

## Screening av perfluoralkylerade ämnen och flamskyddsmedel i svenska vattendrag

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<p><b>Sammanfattning</b></p> <p>Syftet med projektet var att studera förekomst av perfluoralkylerade ämnen (PFASs) samt relativt nya flamskyddsmedel (FRs) i svenska vattendrag. Vi provtog på 44 platser (totalt 41 vattendrag) och bestämde innehållet av PFASs (alla platser) och FRs (25 platser).</p> <p>Av de 12 utvalda FRs, kunde 3 kvantifieras. TCIPP var det klart dominerade ämnet med en halt på upp till 3900 ng L<sup>-1</sup> (Fyrisån). 2,4,6-TBP uppvisade högre halter i åar i södra Sverige. Vattendragen med de högsta av ΣFRs var Fyrisån och Norrström. Den totala belastningen på Östersjön av ΣFRs uppskattades till 38 kg dag<sup>-1</sup>, där Ångermanlandsälven och Norrström stod för de största bidragen. Det ska noteras att i dessa belastningssiffror ingår inte äldre FRs med omfattande historisk användning, t.ex. PBDE.</p> <p>Totalt 13 av 25 de analyserade PFASs kunde kvantifieras. Medelvärdet av ΣPFASs i alla vattendrag var 9,5 ng L<sup>-1</sup>, och de högsta medelhalterna uppmättes för PFBS och PFHxS (~2 ng L<sup>-1</sup>). Det sammanlagda utflödet av ΣPFASs uppgick till 3,2 kg dag<sup>-1</sup>. PFOS överskred miljö kvalitetsnormen på 0,65 ng L<sup>-1</sup> (årligt medelvärde; AA-EQS; 2013/39/EU) på 12 av 44 platser.</p> <p>Den här fältstudien baseras på en provtagningskampanj med ögonblicksprovtagning, och därför ska alla rapporterade värden tolkas med försiktighet. Verifikation av höga resultat och mer detaljerade studier på platser med förhöjda värden rekommenderas. Studien pekar också på att uppströmsmätningar är nödvändiga för att finna viktiga föroreningskällor.</p>	

**Screening of perfluoroalkyl substances and organic flame retardants in  
Swedish rivers**

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## Summary

The occurrence and effects of ubiquitously present persistent organic pollutants (POPs) in the environment is one of the challenges the society is facing today. Two categories of chemicals that have gained increased public attention during the last decades are organic flame retardants (FRs) and perfluoroalkyl substances (PFASs). Many representatives from these compound groups have bioaccumulative, persistent and toxic properties. This has led to a ban of some of these compounds based on international agreements.

FRs and PFASs end up in surface waters and sometimes also in ground water due to their widespread distribution, disinclination of getting removed at wastewater treatment plants (WWTPs), and persistence. However, the knowledge of the occurrence, fate, and effect in the environment of FRs and PFASs is still in great need of research, especially for recently introduced compounds (such as novel FRs). The objective of this project was to provide a snapshot of the current pollution situation of PFASs and selected novel FRs in Swedish surface waters. We sampled at 44 sites (representing 41 rivers and streams) along the whole coastline of Sweden and analysed their content of PFASs (all sites) and FRs (25 sites representing 23 rivers).

Among the 12 target FRs, 3 could be quantified (2,4,6-TBP, TCIPP, and TPHP). TCIPP was the predominant compound with a level up to 3 900 ng L<sup>-1</sup>. The 2,4,6-TBP showed higher levels in southern rivers. The river with highest levels of ΣFRs was Fyrisån, and the total riverine input of the targeted FRs into the Baltic Sea was estimated to 38 kg day<sup>-1</sup> with Ångermanlandsälven and Norrström as major contributors. It should be noted that these values only include the targeted, relatively novel FRs, while historically more important FRs such as the polybrominated diphenyl ethers (PBDEs), are not included.

In total 13 PFASs were detected (PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, FOSA, PFBS, PFHxS, PFOS) among the 25 target compounds. The mean ΣPFAS level of all sampled rivers was 9.5 ng L<sup>-1</sup> and the median 4.2 ng L<sup>-1</sup>, and the highest mean values were found for PFBS and PFHxS (~2 ng L<sup>-1</sup> for each compound). Streams in the north (e.g. Alterälven, Öre älv, Gide älv, Lögde älv and Ljungan) showed generally higher fractions of the longer chained perfluoroalkyl carboxylic acids (PFCAs; i.e. PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA) whereas in the south the fractions of PFHpA and PFOA were higher. The total riverine input of all PFASs into recipient seas was estimated to 3.2 kg day<sup>-1</sup> (1150 kg yr<sup>-1</sup>).

PFOS exceeded the annual average Environmental Quality Standard (AA-EQS; 2013/39/EU) of 0.65 ng L<sup>-1</sup> at 12 of 44 sampling sites, which are located in all parts of Sweden (Ume älv at Gubböle, Ångermanälven, Delångersån, Fyrisån, Norrström, Nyköpingsån, Emån, Lyckebyån, Rönneån, Nissan, Viskan and Göta älv at Alelyckan).

As this study was a one-time grab sampling campaign for screening purposes, all values should be interpreted with care. A screening study like the current may, however, reveal hot spots. Verification and more detailed studies over a longer time period are recommended for sites with elevated levels. Our study also suggests that upstream monitoring is necessary to reveal important pollution sources.

## Sammanfattning

Förekomst och effekter av globalt spridda persistenta organiska miljöföroreningar (POPs) har blivit en mycket uppmärksam fråga. Två kategorier av kemikalier som har fått ökad uppmärksamhet är organiska flamskyddsmedel (FRs) och perfluoroalkylerade substanser (PFASs). Det har visat sig att många av dessa är bioackumulerande, persistenta och giftiga, vilket har lett till att flera av dem fasats ut eller förbjudits under de senaste årtiondena.

Eftersom FRs och PFASs är väl spridda i miljön och dessutom svåra att avlägsna från avloppsvatten, återfinns de regelbundet i ytvatten och i vissa fall även i grundvatten. Kunskap om FRs och PFASs i miljön är begränsad, både vad gäller förekomst, spridning och effekter, och särskilt då för ämnen som introducerats relativt nyligen (t.ex. nya FRs). Det finns alltså ett behov av att lära mer om dessa ämnen. Syftet med detta projekt var att studera förekomst av PFASs samt relativt nya FRs i vattendrag längs hela kusten. Vi provtog på 44 platser (totalt 41 vattendrag) och bestämde innehållet av PFASs (alla platser) och FRs (25 provtagningsplatser som representerar 23 vattendrag).

Av de 12 utvalda FRs, kunde 3 kvantifieras (2,4,6-TBP, TCIPP och TPHP). TCIPP var det klart dominerade ämnet med en halt på upp till 3 900 ng L<sup>-1</sup> (Fyrisån). 2,4,6-TBP uppvisade högre halter i åar i södra Sverige. Vattendraget med den högsta halten av FRs var Fyrisån, och den totala belastningen på Östersjön av FRs uppskattades till 38 kg dag<sup>-1</sup>, där Ångermanlandsälven och Norrström stod för de största bidragen. Det ska noteras att dessa i belastningssiffror ingår bara de utvalda, relativt nya FRs, medan äldre med omfattande historisk användning, t.ex. PBDE, inte ingår.

