as the other precipitation samples in the study. Poor mean accuracy was observed for PFTriDA, PFTeDA and PFDS (28, 7 and 39% respectively). The mean accuracy was 88-112% and the relative standard deviation (RSD) was  $\leq 6\%$  for all other linear analytes included in the study (Table S4). In the samples spiked with technical mixes of PFOS and PFOA the contribution of the sum of branched isomers ( $\Sigma_{\text{br}}\text{PFOS}$  and  $\Sigma_{\text{br}}\text{PFOA}$ ) and ratios of individual branched isomers to the linear isomer (6-, 5-, and 4-PFOA to n-PFOA and 6-, 5-, 3+4- and 1-PFOS to n-PFOS) had a mean accuracy of 80-117% and a RSD of <12% (Table S5). The unspiked triplicate samples showed excellent precision ( $\leq 8\%$ ) at low concentrations (77-287 pg/L) for those analytes that were present in the samples at quantifiable levels (C7-C10 PFCAs and PFOS, Table S6).

The deviation between analyte concentrations was generally below 20% in the Chinese duplicate samples (Table S7). However, high deviation was observed for PFNA in one sample (110%, B5) and PFUnDA in another (54%, W4).

Standard addition was performed by spiking 6000 pg of TPFOA to extracts of samples S2, S5, S7 and S9. The average sum of branched PFOA isomers was 20.7% in the spiked samples, i.e. the mean accuracy for  $\Sigma_{\text{br}}\text{PFOA}$  was 99% (Table S8). The RSD was 6%, same as in the 40 injections of TPFOA standard solution made to determine the dynamic range. This showed that, and at this spike level, the analysis of the distribution between branched and linear PFOA isomers was not confounded by sample matrix.

*Calculation of deposition rates*

Deposition rates (ng/m<sup>2</sup> day) were calculated using the following equation

$$D = \frac{C R}{t}$$

where

C is concentration of substance in deposition samples (ng/m<sup>3</sup>)

R is rainfall amount during the sampling period (m)

t is the duration of the sampling period (days)

Table S1. Precipitation samples included in study. Duplicate sampling and sample analysis was performed from samples W1-4 and B1-5. Samples S11 and S12 represent snow collected from box.

Sample ID	Sample site	Start Date	End Date	No of days	Precipitation (mm)
C1	Corvo,	11/01/2016	12/01/2016	1	51
C2	Azores,	12/01/2016	19/01/2016	7	48
C3	Portugal	19/01/2016	02/02/2016	14	23
C4	39° 40' N	02/02/2016	14/03/2016	12	19
C5	31° 6' W	14/03/2016	24/03/2016	10	37
W1	Wuhan,	22/08/2015	22/09/2015	31	45
W2	China	22/09/2015	08/10/2015	16	128
W3	30° 36' N	08/10/2015	12/11/2015	35	78
W4	114° 17' E	12/11/2015	26/11/2015	14	75
B1		13/07/2015	17/07/2015	4	8.5
B2	Beijing,	17/07/2015	22/07/2015	5	63
B3	China	22/07/2015	31/07/2015	9	40
B4	40° 0' N	31/07/2015	10/08/2015	8	41
B5	116° 20' E	17/08/2015	06/09/2015	20	97
R1		02/01/2015	26/01/2015	24	89
R2		26/01/2015	02/03/2015	35	62
R3	Råö,	29/06/2015	27/07/2015	28	70
R4	Sweden	27/07/2015	31/08/2015	35	94
R5	57° 23' N	31/08/2015	28/09/2015	28	103
R6	11° 54' E	02/11/2015	30/11/2015	28	118
R7		30/11/2015	28/12/2015	28	75
S1		04/05/2015	18/05/2015	14	77
S2		16/06/2015	01/07/2015	15	42
S3		07/07/2015	09/07/2015	2	30
S4		09/07/2015	29/07/2015	20	23
S5		18/08/2015	04/09/2015	16	19
S6	Stockholm,	04/09/2015	14/09/2015	10	61
S7	Sweden	14/09/2015	05/10/2015	21	36
S8	59° 21' N	15/10/2015	23/11/2015	39	46
S9	18° 3' E	16/11/2015	11/12/2015	25	43
S10		08/01/2016	02/02/2016	25	24
S11		08/01/2016	11/01/2016	3	6.9
S12		11/01/2016	14/01/2016	3	5.0
S13		02/02/2016	24/03/2016	51	42
S14		24/03/2016	03/05/2016	42	49

Table S2. Target analyte quantifier and qualifier precursor/product ion transitions ions, as well as internal standard transitions (m/z).

