

1 Supplementary Information

2 Point source characterization of per- and polyfluoroalkyl substances (PFASs) and  
3 extractable organofluorine (EOF) in freshwater and aquatic invertebrates

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## 14 Sampling site description

### 15 Stockholm Arlanda Airport

16 Arlanda Airport is Sweden's largest airport and located at the vicinity of Stockholm (Figure S1). It is  
17 used by more than 26.8 million people annually.<sup>1</sup> Firefighting training facilities are situated at the north  
18 part of the airport area. Between the 1980s and 2003, PFOS-containing AFFFs (STHMEX-AFFF 3%, Dr.  
19 Richard Sthamer GmbH & Co. KG, Hamburg, Germany) were frequently applied during training  
20 excersises.<sup>2</sup> After 2003, the STHMEX-AFFF 3% was used until the stocks were emptied and then  
21 replaced by PFOS-free AFFFs (Presto AFFF and Moussol APS-P, Dr. Richard Sthamer GmbH & Co. KG,  
22 Hamburg, Germany).<sup>2</sup> The PFOS-free AFFFs, however, still contained PFASs (<10 % according to the  
23 manufacturer). From 2011 on, fluorine-free (FF)-AFFF (Moussol FF 3/6, Dr. Richard Sthamer GmbH &  
24 Co. KG, Hamburg, Germany) are in use. Because of the long-term usage of PFAS-containing AFFFs, the  
25 airport area and its surrounding have been contaminated with PFASs. A study about temporal trends  
26 of PFASs at the airport concluded that the area is an important point source for long-term  
27 contamination of PFASs the surrounding environment.<sup>2</sup>

### 28 Ronneby Airport

29 Ronneby airport is used for commercial as well as for military purposes and is located at the south of  
30 Sweden. Armed forces (F17 Air Wing) have been active since 1944 and use of PFAS containing AFFFs  
31 have been documented from 1980 to 2003.<sup>3</sup> An old fire-training site, a gravel field, was used for fire  
32 training until mid-1990s. Afterwards, a new fire-training site with a cemented plate replaced the old  
33 training site (Figure 1). Local, regional and international fire exercises have been performed at that  
34 site. The groundwater located under the airport was used as drinking water that supplied parts of the  
35 Ronneby municipality until the contamination of PFAS was discovered in 2013. The contamination was  
36 found by the county administrative board due to an extended environmental monitoring.<sup>4</sup>  
37 Concentrations up to 140,000 ng L<sup>-1</sup> PFOS were detected in groundwater close to the fire training site  
38 and concentrations up to 17,000 ng L<sup>-1</sup> PFOS were found in the local drinking water, thus leading to  
39 high concentration of PFASs in in blood serum of 5000 inhabitants. As an action the affected drinking  
40 water treatment plant (Brantfors vattenverk) was closed.<sup>4</sup> Several parties participate in the  
41 coordinated investigations, including Environmental Engineering, F17 Air Wing of the Swedish Armed  
42 Forces, Ronneby Municipality, County Administrative Board and Labor, Environmental Medicine in  
43 Lund, the Food Administration and the Swedish Chemicals Agency.

### 44 Söderhavet in Kumla

45 Söderhavet is an open pit mining lake and recipient of an industrial area called Kvarntorp in the  
46 municipality of Kumla, Sweden. In the Kvarntorp area, industrial activities have been in operation since  
47 1940s. Among other industries, shale oil was recovered and ammonia produced. These activities  
48 caused land and water to be polluted to a large extent mostly by petroleum hydrocarbon and heavy  
49 metals, but also e.g. PAH, solvents, PCBs and dioxins <sup>5</sup>. Nowadays, industries such as paper industry  
50 (rolling and punching of paper and cardboard – Millcon), a color and chemistry company (AkzoNobel)  
51 and Fortum, a large hazardous waste management facility are active. Fortum offers high temperature  
52 combustion, treatments such as evaporation, treatment of polluted soils, wet chemical treatment,  
53 mercury stabilization and disposal for hazardous waste. All wastewater is treated on site and released  
54 afterwards into a small stream that enters Söderhavet. Additionally a stretch of about 500 m along the  
55 stream is a sewage sludge deposit from the municipality's wastewater treatment plant (WWTP, Figure