Totalt 13 av 25 de analyserade PFASs kunde kvantifieras (PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTeDA, FOSA, PFBS, PFHxS, PFOS). Medelvärdet av ΣPFASs i alla vattendrag var 9,5 ng L<sup>-1</sup> (medianvärdet 4,2 ng L<sup>-1</sup>), och de högsta medelhalterna uppmättes för PFHxS och PFBS (~2 ng L<sup>-1</sup> per ämne). Vattendrag i norr (t.ex. Alterälven, Öre älv, Gide älv, Lögde älv och Ljungan) uppvisade i regel en högre fraktion av perfluorerade karboxylater (PFCAs) med långa kolkedjor (dvs. PFNA, PFDA, PFUnDA, PFDODA, PFTeDA), medan i söder var fraktionen av PFHpA och PFOA högre. Det sammanlagda utflödet av ΣPFASs uppskattades till 3,2 kg dag<sup>-1</sup> (1150 kg år<sup>-1</sup>).

PFOS överskred miljö kvalitetsnormen på 0,65 ng L<sup>-1</sup> (årligt medelvärde; AA-EQS; 2013/39/EU) på 12 av 44 provtagningsplatser, och dessa återfinns i alla delar av Sverige (Ume älv vid Gubböle, Ångermanälven, Delångersån, Fyrisån, Norrström, Nyköpingsån, Emån, Lyckebyån, Rönneån, Nissan, Viskan och Göta älv vid Alelyckan).

Eftersom den här fältstudien baseras på en provtagningskampanj med ögonblicksprovtagning, ska alla värden som redovisas tolkas med försiktighet. En screening-studie som den här kan dock avslöja s.k. hotspots. Vi rekommenderar verifikation av höga resultat och mer detaljerade studier kring dessa provtagningsplatser för att säkerställa föroreningsituationen. Vår studie pekar också på att uppströmsmätningar är nödvändiga för att finna viktiga föroreningskällor.

# 1. Introduction

This field study was carried out by the Department of Aquatic Sciences and Assessment (Institutionen för vatten och miljö, IVM) at the Swedish University of Agricultural Sciences (SLU). The overall objective was to screen for perfluoroalkyl substances (PFASs) and selected novel organic flame retardants (FRs) in Swedish streams and rivers. We also made estimates of the loadings of FRs and PFASs from these streams and rivers to their recipient seas and discuss sources and pollution patterns.

## 2. Background

### 2.1 Flame retardants (FRs)

Flame retardants (FRs) are extensively used for protection of daily life products such as carpets, furniture, textiles and IT products (Papachlimitzou et al. 2012). The use of FRs has led to significantly reduced incidents of fire- and smoke-related fatalities (Birnbaum and Staskal, 2004; Kolic et al. 2009). However, FRs are not free of disadvantages, with its unsolicited release to the environment as the key issue (Birnbaum and Staskal, 2004).

FRs are chemicals that either inhibit, slow down or suppress the proliferation of fires (URL1). The FRs used today are of two different types: additive or reactive. Additive FRs are normally added to the product after polymerisation; thus they are not chemically bound to the plastic and can easily be released from the product (Schlabach et al. 2011). The reactive FRs, on the other hand, react chemically with the thermoplastic, and release to the environment is therefore less problematic (Schlabach et al. 2011; Papachlimitzou, 2012).

Today, halogenated and phosphorous flame retardants are the most frequently used FRs (Bergman et al. 2012). Structurally, brominated FRs (BFRs) usually consist of one or two phenyl rings with some of the hydrogens substituted by bromine. For instance, polybrominated diphenyl ethers (PBDEs) consist of two phenyl rings with 1-10 bromine atoms (Birnbaum and Cohen Hubal, 2006). They were among the first additive organic FRs used, and the peak production and usage occurred in the 1960s and 1970s (Boon et al. 2002). However, also non-phenylic BFRs exist, with hexabromocyclododecane (HBCDD) and dibromoethyl-dibromocyclohexane (DBE-DBCH) as the most widely used (Bergman et al. 2012).

Phosphorous FRs (PFRs) are compounds that includes phosphorous and different types of functional groups. They can also include covalent bounds to halogenated functional groups (e.g., tri(1-chloro-2-propyl) phosphate, TCIPP). PFRs can be found in lubricants, concrete and hydraulic fluids (Andresen et al. 2004; US EPA, 1985).

BFRs have low water solubility (although for some it is pH-dependent) and high octanol-water

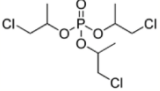
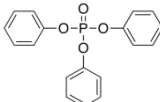
partition coefficients ( $\log K_{OW} \geq 4.4$ ) (Birnbaum and Staskal, 2004; Birnbaum and Cohen Hubal, 2006) as shown in Table 1. The corresponding values for PFRs are distinctly lower ( $\log K_{OW} < 5$ ) (Bergman et al. 2012) as shown in Table 2.

**Table 1: Structure and properties of BFRs analysed in this project<sup>a</sup>**

Compound	Name	Structure	Molecular formula	CAS no.	MW	$\log K_{OW}$	$K_{OC}$	Vp (Pa)
2,4,6-TBP	2,4,6-Tribromophenol		$C_6H_3Br_3O$	118-79-6	330.8	4.4	pH-dep.	2.00E-01
PBP	Pentabromophenol		$C_6HBr_5O$	608-71-9	488.59	5.2	pH-dep.	2.55E-03
TBBPA	Tetrabromobisphenol A		$C_{15}H_{12}Br_4O_2$	79-94-7	543.87	9.7	4.47E+06	1.88E-05
HBB	Hexabromobenzene		$C_6Br_6$	87-82-1	551.42	6.1	50300	1.14E-04
BEHTBP	Bis(2-ethyl-1-hexyl)tetrabromophthalate		$C_{24}H_{34}Br_4O_4$	706.14	706.15	9.3	2.88E+06	1.55E-11
DBDPE	1,2-Bis(2,3,4,5,6-pentabromophenyl)ethane		$C_{14}H_4Br_{10}$	84852-53-9	971.22	11	1.00E+07	n.a.
EHTBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate		$C_{15}H_{18}Br_4O_2$	183658-27-7	549.92	7.7	3.82E+05	3.71E-07
PBT	Pentabromotoluene		$C_7H_3Br_5$	87-83-2	486.62	5.2	60 200	6.00E-04
HBCDD	Hexabromocyclododecane		$C_{12}H_{18}Br_6$	3194-55-6	641.73	7.9	4.86E+05	1.04E-07
BTBPE	Benzene 1,1'-[1,2-ethanediylbis(oxy)]bis[2,4,6-tribromophenoxy]ethane		$C_{14}H_8Br_6O_2$	37853-59-1	687.64	8.3	7.92E+05	n.a.

<sup>a</sup>MW = molecular weight;  $K_{OW}$  = octanol-water coefficient; Vp = vapour pressure; calculated from log pressure in liquid phase ( $\log P_L$ ) values.  $K_{OC}$  = organic carbon – water partition coefficient. The acid dissociation coefficient ( $pK_a = -\log_{10} K_a$ ; only relevant for phenolic FRs) for 2,4,6-TBP, PBP and TBBPA is  $6.32 \pm 0.23$ ,  $4.43 \pm 0.33$  and  $7.7$  or  $8.5 \pm 0.10$ , respectively (values from Birnbaum and Staskal, 2004; Kolic et al. 2009; Schlabach et al. 2011; Bergman et al. 2012 and URL2).

**Table 2: Structure and properties of PFRs analysed in this project<sup>a</sup>**

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow}$	$K_{oc}$	Vp (Pa)
TCIPP	Tri(1-chloro-2-propyl) phosphate		C <sub>9</sub> H <sub>12</sub> O <sub>4</sub> Cl <sub>3</sub> P	13674-84-5	327.56	2.59	275	2.69E-03
TPHP	Triphenyl phosphate		C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	115-86-6	326.28	4.59	2630	8.37E-04

<sup>a</sup>MW = molecular weight;  $K_{ow}$  = octanol-water coefficient; Vp = vapour pressure; calculated from log pressure in liquid phase (log P<sub>L</sub>) values.  $K_{oc}$  = organic carbon – water partition coefficient. Values from Bergman et al. (2012).