Target Analyte	Quant Ion	Qual Ion	IS	IS Ion
PFBS	299/99	299/80	<sup>18</sup> O <sub>2</sub> -PFHxS	403/84
PFHxS	399/80	399/99	<sup>18</sup> O <sub>2</sub> -PFHxS	403/84
PFOS	499/99	499/80	<sup>13</sup> C <sub>4</sub> -PFOS	503/80
1-PFOS	499/419	499/99		
3/4-PFOS	499/130	499/99		
5-PFOS	499/130	499/99		
6-PFOS	499/80	499/99		
PFDS	599/99	599/80	<sup>13</sup> C <sub>4</sub> -PFOS	503/80
PFBA	213/169		<sup>13</sup> C <sub>4</sub> -PFBA	217/172
PFPeA	263/219		<sup>13</sup> C <sub>4</sub> -PFPeA	261/222
PFHxA	313/269	313/119	<sup>13</sup> C <sub>4</sub> -PFHxA	315/270
PFHpA	363/319	363/169	<sup>13</sup> C <sub>4</sub> -PFHpA	363/319
PFOA	413/369	413/169	<sup>13</sup> C <sub>4</sub> -PFOA	417/372
3-PFOA	413/169	413/369		
4-PFOA	413/119	413/369		
5-PFOA	413/219	413/369		
6-PFOA	413/169	413/369		
PFNA	463/419	463/219	<sup>13</sup> C <sub>5</sub> -PFNA	468/423
PFDA	513/469	513/269	<sup>13</sup> C <sub>2</sub> -PFDA	515/470
PFUnDA	563/519	563/269	<sup>13</sup> C <sub>2</sub> -PFUnDA	565/520
PFDoDA	613/569	613/169	<sup>13</sup> C <sub>2</sub> -PFDoDA	615/570
PFTriDA	663/619	663/169	<sup>13</sup> C <sub>2</sub> -PFDoDA	615/570
PFTeDA	713/669	713/169	<sup>13</sup> C <sub>2</sub> -PFDoDA	615/570

Table S3. Recovery of internal standard (%), used to monitor loss and matrix effects in individual samples. The mass of internal standard in each final extract is quantified relative to the volumetric standard (added just before analysis) and compared to the mass of internal standard initially spiked to the sample (400 pg). That is, recovery = 100 \* (mass of internal standard in final extract / mass of internal standard initially spiked to sample). Sample concentrations with corresponding internal standard recovery <20% and >130% are designated in Table S9.

		MPFHxA	MPFHpA	MPFOA	MPFNA	MPFDA	MPFUnDA	MPFHxS	MPFOS
C1-5	Mean	42	78	126	58	36	40	77	48
	RSD	11	8	3	22	49	32	10	49
W1-4, B1-5	Mean	94	65	110	101	90	55	97	92
	RSD	17	13	6	10	17	24	9	19
R1-7	Mean	49	81	117	90	75	29	103	110
	RSD	10	8	10	16	32	57	28	11
S1, S3-8, S10-12	Mean	45	55	82	80	56	16	80	48
	RSD	28	29	29	32	64	96	30	45
S2, S9, S13, S14	Mean	51	87	139	93	59	51	82	82
	RSD	40	21	7	21	51	34	24	53

Table S4. Spike-recovery experiment. Mean accuracy (%) and relative standard deviation (RSD, %) for triplicate Stockholm rain water sample spiked to 8 ng/L with native linear PFAAs.

	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxS	PFOS	PFDS
Accuracy	108	112	99	94	98	98	88	28	7	101	99	39
RSD	1.1	0.9	4.4	3.8	3.2	2.0	5.7	12	29	1.8	5.9	5.6

Table S5. Spike-recovery experiment. Mean accuracy (%) and relative standard deviation (RSD, %) for the concentration of linear homologue, the contribution of the sum of branched isomers ( $\Sigma$ br,%) and ratios of individual branched isomers to the linear isomer (6-, 5-, and 4-PFOA to *n*-PFOA and 6-, 5-, 3+4- and 1-PFOS to *n*-PFOS) in triplicate Stockholm rain water samples spiked to 9 ng/L with technical standards of PFOS and PFOA (TPFOS and TPFOA).

	PFOA					PFOS					
	6/n	5/n	4/n	$\Sigma$ br	linear	6/n	5/n	3+4/n	1/n	$\Sigma$ br	linear
Accuracy	85	92	92	87	103	92	117	80	80	95	111
RSD	6	1	2	3	7	2	3	11	12	1	3

Table S6. Precision of quantification at low sample concentration. Mean concentration (pg/L) and relative standard deviation (RSD, %) in triplicate Stockholm rainwater sample. Only analytes exceeding the MQL in all samples are included.

	PFHpA	PFOA	PFNA	PFDA	PFOS
Concentration	200	287	177	77	111
RSD	5	2	3	3	8

Table S7. Deviation between duplicate samples (%). The deviation was determined by comparison of the difference in analyte concentration between duplicate samples to the mean analyte concentration in duplicate samples. Only analytes exceeding the MQL in both samples are included.

	PFHxA	PFHpA	<i>n</i> -PFOA	totPFOA	PFNA	PFDA	PFUnDA
W1	10	9	5	5	2		
W4	2	6	2	1	0.3		
B1	5	5	3	3	0.3	25	
B2	5	12	4	6	14	3	24
B3	17	9	14	14	3	14	16
B4	4	10	17	19	3		
B5	12	20	8	5	110		

Table S8. Standard addition of samples S2, S5, S7 and S9. Sample extracts were spiked with 6000 pg TPFOA (corresponding to approximately 6 ng/L). The average sum of branched PFOA isomers (%) and average ratios of 6-, 5-, and 4-PFOA and *n*-PFOA is displayed for spiked sample extracts ( $n = 4$ ), as well as injections of TPFOA standard ( $n = 40$ ), along with relative standard deviation (RSD, %).