56 1), which should also be consider as a potential PFAS source. An investigation of lake Söderhavet in  
57 2015 found high PFOS concentration in fish with an average concentration of  $750 \mu\text{g kg}^{-1} \text{ ww}$ .<sup>6</sup>

## 58 Instrumental analysis

59 The instrumental analysis was conducted on ultra-performance liquid chromatography coupled to a  
60 tandem mass spectrometer (UPLC-MS/MS Waters Xevo TQ-S, MA, USA). Target PFASs were separated  
61 on a 100 mm C18 BEH column ( $1.7 \mu\text{m}$ ,  $2.1 \text{ mm}$ ) in negative electrospray. A gradient elution was used  
62 beginning with 100% mobile phase A that was hold for 0.57 min, after that ramped to 0% A in 13 min,  
63 which was hold for 1 min and at minute 14.2 ramped to 100% A, followed by equilibration until 17 min.  
64 The mobile phases were methanol (B) and 30:70 methanol:water mixture (A), both with  $2 \text{ mmol L}^{-1}$   
65 ammonium acetate as an additive. Instrumental settings were: desolvation temperature  $400^\circ\text{C}$ ,  
66 desolvation gas flow  $800 \text{ L h}^{-1}$ , source temperature  $150^\circ\text{C}$ , mobile phase flow rate  $0.3 \text{ mL min}^{-1}$  and  
67 capillary voltage  $3.0 \text{ kV}$ .

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69 Tables

70 Table S1. Overview on sampling sites including sample ID, stream names, sampling dates,  
71 coordinates, measured pH, TOC, DOC and surface temperature (T).

Sample ID	Stream	Sampling date	Coordinates		pH	TOC [mg L <sup>-1</sup> ]	DOC [mg L <sup>-1</sup> ]	Surface water T [°C]
			Latitude	Longitude				
A1	Märsta river	2016-09-20	59°37'53.68"N	17°52'58.07"O	7.9	12.3	12.7	14.1
A2	Ditch	2016-09-20	59°39'32.85"N	17°55'51.32"O	7.5			12.8
A3	Märsta river	2016-09-20	59°36'13.93"N	17°48'55.55"O	7.4			13.0
ARef	unkown	2016-09-20	59°39'38.40"N	17°45'7.49"O	7.3	13.7	13.3	12.3
R1	Klintabäcken	2016-09-14	56°15'54.62"N	15°17'26.40"O	6.8	12.1	12.9	10.9
R2	Hässelstadsbäcken	2016-09-14	56°15'41.09"N	15°15'22.05"O	6.1			13.4
R3	Hässelstadsbäcken	2016-09-14	56°15'36.97"N	15°15'10.78"O	7.5			7.6
RRef	Ronneby river	2016-09-14	56°18'31.88"N	15°16'51.15"O	7.1	8.7	9.2	21.2
K1	Söderhavet outlet	2016-09-26	59° 6'45.03"N	15°14'54.02"O	7.9			16.6

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73 Table S2. The aquatic invertebrate samples, listed are sampling sites, dry weight (dw) of the  
74 composite samples, number of individuals and species taxa order.

Sampling site	Weight (mg dw)	Number of invertebrates	Species (order) of aquatic invertebrates
A1	148	4	Waterlouse (Isopoda)
		10	Water boatmen (Hemiptera)
		74	Fresh water amphipods (Amphipoda)
		4	Roundworm (Nematoda)
R1	151	189	Fresh water amphipods (Amphipoda)
K1	125	12	Mayflies (Ephemeroptera)
		1	Caddisflies (Trichoptera)
		2	Damselflies/dragonflies (Odonata)
		1	Water boatmen (Hemiptera)
		51	Waterlouse (Isopoda)
		6	Fresh water amphipods (Amphipoda)

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77 Table S3. Target PFASs listed in compound groups (PFCAs, PFSAs, FOSAs and FTSA), their chemical  
 78 formula, parent ion, chosen quantification ion, qualification ion and the corresponding IS compound  
 79 chosen for quantification.