**Transport and fate of FRs in the environment:** Highly brominated PBDEs have shown to degrade to lower brominated derivatives (Darnerud, 2003). The transformation of PBDEs in the atmosphere is an issue of concern, as less brominated PBDEs are known to be more toxic (de Wit, 2002; Harju et al. 2009). PBDEs have been detected globally, both close to point sources as well as far from their production, demonstrating long-range transport (LRT) potential (Birnbaum and Staskal, 2004; Kolic et al. 2009). Studies have primarily been carried out in North America, Europe and Japan (de Wit, 2002; Harju et al. 2009).

## 2.2 Perfluoroalkyl substances (PFASs)

PFASs are anthropogenic substances that have been used widely since the early 1950s due to surfactant properties (both lipo- and hydrophobic). Because of their unique properties (repelling both water and grease), PFASs are used in a variety of industry and consumer products, e.g. in paint, leather and textile coating, clothes, shoes and carpets, as lubricants in floor- and car waxes, and as aqueous fire-fighting foams (AFFFs) at airports and oil platforms (Kissa, 2001; Jensen and Leffers, 2008).

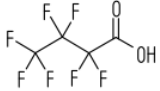









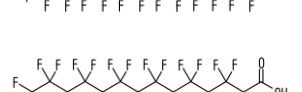
PFASs are also known to be persistent, bioaccumulative and toxic, and they distribute in the environment through LRT and water currents (Jensen and Leffers, 2008; Vierke et al. 2012). They are ubiquitously present, and are detected in wildlife even in remote areas (Giesy and Kannan, 2002; Kannan et al. 2002). The most studied PFASs, perfluorooctane sulfonate (PFOS) was classified as a substance of very high concern (SVHC) under REACH, and its use was prohibited in the EU in 2008 and added to the Stockholm Convention list in 2009 (KemI, 2009; Ahrens, 2010; Vierke et al. 2012).

The general formula of per-FASs is C<sub>n</sub>F<sub>2n+1</sub>R; thus, they consist of a fully fluorinated carbon chain and a functional group (R). Common functional groups include carboxylic acids (-CO<sub>2</sub>H; perfluoroalkyl carboxylic acids; PFCAs) or sulfonic acids (-SO<sub>3</sub>H; perfluoroalkyl sulfonic acids; PFASs). Poly-FASs have at least one C atom in the chain that is not fully fluorinated. Experiments have shown that both the number of F atoms as well as their location is important for the physiochemical properties of the individual substance (Kissa, 2001). The fluorine atoms (F) are attached to the carbon chain by a strong covalent bonds. As F has the highest electronegativity

(EN) in the whole periodic system (EN=3.98 on Pauling scale), PFASs are very persistent to natural degradation. It has been shown that PFASs resist to e.g. heat and hydrolysis, although some degradation from longer to shorter C-chains occur when exposed to UV light (Taniyasu et al. 2013).

Despite long time of PFASs usage, little attention was paid to the environmental aspects prior to the last decade (Kannan, 2011). Since then, more than 2500 research articles on properties, fate and occurrence have been published (Kannan, 2011). Although numerous environmental studies of PFASs (e.g. Prevedouros et al. 2006; Loos et al. 2009; Ahrens et al. 2009a; Ahrens et al. 2009b; Ahrens, 2010; Loos et al. 2010; Filipovic et al., 2013), there is a need of more screening studies to increase the knowledge about point sources and related problems. The current study focuses on fully (per-)fluorinated compounds, including PFCAs (Table 3), perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols, perfluorooctane sulfonamidoacetic acid (FOSAAs) (Table 4), and PFSAAs (Table 5).

**Table 3: PFCAs included in the current study**

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow, dry}$	Vp (Pa)
PFBA	Perfluorobutanoic acid		C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> H	45048-62-2	213.04	2.82	3890
PFPeA	Perfluoropentanoic acid		C <sub>4</sub> F <sub>9</sub> CO <sub>2</sub> H	2706-90-3	263.05	3.43	1349
PFHxA	Perfluorohexanoic acid		C <sub>5</sub> F <sub>11</sub> CO <sub>2</sub> H	92612-52-7	313.06	4.06	457
PFHpA	Perfluorheptanoic acid		C <sub>6</sub> F <sub>13</sub> CO <sub>2</sub> H	120885-29-2	363.07	4.67	158
PFOA	Perfluorooctanoic acid		C <sub>7</sub> F <sub>15</sub> CO <sub>2</sub> H	45285-51-6	413.08	5.30	53.7
PFNA	Perfluorononanoic acid		C <sub>8</sub> F <sub>17</sub> CO <sub>2</sub> H	72007-68-2	463.09	5.92	18.6
PFDA	Perfluorodecanoic acid		C <sub>9</sub> F <sub>19</sub> CO <sub>2</sub> H	73829-36-4	513.10	6.50	6.61
PFUnDA	Perfluoroundecanoic acid		C <sub>10</sub> F <sub>21</sub> CO <sub>2</sub> H	196859-54-8	563.11	7.15	2.19
PFDoDA	Perfluorododecanoic acid		C <sub>11</sub> F <sub>23</sub> CO <sub>2</sub> H	171978-95-3	613.12	7.77	0.741
PFTTrDA	Perfluorotridecanoic acid		C <sub>12</sub> F <sub>25</sub> CO <sub>2</sub> H	72629-94-8	663.13	-0.57	n.a.
PFTeDA	Perfluorotetradecanoic acid		C <sub>13</sub> F <sub>27</sub> CO <sub>2</sub> H	376-06-7	713.14	-0.99	n.a.



Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow, dry}$	Vp (Pa)
PFHxDA	Perfluoro-hexadecanoic acid		$C_{15}F_{31}CO_2H$	n.a.	813.16	n.a.	n.a.
PFOcDA	Perfluoro-octadecanoic acid		$C_{17}F_{35}CO_2H$	n.a.	913.18	n.a.	n.a.

MW = Molecular weight;  $K_{OW}$  = octanol-water coefficient; Vp = vapour pressure; calculated from log pressure in liquid phase (log  $P_L$ ) values. Values from Wang et al. (2011).



**Table 4: FOSAs, FOSEs, and FOSAAs included in the current study**

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow}$	Vp (Pa)
FOSA	Perfluorooctane sulfonamide		$C_8F_{17}SO_2NH_2$	754-91-6	499.18	5.62	0.245
FOSAA	Perfluorooctane sulfonamidoacetic acid		$C_8F_{17}SO_2NHCH_2CO_2$	n.a.	n.a.	n.a.	n.a.
EtFOSA	N-ethylperfluoro-1-octanesulfonamide		$C_8F_{17}SO_2NHCH_2CH_3$	4151-50-2	527.20	n.a.	5.71E-05
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid		$C_8F_{17}SO_2N(CH_2)_2CH_3CO_2$	n.a.	n.a.	n.a.	n.a.
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol		$C_8F_{17}SO_2N(CH_2)_2CH_2OH$	1691-99-2	571.25	n.a.	n.a.
MeFOSA	N-methylperfluoro-1-octanesulfonamide		$C_8F_{17}SO_2NHCH_3$	31506-32-8	n.a.	n.a.	n.a.
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid		$C_8F_{17}SO_2NCH_3CH_2CO_2$	n.a.	n.a.	n.a.	n.a.
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol		$C_8F_{17}SO_2N(CH_3)CH_2OH$	24448-09-7	557.22	n.a.	n.a.

MW = Molecular weight;  $K_{OW}$  = octanol-water coefficient; Vp = vapour pressure; calculated from log pressure in liquid phase (log  $P_L$ ) values. Values from Wang et al. (2011).