Sample		brPFOA	6/n	5/n	4/n	5/6	4/6	4/5
Spiked sample	Mean	21	0.06	0.05	0.01	0.8	0.2	0.2
	RSD	6	7	4	6	9	11	3
TPFOA STD	Mean	21	0.07	0.06	0.01	0.8	0.2	0.2
	RSD	6	10	9	7	4	10	11



Table S9. Concentrations (pg/L) of PFAAs in precipitation samples. Values in bold represent concentrations below the quantification limit. PFHxA was not quantified in samples S12 due to interference of matrix. <sup>1</sup>Recovery of internal standard <20% <sup>2</sup>Recovery of internal standard <30% <sup>3</sup>Recovery of internal standard >130% <sup>4</sup>Not within dynamic range.

Sample ID	PFHxA	PFHpA	% brPFOA	n-PFOA	totPFOA	PFNA	PFDA	PFUnDA	PFHxS	% brPFOS	n-PFOS	totPFOS
C1	70	97	<12	238	238	187	75 <sup>2</sup>	<212	25	<b>45</b>	<b>111</b>	201
C2	236	545	8	1350	1460	1147	549	<b>131</b>	80	44	353	628
C3	225	326	8	1593	1728	1483	341 <sup>2</sup>	<b>196</b>	138	47	666	1262
C4	165	415	9	1215	1330	1349	347	237	112	40	677	1126
C5	274	389	10	1011	1129	1092	309	213	91	37	504	795
W1a	1630	960	17	3769	4551	979	<b>165</b>	<212	<b>106</b>		<b>514</b>	
W1b	1798	1050	17	3976	4807	1003	<b>268</b>	<b>296</b>	<b>679</b>		<b>640</b>	
W2	385	443	24	1257	1647	484	<b>126</b>	<b>226</b>	<88		<444	
W3	2397	1465	20	7652	9529	1102	<b>326</b>	498	<88		<444	
W4a	7447	481	19	3344	4128	672	<b>109</b>	<b>343</b>	<88		<444	
W4b	7286	453	20	3273	4111	670	<b>87</b>	<212	<88		<444	
B1a	1508	1392	16	6389	7633	1828	782	<b>448</b>	<88		<444	
B1b	1587	1319	15	6203	7263	1833	1001	<b>637</b>	<88		<444	
B2a	1308	1291	18	5521	6757	1964	560	589	<88		<b>447</b>	
B2b	1371	1457	19	5745	7127	2259	578	747	<88		<444	
B3a	440	349	21	2597	3275	974	518	392	<88		<444	
B3b	520	383	21	2255	2837	949	450	333	<b>135</b>		<444	
B4a	874	831	23	8216	10656	694	<b>270</b>	<b>220</b>	<88		<b>505</b>	
B4b	913	751	25	9695	12978	671	390	<b>232</b>	<b>88</b>		<b>624</b>	
B5a	765	889	24	6439	8450	1130	<b>220</b>	<b>151</b>	<88		<444	
B5b	861	1088	23	6941	8991	3868	397	418	<88		<444	
R1	168	246	<b>12</b>	1137	1297	473	97	<28 <sup>1</sup>	237 <sup>3</sup>	42	1152	1986
R2	201	302	<b>12</b>	716	814	371	98	<b>56</b> <sup>1</sup>	132 <sup>3</sup>	40	611	1018
R3	331	461	<11	699	699	839	171	173 <sup>1</sup>	53	37	494	783
R4	194	269	<14	436	436	389	92	<b>40</b>	<b>28</b>	35	284	438
R5	125	295	<9	303	303	392	65	<b>62</b> <sup>1</sup>	<b>30</b>	38	311	501
R6	51	156	<b>13</b>	730	843	360	65	<b>30</b>	155	36	1040	1625
R7	87	152	13	925 <sup>3</sup>	1059	397	64	<b>31</b>	203	37	1120	1778
S1	183	344	<b>12</b>	242	274	342	90	<b>87</b> <sup>1</sup>	<12	<b>42</b> <sup>4</sup>	<b>75</b>	129
S2	266	583	<8	425 <sup>3</sup>	425	460	181 <sup>2</sup>	<b>28</b>	<12		299	
S3	264	377	<8	347	347	707	140	<b>161</b> <sup>1</sup>	<12	<b>31</b> <sup>4</sup>	137	198
S4	201	373	<4	368	368	628	<b>30</b>	127 <sup>1</sup>	<12	<b>38</b> <sup>4</sup>	<b>98</b>	158
S5	398 <sup>1</sup>	579 <sup>2</sup>	<14	475 <sup>2</sup>	475	627 <sup>2</sup>	194	163 <sup>1</sup>	<b>69</b>	38 <sup>4</sup>	<b>47</b>	76
S6	189	210	<3	168	168	223	90	<b>91</b> <sup>1</sup>	<12	41 <sup>4</sup>	117	198
S7	251	369	<8	377	377	591	156	136 <sup>2</sup>	<b>75</b>	36 <sup>4</sup>	<b>76</b>	120
S8	139	224	<b>12</b>	248	280	495	75 <sup>2</sup>	70 <sup>1</sup>	<12		<b>96</b> <sup>2</sup>	
S9	135	147	<12	324	324	642	75	<28	<b>17</b>		<b>56</b>	
S10	396	373	8	1263	1377	1478	244	198 <sup>1</sup>	<b>65</b>	<b>35</b>	391	601
S11	245	135	<11	588	588	233	149 <sup>3</sup>	79 <sup>1</sup>	<b>39</b>	<b>34</b>	331	502
S12	NA	59	<9	222	222	102	<b>45</b>	<b>25</b> <sup>2</sup>	<b>19</b>	<b>32</b> <sup>4</sup>	<b>104</b>	153
S13	471	705	9	831	916	868	169	104	<b>30</b>	41 <sup>4</sup>	134	229
S14	246	556	<8	428 <sup>3</sup>	428	411	175	<b>105</b>	<12	<b>35</b> <sup>4</sup>	<b>105</b>	161