Acronym	Compound	Chemical formula	Parent ion (m/z)	Product ion quantification (m/z)	Product ion qualification (m/z)	Corresponding IS
<b>PFCAs</b>						
PFBA	Perfluorobutanoate	C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> <sup>-</sup>	213	169	-	<sup>13</sup> C <sub>4</sub> PFBA
PFPeA	Perfluoropentanoate	C <sub>4</sub> F <sub>9</sub> CO <sub>2</sub> <sup>-</sup>	263	219	-	<sup>13</sup> C <sub>2</sub> PFPeA
PFHxA	Perfluorohexanoate	C <sub>5</sub> F <sub>11</sub> CO <sub>2</sub> <sup>-</sup>	313	269	119	<sup>13</sup> C <sub>2</sub> PFHxA
PFHpA	Perfluoroheptanoate	C <sub>6</sub> F <sub>13</sub> CO <sub>2</sub> <sup>-</sup>	363	169	319	<sup>13</sup> C <sub>2</sub> PFHxA
PFOA	Perfluorooctanoate	C <sub>7</sub> F <sub>15</sub> CO <sub>2</sub> <sup>-</sup>	413	369	169	<sup>13</sup> C <sub>4</sub> PFOA
PFNA	Perfluorononanoate	C <sub>8</sub> F <sub>17</sub> CO <sub>2</sub> <sup>-</sup>	463	419	219	<sup>13</sup> C <sub>5</sub> PFNA
PFDA	Perfluorodecanoate	C <sub>9</sub> F <sub>19</sub> CO <sub>2</sub> <sup>-</sup>	513	469	219	<sup>13</sup> C <sub>2</sub> PFDA
PFUnDA	Perfluoroundecanoate	C <sub>10</sub> F <sub>21</sub> CO <sub>2</sub> <sup>-</sup>	563	269	519	<sup>13</sup> C <sub>2</sub> PFUnDA
PFDoDA	Perfluorododecanoate	C <sub>11</sub> F <sub>23</sub> CO <sub>2</sub> <sup>-</sup>	613	169	569	<sup>13</sup> C <sub>2</sub> PFDoDA
PFTrDA	Perfluorotridecanoate	C <sub>12</sub> F <sub>25</sub> CO <sub>2</sub> <sup>-</sup>	663	619	169	<sup>13</sup> C <sub>2</sub> PFDoDA
PFTeDA	Perfluorotetradecanoate	C <sub>13</sub> F <sub>27</sub> CO <sub>2</sub> <sup>-</sup>	713	669	169	<sup>13</sup> C <sub>2</sub> PFTeDA
PFHxDA	Perfluorohexadecanoate	C <sub>15</sub> F <sub>31</sub> CO <sub>2</sub> <sup>-</sup>	813	769	169	<sup>13</sup> C <sub>2</sub> PFHxDA
PFOcDA	Perfluorooctadecanoate	C <sub>17</sub> F <sub>35</sub> CO <sub>2</sub> <sup>-</sup>	913	869	169	<sup>13</sup> C <sub>2</sub> PFHxDA
<b>PFSAs</b>						
PFBS	Perfluorobutane sulfonate	C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> <sup>-</sup>	299	80	99	<sup>18</sup> O <sub>2</sub> PFHxS
PFPeS	Perfluoropentane sulfonate	C <sub>5</sub> F <sub>11</sub> SO <sub>3</sub> <sup>-</sup>	349	80	99	<sup>18</sup> O <sub>2</sub> PFHxS