**Table 5: PFSAs included in the study**

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow}$	Vp (Pa)
PFBS	Perfluorobutane sulfonic acid		$C_4F_9SO_3H$	375-73-5 or 59933-66-3	300.12	3.90	631
PFHxS	Perfluorohexane sulfonic acid		$C_6F_{13}SO_3H$	355-46-4	400.14	5.17	58.9

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow}$	Vp (Pa)
PFOS	Perfluorooctane sulfonic acid		C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H	1763-23-1	500.16	6.43	6.76
PFDS	Perfluorodecane sulfonic acid		C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub> H	335-77-3	600.18	7.66	n.a.

MW = Molecular weight;  $K_{OW}$  = octanol-water coefficient; Vp = vapour pressure; calculated from log pressure in liquid phase (log  $P_L$ ) values. Values from Wang et al. (2011).

**Sources of PFASs:** WWTPs have been found to be a major source of PFASs in the environment (Filipovic et al. 2013, Loos et al. 2010). Other important sources of PFASs are atmospheric deposition, contaminated soil/sediment and landfills (Llorca et al. 2012).

**Transport, fate and occurrence in the environment:** PFASs distribute in the environment through LRT and water currents (Jensen and Leffers, 2008; Vierke et al. 2012). During transport, PFASs is partly bound to particles. Ahrens et al. (2009a) found that the northern part of the Atlantic ocean have moderate PFAS concentrations in the sub-surface water, whereas below-equator PFAS concentrations were below the detection limit. PFASs have been detected in >90% of the European rivers at concentrations between 3-1400 ng/L (Loos et al. 2009; Loos et al. 2010; Möller et al. 2010). PFASs have also been found in treated wastewater, tap water, and bottled drinking water (Llorca et al. 2012) as well as in humans and wildlife (e.g. minks, otters, polar bears; Giesy and Kannan, 2002; Kannan et al. 2002; Roos et al. 2013, Persson et al. 2013).

**Exposure and health aspects:** Drinking water, food packaging and food may contain PFASs (Boon et al. 2002; KemI, 2009; Thompson et al. 2011; Llorca et al. 2012). It has been estimated that 80% of the PFCAs historically produced have been emitted to the environment, and as a consequence, trace levels of PFASs are ubiquitously detected in humans (Prevedouros et al. 2006; Loos et al. 2009; Ahrens et al. 2009b). PFASs have been suggested to be toxic to humans and wildlife, e.g. carcinogenic and endocrine disrupting (Jensen and Leffers, 2008; Ahrens, 2010; Kannan, 2011). The toxicity is known to be related to chain length (long chains are more toxic), and the sulfonates (PFSAs) have been found to be more toxic than the PFCAs (Ulhaq et al. 2013a; Ulhaq et al. 2013b).

### 3. Materials and methods

The overall goal of this project was to carry out a screening of selected novel FRs as well as a number of PFASs in Swedish rivers and streams. We also aimed for an estimation of loadings of FRs and PFASs to the sea through Swedish river and stream transport. The plan was to give a snapshot of the situation during a short period of time, and for this purpose, grab samples was considered as the best sampling method. The rivers and streams were sampled in October 2013, and then extracted and analysed for FRs and PFASs at the POPs laboratory at IVM, SLU (Uppsala).

### 3.1 Chemicals

Solvents used were: Acetone (SupraSolv® for GC-ECD and FID), dichloromethane (DCM; SupraSolv®), isooctane (SupraSolv® for GC- ECD and FID), methanol (LiChrosolv® hypergrade for LC-MS) and toluene (SupraSolv® for GC), all purchased from Merck KGaA, Darmstadt, Germany. Acetic acid solution ( $\geq 99.7\%$ ), ethyl acetate (for pesticide residue analysis), ammonium acetate and ammonium hydroxide solution 28-30% were purchased from Sigma-Aldrich, Steinheim, Germany. Ethanol (95%) was purchased from Solveco, Rosersberg, Sweden. MilliPore water was available at the laboratory and filtered with MilliPak® 0.22  $\mu\text{m}$  filter.

Other laboratory consumables used were: boiling chips granules (2-8 mm) and glass wool (Merck KGaA), and glass beads (diameter $\approx$ 5 mm; Sigma-Aldrich). The FR sorbent XAD-2 was purchased from Supelco, Bellefonte, USA.

The following laboratory equipment was used: Biotage TurboVap™ II, Branson 5500 sonication bath, centrifuge 5810 from Eppendorf (Hamburg, Germany), glass columns from Werner Glas (inner diameter 3.5 cm, length 26.5 cm, width at in- and outlet 1 cm), nitrogen evaporator N-Evap™112 (from Organomation Associates, Inc., Berlin, USA), Oasis weak anion exchange (WAX) 6 cc cartridge 500 mg, 60  $\mu\text{m}$  (Waters, Wexford, Ireland), peristaltic pump MasterFlex® (model 77800-62 Cole-Parmer easyload®3 from Barnant Company, Barrington, USA), pH-meter VWR pHenomenal™, rubber tubing from Saint Gobain (MasterFlex® 06404-15 Norprene®, 5 mm inner diameter), Shimadzu TOC-VCPH and ASI autosampler, silicone tubing from Saint Gobain (Platinum-curved silicone MasterFlex® 96420-15, 5 mm inner diameter) and Whatman™ glass microfibre filters (GF, 47 mm  $\varnothing$ , GE Healthcare UK Limited, Buckinghamshire, United Kingdom).

**References compounds used for FRs:** Native compounds ( $n=12$ ) used in the calibration samples were in the range of 0.25  $\text{pg } \mu\text{L}^{-1}$  to 450  $\text{pg } \mu\text{L}^{-1}$ . The compounds included in the calibration were 2,4,6-TBP, PBP, TBBPA, HBB, BEHTBP, DBDPE, EHTBB, PBT,  $\alpha$ -HBCDD, TCIPP, TPHP, and BTBPE. More information on these compounds as well as chemical formulas and their full names can be found in Tables 1 and 2. The samples were spiked with the isotope labelled internal standard (IS) BDE99. This was done in order to be able to identify and correct for losses during sample processing. Lastly, the injection standard (InjS) Mirex was added to all samples prior to analysis. The ISs and Mirex were purchased from Wellington laboratories, Ontario, Canada.