Table S10. Deposition rates (ng/m<sup>2</sup> day) of PFAAs in precipitation samples. Data for PFOA and PFOS represent the sum of branched and linear isomers. PFHxA was not quantified in samples S12 due to interference of matrix.

Sample ID	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFHxS	PFOS	ΣPFAAs
C1	3.5	4.9	12	9.4	3.8	<11	1.3	10.1	45
C2	1.6	3.7	9.9	7.8	3.7	0.89	0.54	4.3	32
C3	0.37	0.53	2.8	2.4	0.56	0.32	0.23	2.1	9.3
C4	0.27	0.67	2.1	2.2	0.56	0.38	0.18	1.8	8.2
C5	1.0	1.5	4.2	4.1	1.2	0.80	0.34	3.0	16
W1a	2.3	1.4	6.5	1.4	0.24	<0.30	0.15	<0.74	12
W1b	2.6	1.5	6.9	1.4	0.4	0.42	0.97	<0.92	14
W2	3.1	3.5	13	3.9	1.0	1.8	<0.71	<3.6	27
W3	5.4	3.3	21	2.5	0.73	1.1	<0.2	<1.0	34
W4a	40	2.6	22	3.6	0.58	1.8	<0.47	<2.4	70
W4b	39	2.4	22	3.6	0.47	<1.1	<0.47	<2.4	67
B1a	3.2	3.0	16	3.9	1.7	0.95	<0.19	<0.94	29
B1b	3.4	2.8	15	3.9	2.1	1.4	<0.19	<0.94	29
B2a	16	16	85	25	7.0	7.4	<1.1	5.6	162
B2b	17	18	89	28	7.2	9.4	<1.1	<5.6	170
B3a	2.0	1.6	15	4.3	2.3	1.7	<0.39	<2.0	26
B3b	2.3	1.7	13	4.2	2.0	1.5	0.60	<2.0	25
B4a	4.5	4.3	55	3.6	1.4	1.1	<0.45	2.6	72
B4b	4.7	3.9	67	3.4	2.0	1.2	0.45	3.2	86
B5a	3.7	4.3	41	5.5	1.1	0.73	<0.43	<2.2	56
B5b	4.2	5.3	44	19	1.9	2.0	<0.43	<2.2	76
R1	0.63	0.91	4.8	1.8	0.36	<0.79	0.88	7.4	17
R2	0.35	0.53	1.4	0.65	0.17	0.10	0.23	1.8	5.3
R3	0.83	1.15	1.8	2.1	0.43	0.43	0.13	2.0	8.8
R4	0.52	0.72	1.2	1.0	0.25	0.11	0.08	1.2	5.1
R5	0.46	1.08	1.1	1.4	0.24	0.23	0.11	1.8	6.5
R6	0.22	0.66	3.6	1.5	0.28	0.13	0.65	6.9	14
R7	0.23	0.41	2.8	1.1	0.17	0.08	0.54	4.8	10
S1	1.0	1.9	1.5	1.9	0.49	0.48	<0.07	0.70	7.9
S2	0.75	1.6	1.2	1.3	0.51	0.08	<0.03	0.84	6.3
S3	4.0	5.7	5.2	11	2.1	2.4	<0.18	3.0	33
S4	0.23	0.42	0.42	0.71	0.03	0.14	<0.01	0.18	2.1
S5	0.47	0.68	0.56	0.74	0.23	0.19	0.08	0.09	3.0
S6	1.2	1.3	1.0	1.4	0.55	0.56	<0.07	1.21	7.1
S7	0.43	0.63	0.64	1.0	0.27	0.23	0.13	0.21	3.5
S8	0.16	0.26	0.33	0.59	0.09	0.08	<0.01	0.19	1.7
S9	0.23	0.25	0.55	1.1	0.13	0.36	0.03	0.10	2.7
S10	0.37	0.35	1.3	1.4	0.23	0.19	0.06	0.57	4.4
S11	0.56	0.31	1.4	0.53	0.34	0.18	0.09	1.2	4.5
S12	NA	0.10	0.37	0.17	0.08	0.04	0.03	0.25	1.0
S13	0.39	0.58	0.69	0.72	0.14	0.09	0.02	0.19	2.8
S14	0.29	0.65	0.50	0.48	0.21	0.12	<0.01	0.19	2.4

Table S11. Pattern of individual branched PFOA isomers. Ratios of 5- and 4-PFOA to 6-PFOA and ratio of 4-PFOA to 5-PFOA in each sample. Ratios are based on peak areas in isomer-specific mass transitions. Numbers in bold correspond to values calculated using peak areas of signal-to-noise < 10.