PFHxS	Perfluorohexane sulfonate	C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub> <sup>-</sup>	399	99	80, 119	<sup>18</sup> O <sub>2</sub> PFHxS
PFHpS	Perfluoroheptane sulfonate	C <sub>7</sub> F <sub>15</sub> SO <sub>3</sub> <sup>-</sup>	449	99	80	<sup>13</sup> C <sub>4</sub> PFOS
PFOS	Perfluorooctane sulfonate	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	499	99	80, 169	<sup>13</sup> C <sub>4</sub> PFOS
1 <i>m</i> -PFOS	1 <i>m</i> - perfluorooctane sulfonate	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	499	99	169	<sup>13</sup> C <sub>4</sub> PFOS
6/2 <i>m</i> -PFOS	6/2 <i>m</i> - perfluorooctane sulfonate	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	499	169	80	<sup>13</sup> C <sub>4</sub> PFOS
3/4/5 <i>m</i> -PFOS	3/4/5 <i>m</i> - perfluorooctane sulfonate	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	499	80	99	<sup>13</sup> C <sub>4</sub> PFOS
4.4/4.5/5.5- <i>m</i> <sub>2</sub> -PFOS	4.4/4.5/5.5- perfluorooctane sulfonate	C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	499	80	99	<sup>13</sup> C <sub>4</sub> PFOS
PFNS	Perfluorononane sulfonate	C <sub>9</sub> F <sub>19</sub> SO <sub>3</sub> <sup>-</sup>	549	80	99	<sup>13</sup> C <sub>4</sub> PFOS
PFDS	Perfluorodecane sulfonate	C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub> <sup>-</sup>	599	99	80	<sup>13</sup> C <sub>4</sub> PFOS
PFDoDS	Perfluorododecane sulfonate	C <sub>12</sub> F <sub>25</sub> SO <sub>3</sub> <sup>-</sup>	699	99	80	<sup>13</sup> C <sub>4</sub> PFOS
<b>FOSAs</b>						
FOSA	Perfluorooctanesulfonamide	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> NH <sub>2</sub>	499	78	169	<sup>13</sup> C <sub>8</sub> -FOSA
<b>FTSAs</b>						
4:2 FTSA	4:2 fluorotelomer sulfonate	C <sub>6</sub> H <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> <sup>-</sup>	327	307	81	<sup>13</sup> C <sub>2</sub> 4:2 FTSA
6:2 FTSA	6:2 fluorotelomer sulfonate	C <sub>8</sub> H <sub>4</sub> F <sub>13</sub> SO <sub>3</sub> <sup>-</sup>	427	407	81	<sup>13</sup> C <sub>2</sub> 6:2 FTSA
8:2 FTSA	8:2 fluorotelomer sulfonate	C <sub>10</sub> H <sub>4</sub> F <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	527	507	81	<sup>13</sup> C <sub>2</sub> 8:2 FTSA