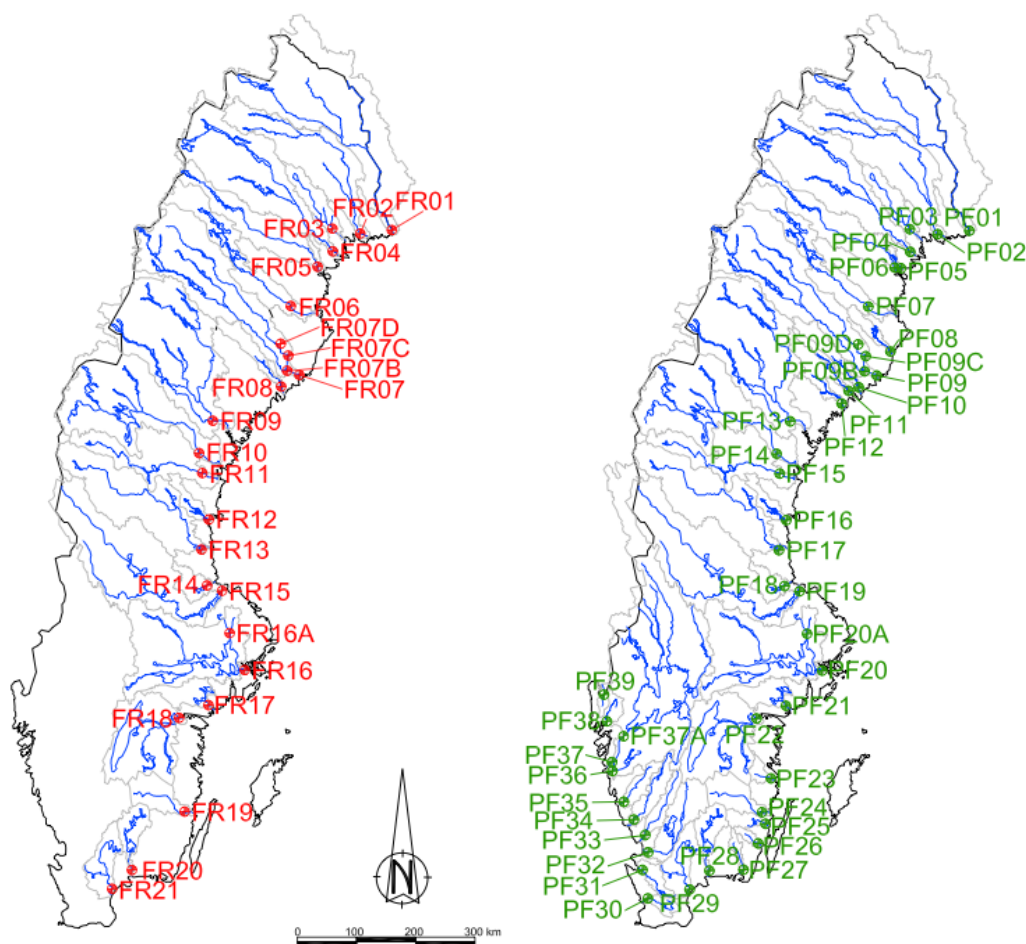
**Reference compounds used for PFASs analysis:** Native compounds ( $n=25$ ) used in the calibration samples were in the range of 0.05  $\text{pg } \mu\text{L}^{-1}$  to 40  $\text{pg } \mu\text{L}^{-1}$  (i.e. PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFTeDA, PFHxDA, PFOcDA, FOSA, FOSAA, EtFOSA, EtFOSAA, EtFOSE, MeFOSA, MeFOSAA, MeFOSE, PFBS, PFHxS, PFOS, PFDS). Mass-labelled ( $^{13}\text{C}$ ) IS ( $n=14$ ) included PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, FOSA, MeFOSAA, MeFOSE, EtFOSAA, N-EtFOSE, PFHxS, PFOS. All reference standards were purchased from Wellington laboratories, Ontario, Canada. More information on these compounds as well as chemical formulas and full names can be found in Tables 3, 4 and 5.

### 3.2 Sampling sites

The goal was to screen a variety of different water bodies, including small and large streams/ivers as well as representatives of both urban and remote areas. Sampling sites were selected on the basis of the following criteria. Firstly, catchment size and riverine discharge was of vital importance. All rivers with a catchment size of 4000 km<sup>2</sup> or more were included. Secondly, rivers of densely populated parts of Sweden were prioritized, as urban areas are supposed to have higher levels of both FRs and PFASs. Additionally, some rivers where high values could be expected (due to e.g., large-scale industrial activities) were added. An overview of the sampling sites is presented in Figure 1, and more details on the sites are given in Tables A1 and A2 (Appendix A).

For the FRs, 25 sampling sites (representing 23 rivers) were chosen from Haparanda (Torne älv) in the north to Kristianstad (Helge å) in the south end of the east coast of Sweden. Three upstream sites were included (Vindelälven at Krycklan and at Rödånäs, and Ume älv at Gubböle) to screen for upstream variation.

The screening of PFASs included 44 sites representing 41 rivers, from Haparanda (Torne älv) in the north to Kristianstad (Helge å) in the south of the Swedish east coast along with some samples from the west coast. Four upstream sites were included (Vindelälven at Krycklan and at Rödånäs, Ume älv at Gubböle and Göta älv near Trollhättan). All rivers screened for FRs were also included in the PFASs screening. All samples were taken by IVM (SLU) or by help from people involved in the national monitoring program "Flodmynningar" (administrated by IVM, SLU).



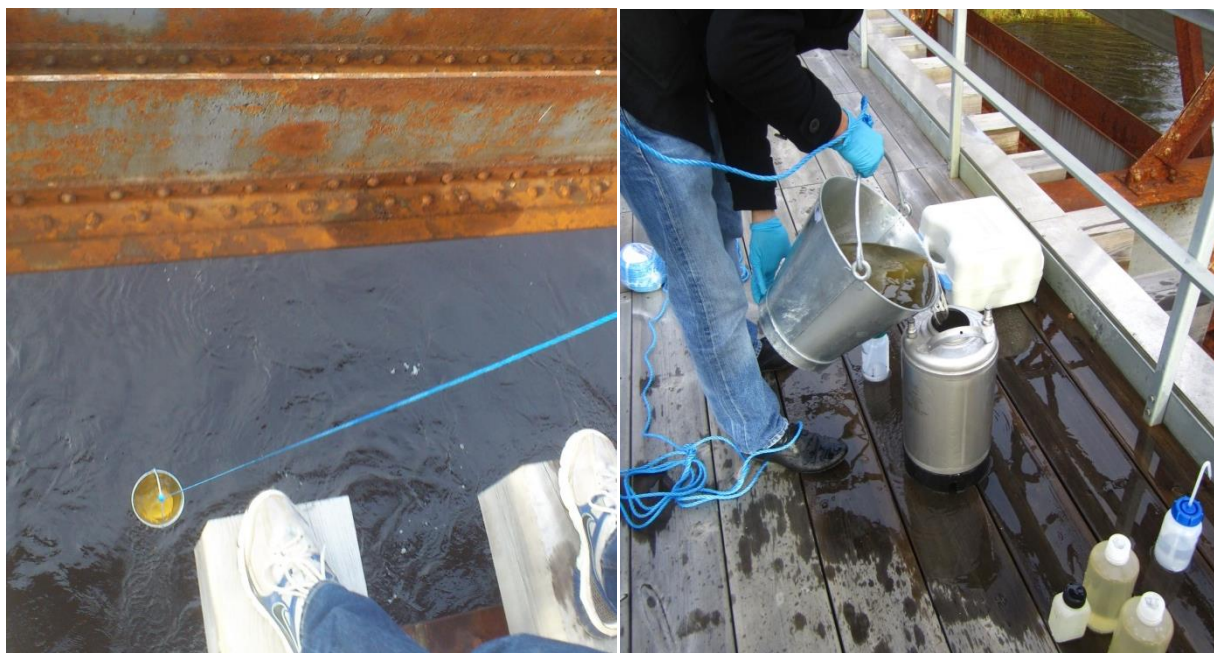
**Figure 1:** Sampling sites for FRs (on the left) and PFASs (on the right). Rivers are displayed in blue, watersheds in grey. Details for the sampling and the sampling sites are given in Tables A1 and A2 (Appendix).

### 3.3 Sample collection

The FRs samples were collected in POP-cans (12 L) (3 US gallons/12 L; Sharpville container/NSF Component®). Samples for PFASs and suspended particulate matter (SPM) were collected in polypropylene (PP) bottles (1 L; VWR International, Radnor, India). The sampling took place October 1-9, and October 25 (Fyrisån), 2013 (for more details see Table A1 in the Appendix).