Sample	5/6	4/6	4/5
C2	<b>0.87</b>	<b>0.22</b>	<b>0.25</b>
C3	0.90	0.26	0.29
C4	0.84	<b>0.20</b>	<b>0.24</b>
C5	0.99	0.24	0.25
W1a	1.07	0.26	0.24
W1b	0.99	0.25	0.25
W2	1.08	0.31	0.29
W3	0.84	0.28	0.34
W4a	0.92	0.30	0.32
W4b	0.88	0.24	0.28
B1a	0.68	0.21	0.30
B1b	0.71	0.21	0.29
B2a	0.76	0.23	0.30
B2b	0.73	0.20	0.27
B3a	0.83	0.22	0.26
B3b	0.77	0.22	0.28
B4a	0.74	0.22	0.30
B4b	0.76	0.21	0.28
B5a	0.69	0.19	0.27
B5b	0.67	0.18	0.26
R1	0.80	<b>0.20</b>	<b>0.25</b>
R2	<b>0.91</b>	<b>0.21</b>	<b>0.23</b>
R6	1.01	<b>0.24</b>	<b>0.24</b>
R7	0.85	<b>0.17</b>	<b>0.19</b>
S1	<b>0.69</b>		
S8	<b>0.78</b>		
S10	0.94	<b>0.22</b>	<b>0.24</b>
S13	0.84	<b>0.27</b>	<b>0.32</b>

Table S12. Pattern of individual branched PFOS isomers. Ratios of 1- and 3+4- and 5-PFOS to 6-PFOS and ratio of 3+4-PFOS to 5-PFOS in samples as well as mean, maximum and minimum values for the same ratios observed for injections of TPFOS standard (n = 25). Ratios are based on peak areas in isomer-specific mass transitions. Numbers in bold correspond to values calculated using peak areas of signal-to-noise < 10. Ratios are not displayed for samples whose PFOS concentrations were outside the dynamic range of the instrument.

Sample	1/6	3+4/6	5/6	3+4/5
C1		<b>0.90</b>	<b>0.99</b>	<b>0.91</b>
C2	0.91	1.1	0.70	1.6
C3	1.0	1.2	0.92	1.3
C4	0.82	0.93	0.77	1.2
C5	0.73	0.75	0.65	1.1
R1	0.86	1.1	0.75	1.5
R2	0.72	1.0	0.75	1.3
R3	0.84	0.94	0.79	1.2
R4		0.37	0.21	1.3
R5	1.2	1.3	1.2	1.1
R6	0.70	0.90	0.73	1.2
R7	0.66	0.98	0.81	1.2
S11	<b>1.2</b>	<b>1.3</b>	<b>0.86</b>	1.5
S13	<b>0.74</b>	<b>1.1</b>	0.77	<b>1.4</b>
Standard	1/6	3+4/6	5/6	3+4/5
Mean	0.7	0.7	0.7	0.9
Min	0.3	0.5	0.5	0.8
Max	1.0	0.9	0.9	1.3
RSD (%)	32	15	15	12

Table S13. Results of MANOVA post hoc test performed on the logarithm of PFOA isomer ratios. p values for pairwise between-location comparison of mean ratios of 5- and 4-PFOA to 6-PFOA are displayed over diagonal and Bonferroni-corrected p values are displayed under diagonal. Numbers in bold indicate p values corresponding to tests significant at the 5% level. The Bonferroni correction compensates for the increased chance of incorrectly rejecting the null hypothesis, which arises when multiple hypotheses are tested. Due to low detection frequency, data from Stockholm were not included in the comparison.

	Corvo	Wuhan	Beijing	Råö
Corvo		0.093	<b>0.017</b>	0.21
Wuhan	0.56		<b>0.0020</b>	<b>0.0040</b>
Beijing	0.10	<b>0.012</b>		<b>0.0062</b>
Råö	1.0	<b>0.024</b>	<b>0.037</b>	