Table S4. PFAS concentrations of surface water samples from Stockholm Arlanda Airport, A1 ± SD (*n*=3), A2, A3, ARef (*n*=3) and A FB (field blank); from Ronneby Airport R1 ± SD (*n*=3), R2, R3, ARef (*n*=3) and R FB (field blank) and from Söderhavet in Kvarntorp, K1 ± SD (*n*=2) in ng L<sup>-1</sup>. Total concentrations, consisting of the joined integration of linear and the detected branched isomers, are shown for T-PFOA, T-PFHxS and T-PFHpS. Concentrations of PFOS are shown as the sum (ΣPFOS) of linear, 1-PFOS, 6/2-PFOS, 3/4/5-PFOS and 4.4/4.5/5.5-*dimethyl*-PFOS. All other PFAS values shown represent the linear PFAS. Values below the method detection limit are marked with <MDL and values above MDL and below the quantification limit (MQL) are marked with \*.

PFAS	Sampling sites											Detection limits	
	A1	A2	A3	ARef	A FB	R1	R2	R3	RRef	R FB	K1	MDL	MQL
<b>PFCAs</b>													
PFBA	2.83±0.78	3.41	5.08	4.110±0.04	<MDL	2.26±0.27	8.41	8.69	<MDL	<MDL	4.88±0.06	0.004	0.013
PFPeA	2.95±0.86	5.77	6.65	1.12±0.10	<MDL	3.34±0.05	24.67	23.80	<MDL	<MDL	6.20±0.09	0.004	0.013
PFHxA	2.63±0.77	5.11	7.71	1.75±0.06	0.05	8.48±0.02	50.40	47.78	0.23±0.01	<MDL	9.08±0.00	0.004	0.013
PFHpA	1.98±0.54	3.05	5.20	1.26±0.02	0.02*	2.73±0.05	18.04	17.17	0.46±0.03	<MDL	4.14±0.04	0.014	0.047
T-PFOA	2.91±0.70	2.92	5.21	1.51±0.05	<MDL	4.52±0.04	34.95	24.98	0.52±0.02	<MDL	3.67±0.03	0.12	0.38
PFNA	0.21±0.06	0.20	0.36	0.31±0.01	<MDL	0.09±0.00	0.36	0.34	0.16±0.01	<MDL	0.34±0.01	0.019	0.064
PFDA	0.1±0.03	0.05	0.15	0.07±0.01	0.02*	0.01*	0.06	0.07	0.03±0.00	<MDL	0.12±0.04	0.007	0.024
PFUnDA	0.02*	0.02*	0.03*	<MDL	0.01*	<MDL	0.01*	<MDL	0.01*	<MDL	0.02*	0.014	0.048
PFDoDA	0.02±0.02	<MDL	0.06	<MDL	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
PFTTrDA	0.01*	<MDL	0.03	<MDL	0.03	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
PFTeDA	<MDL	0.04	0.02	0.01*	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
PFHxDA	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.016	0.052
PFOcDA	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
<b>PFSA</b> s													
PFBS	0.45±0.13	0.85	1.95	0.64±0.01	<MDL	10.20±0.13	36.48	32.66	0.11±0.01	<MDL	13.00±0.28	0.015	0.048
PFPeS	0.4±0.11	0.94	1.78	0.13±0.01	<MDL	11.11±0.12	51.49	45.78	0.02±0.00	<MDL	1.78±0.06	0.004	0.013
T-PFHxS	5.64±1.42	11.15	14.78	1.01±0.01	<MDL	71.83±0.72	273.40	260.73	0.16±0.01	<MDL	15.11±0.32	0.017	0.057
T-PFPpS	0.29±0.02	1.09	1.25	0.07*	<MDL	5.06±0.13	96.51	79.81	<MDL	<MDL	1.40±0.01	0.020	0.068
ΣPFOS	10.37±1.3	54.46	42.06	0.08*	<MDL	161.95±2.30	2288.06	2028.85	<MDL	<MDL	90.13±0.78	0.806	2.69
PFNS	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.40	0.32	<MDL	<MDL	0.02±0.01	0.004	0.013
PFDS	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
PFDoDS	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
<b>FOSA</b> s													
FOSA	0.02±0.01	0.45	0.05	<MDL	<MDL	0.04±0.00	0.04	0.03	<MDL	<MDL	0.31±0.03	0.004	0.013
<b>FTSA</b> s													
4:2 FTSA	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004	0.013
6:2 FTSA	0.13*	3.86	1.24	0.08*	0.06*	<MDL	7.50	5.16	0.01*	<MDL	6.05±0.03	0.004	0.013
8:2 FTSA	<MDL	0.13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.01*	<MDL	0.11±0.02	0.004	0.013

Table S5. PFAS concentrations of aquatic invertebrates from Stockholm Arlanda Airport, A1 ( $n=1$ ), from Ronneby Airport R1 ( $n=1$ ) and from Söderhavet in Kumla, K1 ( $n=1$ ) in  $\text{ng g}^{-1}$  dw. Total concentrations, consisting of the integration of linear and the detected branched isomers, are shown for T-PFOA and T-PFHpS. Concentration of PFOS is shown as the sum ( $\Sigma$ PFOS) of linear, 1-PFOS, 6/2-PFOS, 3/4/5-PFOS and 4.4/4.5/5.5-*dimethyl*-PFOS, all other PFAS values shown represent the linear PFAS. Values below the method detection limit are marked with <MDL and values above MDL and below the quantification limit (MQL) are marked with \*.