All samples were collected according to techniques used in previous screening (Loos et al., 2009; Loos et al., 2010). Prior to the sampling, all stainless steel sampling equipment was rinsed three times with ethanol, Millipore water, and acetone. In the field, buckets, sample bottles and POP-cans were rinsed three times with river water prior to the sampling. A stainless steel bucket connected to a 30 m PP rope was used for the water sampling. All sampling was performed in the middle of the stream (from the upstream side of a bridge), or from the shore when no bridges were available (Figure 2). However, where bridges with just one pillar were used while sampling, samples were taken in the middle between pillar and the shore. Sampling from shores was needed in only two cases (Ume älv near Gubböle and Indalsälven near Timrå), and then the sampling was performed

from a jetty. All FR sites were also sampled for total organic carbon (TOC) and SPM. After sampling, pH and water temperature were measured at each site. Bottles for PFASs, SPM and TOC were wrapped in aluminium foil after sampling in order to prevent exposure to direct sunlight. TOC bottles were stored in a cooling box. All samples were brought to the laboratory within 3 days and then stored at +4 °C. All FR extractions were performed within one month after sample collection, whereas the extractions for PFASs were done within two months.



**Figure 2:** Bucket sampling at Råne älv, Niemisel.

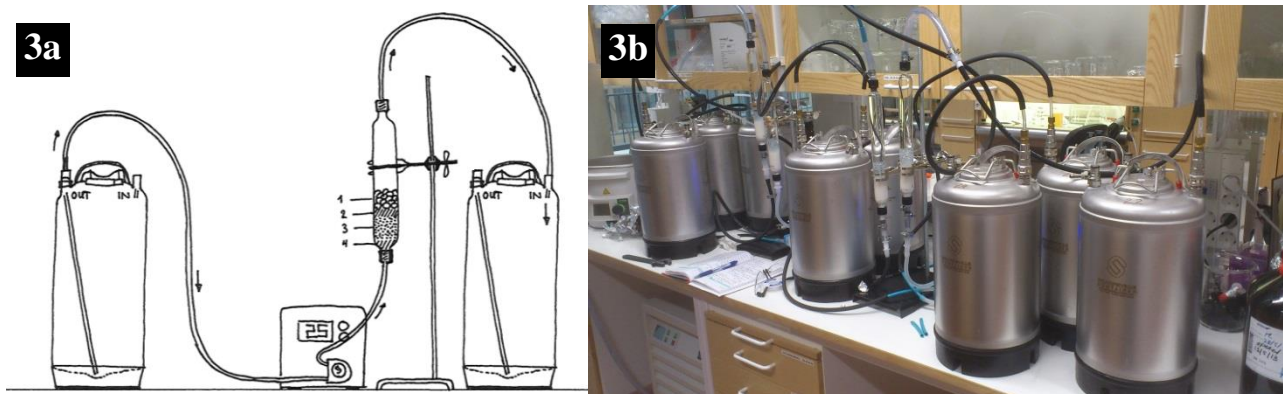
### 3.4 Extraction of FRs and PFASs

**Solid-phase extraction (SPE) for FRs:** Amberlite XAD-2 was pre-cleaned in a Soxhlet apparatus in two steps (methanol 48 hours, ethyl acetate 48 hours), then dried using nitrogen gas (N<sub>2</sub>) and finally stored at -20 °C until analysis. Extraction glass columns were prepared as follows (from bottom and up): 0.5 g glass wool (GW), 20.0 g XAD-2, 0.5 g GW, and 34 g of glass beads. Each sample was spiked with 100 µL (80 pg µL<sup>-1</sup>) of IS, directly into the POP-can. After spiking, the POP-cans were manually shaken 3x30 seconds in order to effectively distribute the IS. Figure 3 illustrates the SPE set up for the FRs. A peristaltic pump was used to pre-clean the tubing (2.5 L MilliPore water) prior to connection to the glass column. The sample was then pumped through the glass column at a speed of 10 (during start-up) to 25 rpm, which corresponds to a flow rate of 0.65 mL s<sup>-1</sup>. This was followed by drying the XAD-2 adsorbent with N<sub>2</sub>-gas flow for 45 minutes and eluting the analytes using 2x70 mL DCM. The eluted extracts were collected in round-bottom flasks, which were sealed and stored at -20 °C until volume reduction. Elution was performed the same day as the extraction occurred.

A Biotage TurboVap™ was used to reduce the volume to 1 mL (water temperature 40 °C; N<sub>2</sub>-pressure 8 bar). To remove water residues, the extract was then passed through a column filled with



1 g Na<sub>2</sub>SO<sub>4</sub> (pre-cleaned with DCM) and eluted with 6 mL DCM. Then, the extract was reduced to 1 mL using a N<sub>2</sub>-stream (N-Evap™112) and transferred to a 1 mL amber glass vial. The injection standard (Mirex) was added, and the samples were stored at -20 °C until instrumental analysis.

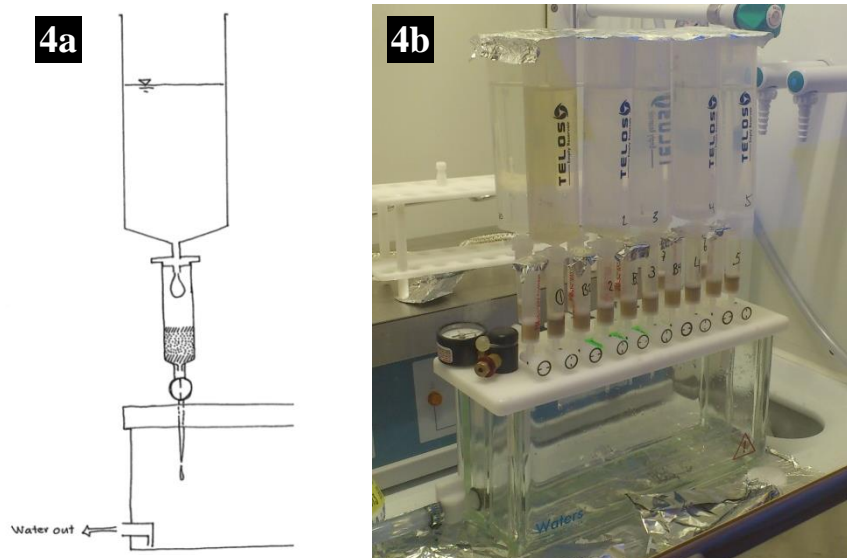


**Figure 3a:** Drawing of the extraction set up for the FRs. 1: glass beads; 2 and 4: GW; 3: XAD-2. **Figure 3b:** The SPE set up with four extractions running in parallel.

**Solid-phase extraction for PFASs:** As PFASs are relatively water soluble, a filtration step was included prior to the SPE. Filtration was done using a glass fibre filter (GFF with the grade GF/C; diameter 47 mm, 1.2 µm pore size, Whatman), Werner Glass filtration equipment, and vacuum. All glass material was heated at 400 °C for four hours and carefully cleaned using methanol prior to use. After filtration, the GFF was packed in aluminium foil and stored in a desiccator in order to remove water. GFFs were weighted before and after drying, but not analysed for PFASs. After filtration, the samples were divided into 2 x 0.5 L and stored at +4 °C until SPE.

The PFASs were extracted using Oasis weak anion exchange (WAX) 6cc cartridges (500 mg, 60 µm) and a SPE workstation as described elsewhere (Ahrens et al. 2009a). The extraction set-up for PFASs is shown in Figure 4a and 4b. Prior to the SPE, each water sample was spiked with 100 µL IS (20 pg µL<sup>-1</sup>), and cartridges and extraction materials were preconditioned (three steps using 4 mL ammonium hydroxide buffer, 4 mL methanol, and 4 mL MilliPore water). The flow during the sample extraction step was low (one drop per second).

After the extraction, the cartridges were washed with ammonium acetate buffer, and the cartridges were dried by centrifugation. The target analytes were eluted using 4 mL methanol (for FOSAs, FOSEs, FOSAAs) and 4 mL 0.1% ammonium hydroxide buffer (for PFCAs, PFSAs). The extracts were collected in 15 mL PP tubes and the volume was reduced to 1 mL using the nitrogen evaporator N-Evap™112. Then, 10 µL InjS was added (200 pg µL<sup>-1</sup>), and the samples were stored at -20°C until instrumental analysis.