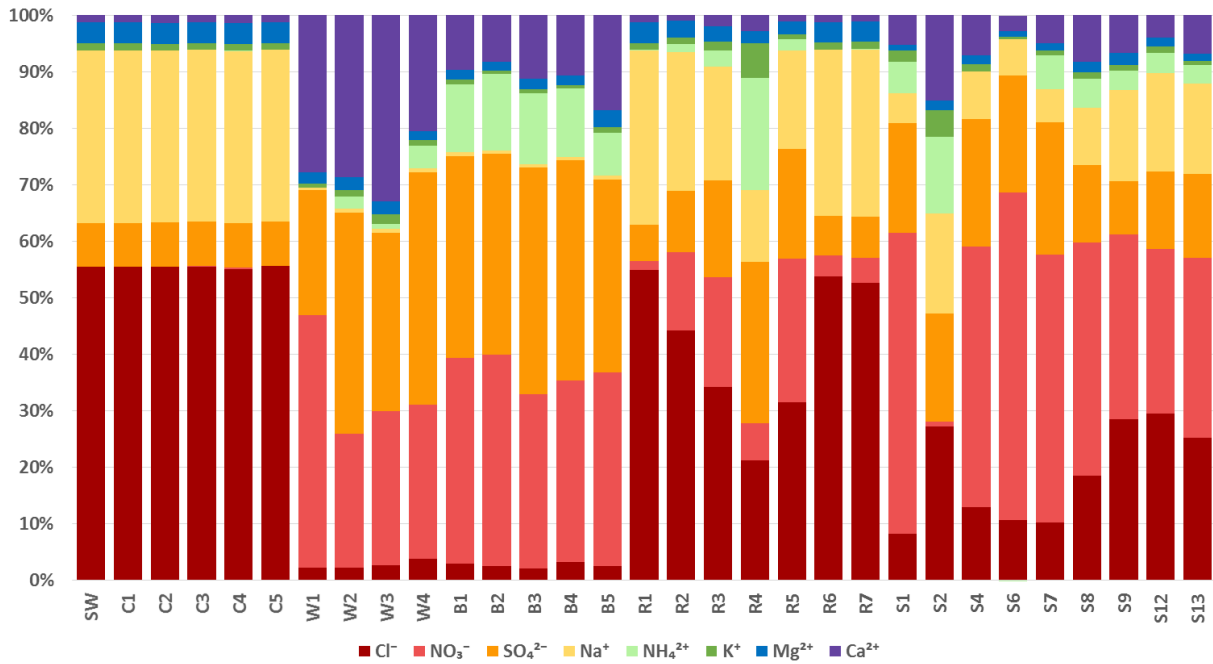


Figure S1. Ion composition (displayed as percentage by weight) in precipitation sampled on Corvo (C), in Wuhan (W), in Beijing (B), on Råö (R) and in Stockholm (S). SW is a seawater reference.

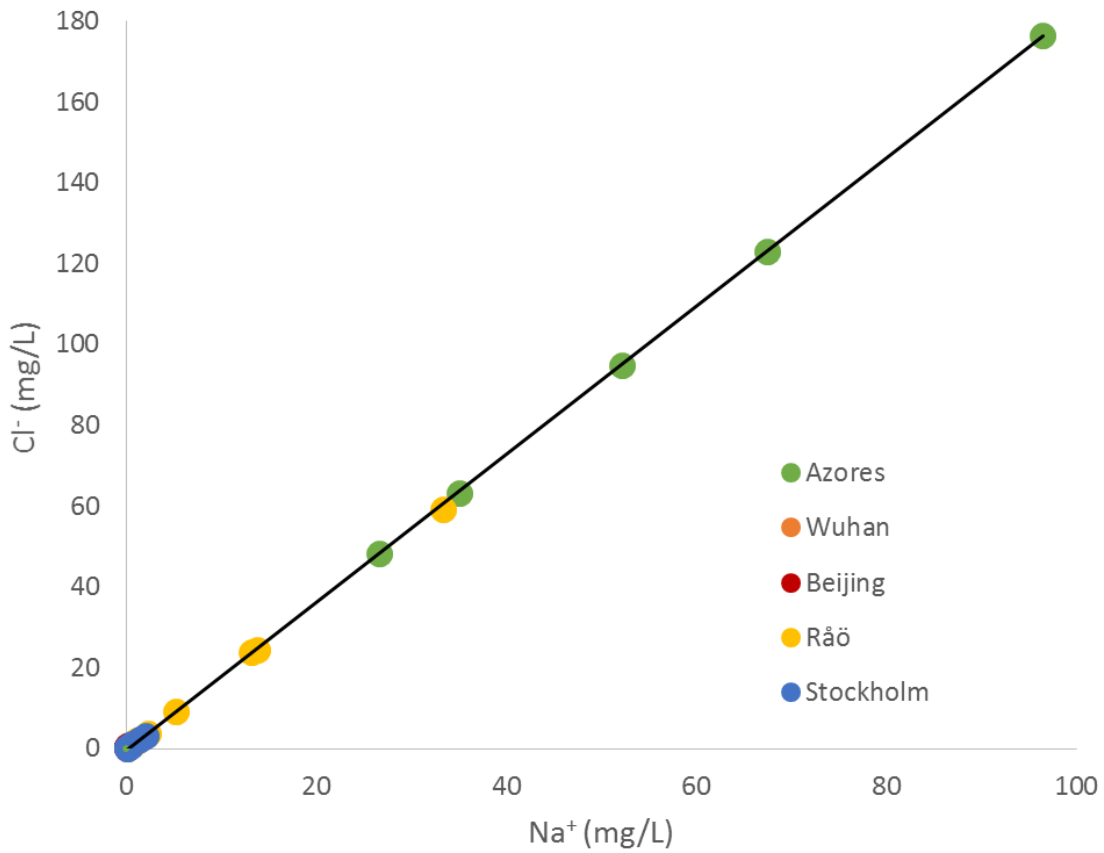


Figure S2. Concentration of chlorine to sodium (mg/L) in precipitation. The black line represents a seawater reference.