	Sampling sites			Detection limits	
	A1	R1	K1	MDL	MQL
PFCAs					
PFBA	0.42	4.23	0.51	0.03	0.09
PFPeA	1.15	8.48	2.20	0.03	0.09
PFHxA	1.01	9.52	1.10	0.03	0.09
PFHpA	0.81	4.86	0.67	0.03	0.09
T-PFOA	4.97	23.53	1.83	0.03	0.09
PFNA	1.78	1.23	0.96	0.03	0.09
PFDA	4.14	0.37	0.73	0.03	0.09
PFUnDA	3.40	0.74	1.00	0.05	0.18
PFDoDA	7.06	0.57	0.78	0.03	0.09
PFTTrDA	3.61	0.95	1.08	0.03	0.09
PFTeDA	1.85	0.35	0.27	0.03	0.09
PFHxDA	0.07*	0.05*	0.05*	0.04	0.14
PFOcDA	<MDL	<MDL	<MDL	0.03	0.09
PFSAs					
PFBS	<MDL	0.45	0.29	0.03	0.09
PFPeS	0.14	1.85	0.19	0.03	0.09
PFHxS	1.97	58.42	5.97	0.03	0.09
T-PFPpS	0.37	10.53	1.16	0.03	0.09
$\Sigma$ PFOS	44.12	624.5	251.1	0.37	1.25
PFNS	0.07*	0.61	0.69	0.03	0.09
PFDS	0.36	0.75	0.44	0.03	0.09
PFDoDS	0.05*	<MDL	0.07*	0.03	0.09
FTSAs					
4:2 FTSA	<MDL	<MDL	<MDL	0.03	0.09
6:2 FTSA	3.49	5.73	10.26	0.03	0.09
8:2 FTSA	0.24	0.13	6.92	0.03	0.09
$\Sigma_{25}$ PFAS	80.4	704	267		

Table S6. Internal standard recoveries of all water and aquatic invertebrate samples (in percent %). Values for A1, ARef, R1, RRef, K1 water samples were replicates and therefore displayed as averages ( $\pm$  their standard deviation). The number of replicates were  $n=2-3$ .

	Surface water												SD	Aquatic invertebrates				
	QA	A1	A2	A3	ARef	A FB	R1	R2	R3	RRef	R FB	K1		QA	A1	R1	K1	SD
IS_PFBA	95	n.a.	75	103	n.a.	108	57 $\pm$ 5	45	81	47 $\pm$ 3	92	n.a.	36	92	67	89	86	n.a.
IS_PFHxA	102	65 $\pm$ 1	69	79	66 $\pm$ 2	119	75 $\pm$ 1	81	77	56 $\pm$ 3	101	68 $\pm$ 6	18	90	91	91	60	n.a.
IS_PFOA	94	99 $\pm$ 2	107	116	100 $\pm$ 3	113	97 $\pm$ 0.3	92	95	91 $\pm$ 3	98	101 $\pm$ 10	8	90	95	89	103	6
IS_PFNA	96	99 $\pm$ 0.1	104	113	98 $\pm$ 4	116	95 $\pm$ 1	93	95	92 $\pm$ 3	100	103 $\pm$ 1	7	90	96	89	104	6
IS_PFDA	91	91 $\pm$ 3	106	125	87 $\pm$ 9	115	92 $\pm$ 1	90	92	89 $\pm$ 5	92	90 $\pm$ 8	12	89	92	83	100	6
IS_PFUxDA	79	65 $\pm$ 12	58	86	60 $\pm$ 4	108	79 $\pm$ 4	83	80	79 $\pm$ 7	80	74 $\pm$ 5	12	88	93	83	96	5
IS_PFTDA	66	20 $\pm$ 8	39	45	19 $\pm$ 5	73	53 $\pm$ 2	53	57	44 $\pm$ 7	59	45 $\pm$ 2	16	50	21	46	27	12
IS_PFDxDA	63	38 $\pm$ 10	40	60	30 $\pm$ 2	92	61 $\pm$ 4	61	57	54 $\pm$ 7	54	50 $\pm$ 1	15	81	25	74	40	23
IS_PFHxDA	98	30 $\pm$ 11	56	87	23 $\pm$ 9	86	53 $\pm$ 4	67	59	41 $\pm$ 8	80	53 $\pm$ 2	22	77	44	58	46	13
IS_PFHxS	92	100 $\pm$ 0.2	108	119	102 $\pm$ 3	117	98 $\pm$ 2	103	108	91 $\pm$ 4	97	101 $\pm$ 8	8	91	93	90	103	5
IS_PFOS	95	96 $\pm$ 4	95	114	93 $\pm$ 7	112	99 $\pm$ 1	94	91	93 $\pm$ 5	96	95 $\pm$ 5	7	89	99	83	100	7
IS_8_2_FTS	57	156 $\pm$ 8	134	192	107 $\pm$ 7	73	105 $\pm$ 2	151	172	107 $\pm$ 6	58	103 $\pm$ 1	42	88	173	121	113	31
IS_6_2_FTS	50	187 $\pm$ 1	201	228	172 $\pm$ 6	59	128 $\pm$ 15	198	235	151 $\pm$ 6	52	179 $\pm$ 7	64	118	137	129	126	7