**Figure 4a.** Drawing of the SPE set-up of for PFASs. **Figure 4b.** Picture of the SPE for the PFASs.

### 3.5 Instrumental analysis and quantification

**Gas chromatography tandem mass spectrometry (GC-MS/MS):** All FR extracts were analysed for the FRs listed in Tables 1 and 2 using gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) according to in-house methods (IVM, SLU). The GC-MS/MS was an Agilent Technologies system (GC 7890A coupled to a Triple Quad 7000). The calibration curve was set up using seven FR calibration solutions at concentrations of 0.25, 1.25, 6, 30, 150, 300 and 450 ng mL<sup>-1</sup>.

**Liquid chromatography tandem mass spectrometry:** All PFAS extracts were analysed for the compounds listed in Tables 3, 4 and 5, using high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) according to methods described by Ahrens et al. (2009a). The LC-MS/MS was an Agilent Technologies system (LC 1200 series and coupled to a 6460 Triple Quad). A calibration curve was set up using six PFAS calibration solutions at concentrations 0.05, 0.25, 1.0, 4.0, 8.0 and 40 ng mL<sup>-1</sup>.

**Quantification:** The quantification was done using the isotope dilution method and the software used was Agilent QQQ MassHunter and Oracle™ OpenOffice. For a positive identification, retention time agreement with calibration standard was required, quantifier/qualifier ratio should be within  $\pm 20\%$  of the ratio in the calibration standard, and the signal to noise (S/N) ratio had to be  $\geq 3$ .

**Quality Assurance/Quality control (QA/QC):** For the FRs, two field blanks were used for calculating the method detection limit (MDL) and method quantification limit (MQL). For the PFASs, a total of five laboratory blanks were used.

MDLs and MQLs were determined as described by Simonsen (2005). The blank concentrations



were used to calculate the MDL using eq. 1:

$$MDL = mean_{\text{blanks}} + 3 \cdot SD_{\text{blanks}} \quad (1)$$

where  $mean_{\text{blanks}}$  is the mean value of the blanks, and  $SD_{\text{blanks}}$  is their standard deviation. If the substance was not detected in the blanks, the MDL was calculated from the lowest calibration standard. MQL was calculated from the MDL, using eq. 2:

$$MQL = \frac{10 \cdot MDL}{3} \quad (2)$$

**Deviations from the contract:** The following compounds were included in the contract but not analyzed for: 2,4-DBP, TPP, Declorane plus (syn and anti), PFPeS, PFHpS, and PFNS. On the other hand, we targeted for some bonus compounds: BEHTBP, BTBPE, DBDPE, ETHBB, PBT, TBBPA, and TCIPP.

## 4. Results and discussion

### 4.1 Quality assurance and quality control (QA/QC)

Recoveries for the PFASs are compiled in Table 6. For FRs, the recovery (of BDE99) was  $72 \pm 0.4\%$ . The MDLs and MQLs for the FRs and PFASs are listed in Tables 7 and 8, respectively.

**Table 6:** Recoveries of PFASs.

<b>Internal Standard:</b>	<b>PFBA</b>	<b>PFHxA</b>	<b>PFOA</b>	<b>PFNA</b>	<b>PFDA</b>	<b>PFUnDA</b>	<b>PFDoDA</b>
Recovery (%)	$105 \pm 5$	$91 \pm 19$	$110 \pm 21$	$106 \pm 20$	$106 \pm 32$	$101 \pm 32$	$89 \pm 38$

<b>Internal Standard:</b>	<b>FOSA</b>	<b>MeFOSAA</b>	<b>MeFOSE</b>	<b>EtFOSAA</b>	<b>EtFOSE</b>	<b>PFHxS</b>	<b>PFOS</b>
Recovery (%)	$94 \pm 31$	$117 \pm 28$	$59 \pm 10$	$109 \pm 28$	$53 \pm 10$	$94 \pm 3$	$110 \pm 21$

**Table 7:** FRs: Method detection limits (MDLs), method quantification limits (MQLs) and mean amounts in blanks

<b>Substance</b>	<b>Blank (ng)</b>	<b>MDL (ng L<sup>-1</sup>)</b>	<b>MQL (ng L<sup>-1</sup>)</b>
2,4,6-TBP	n.d.	0.8	2.5
PBP	0.6	0.2	0.8
TBBPA	n.d.	0.2	0.5
HBB	n.d.	0.03	0.1
BEHTBP	3.9	2.0	6.8
DBDPE	700	220	720

Substance	Blank (ng)	MDL (ng L <sup>-1</sup> )	MQL (ng L <sup>-1</sup> )
EHTBB	6.3	3.3	11
PBT	n.d.	0.03	0.1
HBCDD	20	9.9	33
TCIPP	504	142	476
TPHP	117	37	124
BTBPE	n.d.	0.8	2.5

n.d. = not detected.

**Table 8:** PFASs: Method detection limits (MDLs), method quantification limits (MQLs) and mean amounts in blanks

Substance	Blank (ng)	MDL (ng L <sup>-1</sup> )	MQL (ng L <sup>-1</sup> )
PFBA	0.029	0.20	0.77
PFPeA	n.d.	0.030	0.10
PFHxA	0.058	0.64	2.1
PFHpA	n.d.	0.030	0.10
PFOA	0.051	0.17	0.58
PFNA	n.d.	0.064	0.21
PFDA	n.d.	0.030	0.10
PFUnDA	n.d.	0.036	0.12
PFDoDA	n.d.	0.030	0.10
PFTriDA	n.d.	0.030	0.10
PFTeDA	0.030	0.060	0.20
PFHxDA	n.d.	0.030	0.10
PFOcDA	n.d.	0.030	0.10
FOSA	n.d.	0.030	0.10
FOSAA	n.d.	0.030	0.10
EtFOSA	n.d.	0.030	0.10
EtFOSAA	n.d.	0.030	0.10
EtFOSE	0.058	0.35	1.2
MeFOSA	n.d.	0.030	0.10
MeFOSAA	n.d.	0.060	0.20
MeFOSE	0.061	0.31	1.0
PFBS	n.d.	0.030	0.10
PFHxS	n.d.	0.030	0.10
PFOS	n.d.	0.030	0.10
PFDS	n.d.	0.030	0.10

n.d. = not detected.