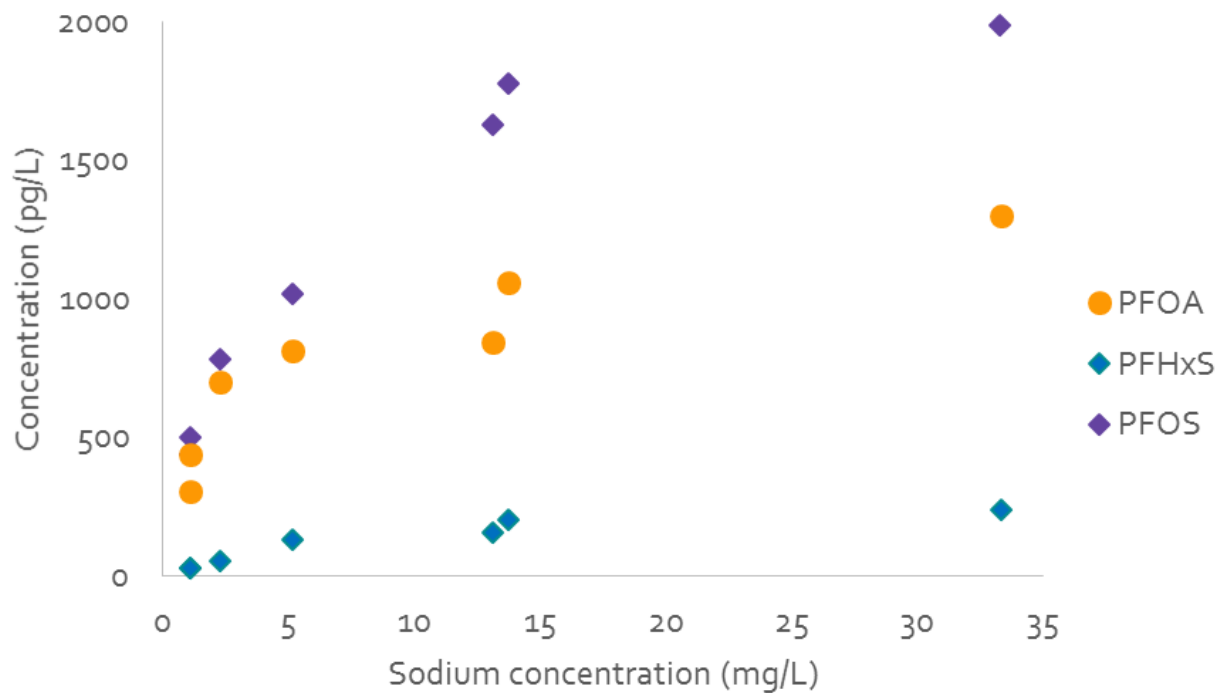


Figure S3. Concentration of PFOA, PFHxS and PFOS (pg/L) to sodium (mg/L) in precipitation sampled on Råö.