Table S7. Percent (%) of linear PFOS (L-PFOS) and branched isomers of the  $\Sigma$ PFOS.

	Surface water							Aquatic invertebrates		
	A1	A2	A3	R1	R2	R3	K1	A1	R1	K1
L-PFOS	39	51	33	31	23	22	40	85	72	76
1-PFOS	3.6	3.2	5.7	6.2	12	12	4.9	1.5	2.3	2.6
6/2-PFOS	20	17	19	21	24	24	18	6.1	9.9	8.9
3/4/5-PFOS	36	28	40	40	37	38	35	7.2	16	12
dimethyl-PFOS	2.2	1.6	2.7	2.8	5.0	4.8	2.5	0.0	0.1	0.1

Table S8. Bioaccumulation factor (BAF) on converted wet weight basis of aquatic invertebrate samples in L kg<sup>-1</sup> determined at site A1, R1 and K1.

	A1	R1	K1
PFCAs			
PFBA	15	188	11
PFPeA	39	254	35
PFHxA	38	112	12
PFHpA	41	178	16
PFOA	171	520	50
PFNA	866	1300	281
PFDA	4280	374	592
PFUnDA	n.a.	n.a.	n.a.
PFDoDA	37000	n.a.	n.a.
PFTTrDA	8450	n.a.	n.a.
PFTDA	11200	n.a.	n.a.
PFSAs			
PFBS	n.a	4.4	2.2
PFPeS	36	17	11
PFHxS	35	81	40
PFHpS	129	208	83
PFNS	n.a.	n.a.	2990
dimethyl-PFOS	n.a	14	8.5
3/4/5-PFOS	85	155	100
6/2-PFOS	131	186	138
1-PFOS	172	141	146
L-PFOS	942	905	534
$\Sigma$ PFOS	813	535	670

n.a. not available

Table S9. Mass discharge of PFOS,  $\Sigma_{25}$ PFASs and EOF [kg year<sup>-1</sup>] calculated with the annual average flow rates [L s<sup>-1</sup>], except for Klintabäcken (R1) that was calculated with one point measured flow rate.

Sampling site	Flow rate [L s <sup>-1</sup> ]	PFOS [kg year <sup>-1</sup> ]	$\Sigma_{25}$ PFASs [kg year <sup>-1</sup> ]	EOF [kg F year <sup>-1</sup> ]
Märsta river (A1)	480 <sup>1</sup>	0.16	0.52	7.5
Märsta river outlet (A3)	480 <sup>1</sup>	0.64	1.4	36
Klintabäcken (R1)	75 <sup>2</sup>	0.38	0.63	1.4
Hässelstadsbäcken (avg. R2/R3)	230 <sup>1</sup>	15±0.92	19±1.1	29±3.0
Ronneby river ( $\Sigma$ R1 and R2/3)		16	20	31