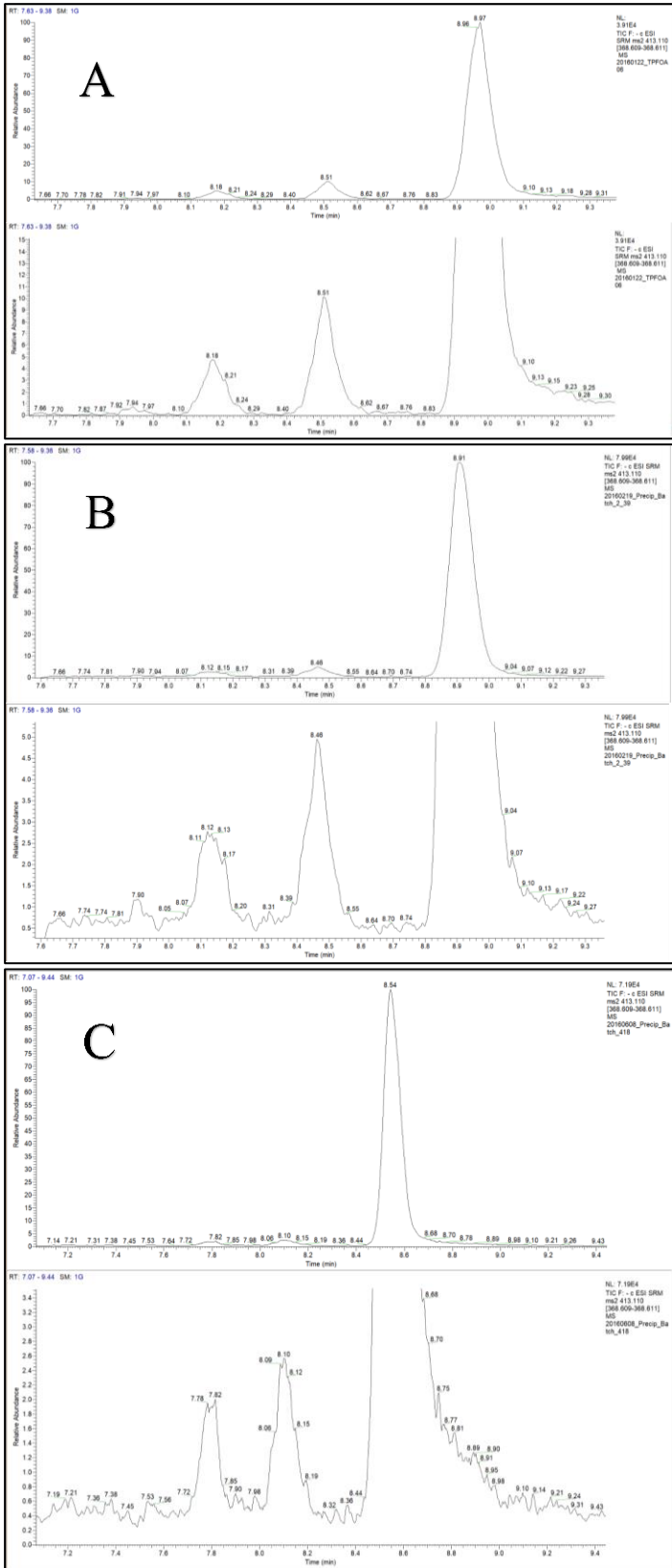


Figure S4. Examples of chromatograms of PFOA in the transition m/z 413/369 a) TPFOA standard b) Sample R7 c) Sample C3

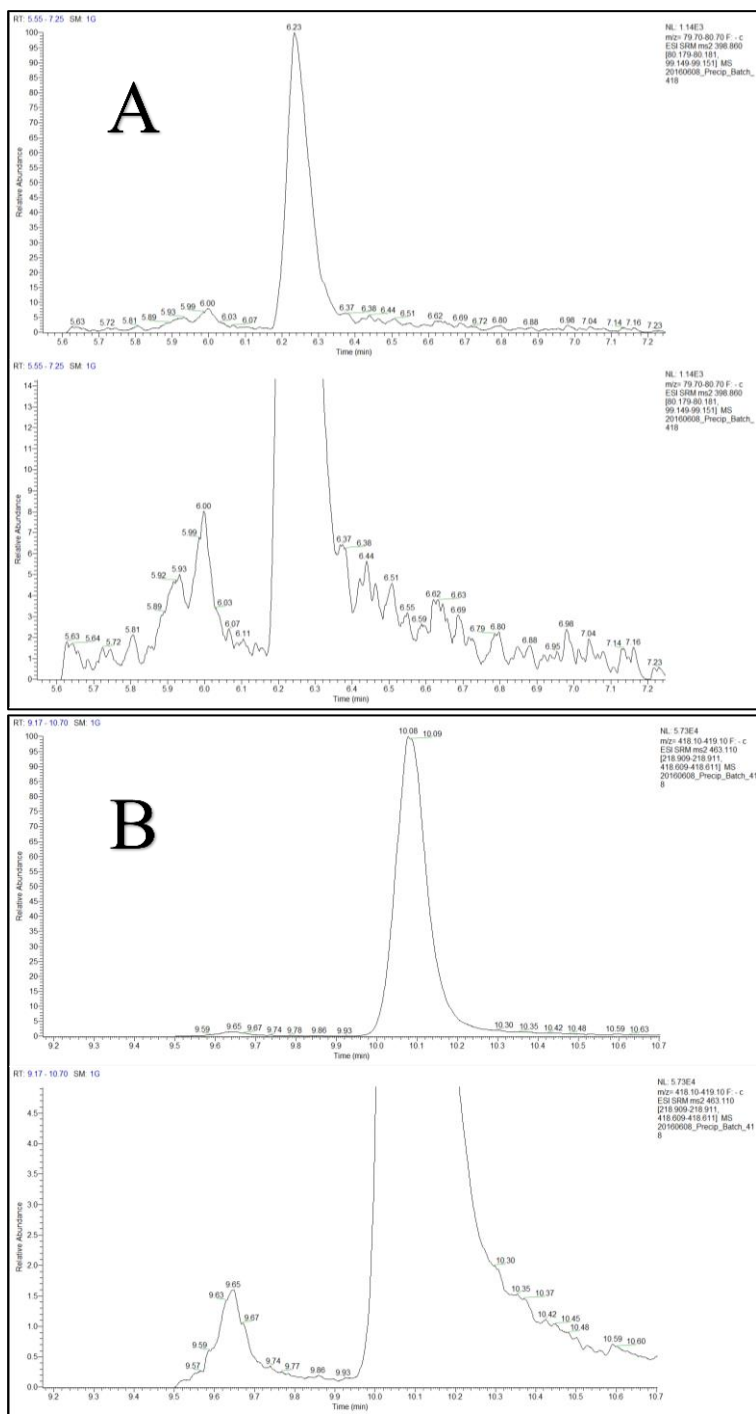


Figure S5. Examples of chromatograms for sample C3 a) PFHxS in the transition m/z 399/80 b) PFNA in the transition m/z 463/419



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