<sup>1</sup>yearly average flow rate at the Märsta river (A3) and Hässelstad watershed <sup>7</sup>, <sup>2</sup> flow rate measured on 14-17<sup>th</sup> Apr. 2015 <sup>3</sup>

## Figures

### Technical PFOS

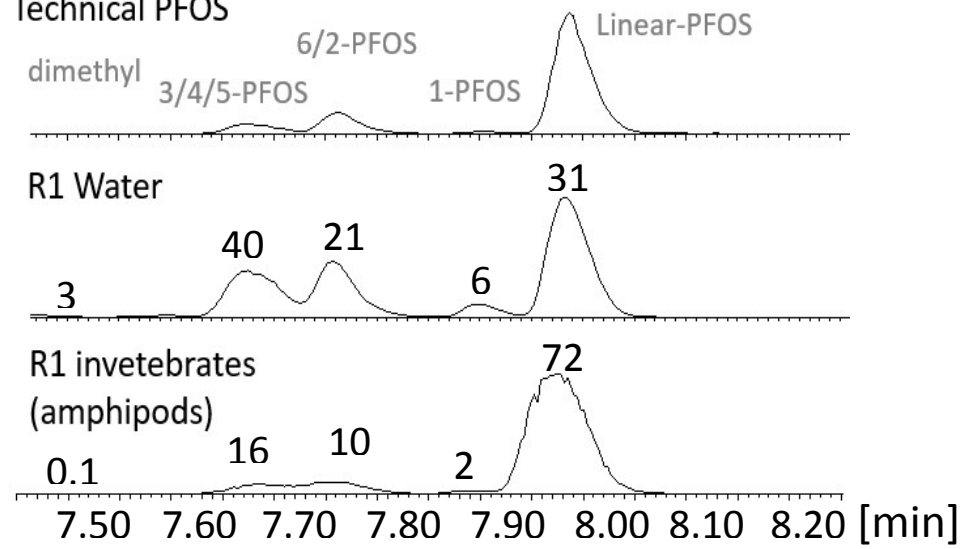


Figure S1. Chromatograms of PFOS isomers and their percentage contribution to the  $\Sigma$ PFOS from the injection of the standard, R1 surface water and R1 aquatic invertebrates.

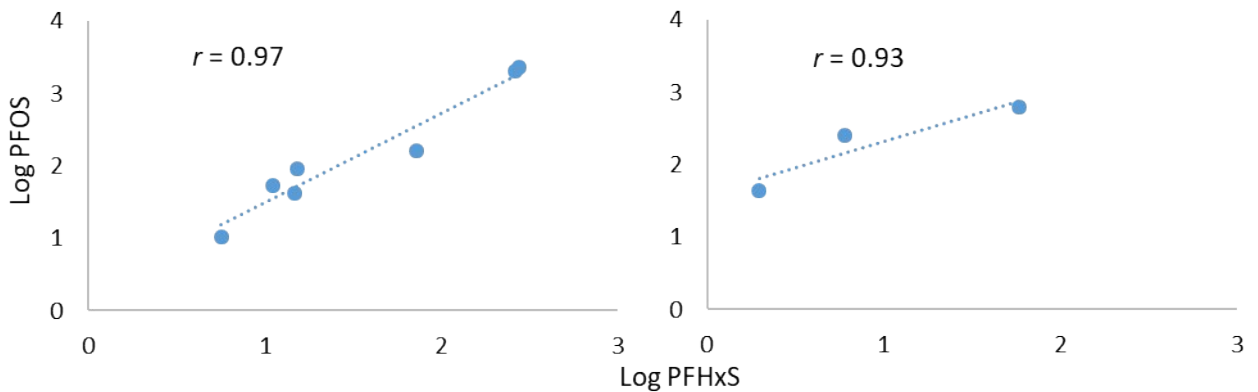


Figure S2. Correlation between  $\Sigma$ PFOS and T-PFHxS concentrations (log transformed) in water (left plot) and aquatic invertebrates (right plot) at sites A, R and K.

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