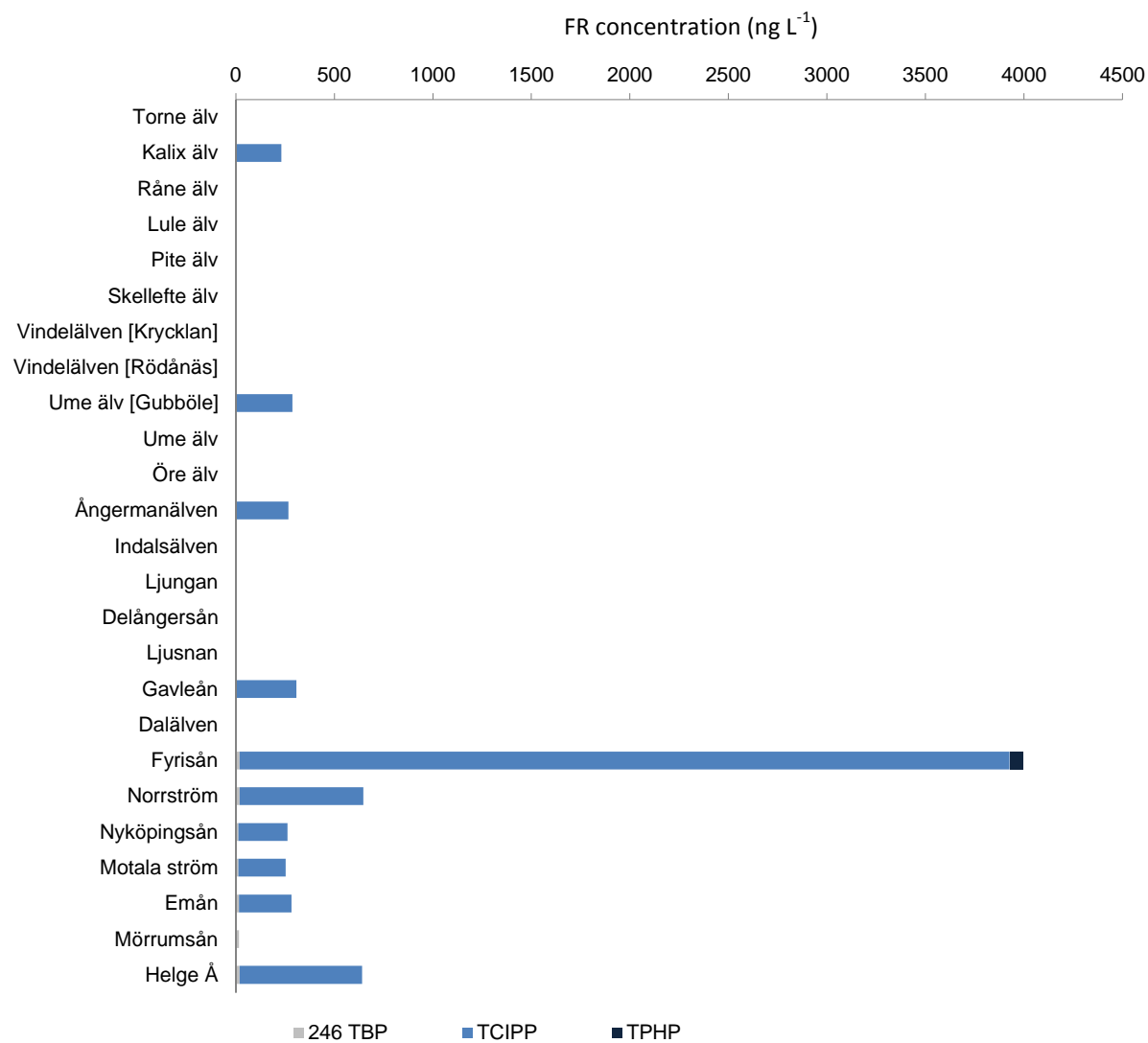
**Blanks:** Levels in PFAS blanks were in general low ( $<1 \text{ ng L}^{-1}$ ; Table 8). Levels in FR field blanks were occasionally high for several FRs (e.g. DBDPE, TCIPP and TPHP) resulting in high MDLs, while the elution blank showed lower values. A possible explanation for the high values in the field blanks is the presence of FRs in the Millipore water processed in the field blanks; however not in real samples.

#### 4.2 Flame retardants (FRs)

Detectable levels of FRs were found at 11 out of 25 sampling sites. In total, levels of 3 FRs could be determined (2,4,6-TBP, TCIPP, and TPHP), while BEHTBP, EHTBB, HBCDD, PBP, PBT, BTBPE, DBDPE, HBB, and TBBPA were all below MDL or not quantified due to interfering chromatographic peaks (Table 7). The levels of FRs are shown in Figure 5, and the raw data are given in Table A3 (Appendix A). The mean  $\Sigma$ FRs level of all sampled rivers was  $288 \text{ ng L}^{-1}$ . The main FR was TCIPP, which was detected at 40% of the sampling sites. The compound 2,4,6-TBP showed a spatial pattern with higher levels in river draining southern areas.

The highest levels of  $\Sigma$ FRs were observed in Fyrisån ( $3993 \text{ ng L}^{-1}$ ) followed by Norrström ( $647 \text{ ng L}^{-1}$ ). Reference values for WWTP in Sweden and other countries can be found in Marklund et al., 2005, Reemtsma et al., 2006; Martínez-Carballo et al., 2007, and levels of FRs in other European rivers are reported in van der Veen and de Boer, 2012, Martínez-Carballo et al., 2007, Andresen et al., 2004, Bacaloni et al., 2007, Regnery and Püttmann, 2010. Influence of wastewater is the likely explanation for the high FR levels in Fyrisån, as the sample was taken downstream the Uppsala municipality WWTP.

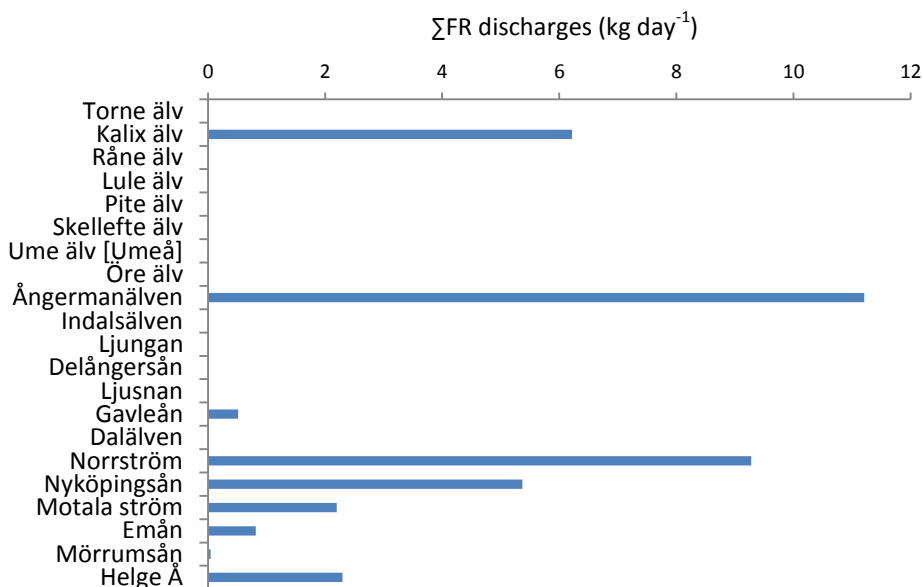
Estimates of daily loads of FRs to the Baltic Sea were calculated using of the snapshot FR concentrations together with the daily average riverine water discharge (based on data from 2002 to 2012 obtained from SMHI via *Datavärdskapet för sjöar och vattendrag*, IVM, SLU; Table 9 and Figure 6). As the sampling was a one-time snapshot for screening purposes, these values should be interpreted with great care. The total riverine input of the targeted FRs into the Baltic Sea was  $38 \text{ kg day}^{-1}$ . The main FR was TCIPP, which accounted for around 89% of the total FR load. Among the rivers, Ångermanlandsälven and Norrström showed the highest loads of FRs to the Baltic Sea, with a daily amount of  $11$  and  $9 \text{ kg day}^{-1}$ , respectively. It should be noted, that the targeted FRs represent only novel FRs and do not include e.g. historically more important FRs such as the PBDEs. Therefore, the reported loads of  $\Sigma$ FRs are not representative for all FRs emitted in Sweden.



**Figure 5:** Levels of FRs (ng L<sup>-1</sup>) at the different sampling stations, from north (upper) to south (lower). Absence of bar indicates that all FRs were <MDL.

**Table 9:** Discharge of ΣFRs from Swedish rivers to the Baltic Sea (kg day<sup>-1</sup>)

Kalix älv	Ångerman- älven	Gavleån	Norrström	Nyköpingsån	Motala ström	Emån	Helge å
6.2	11.2	0.5	9.3	5.4	2.2	0.8	2.3
<b>ΣFRs to the Baltic Sea</b>		<b>Fyrisån</b>					
38		3.5					



**Figure 6:** Discharge of  $\Sigma$ FRs from Swedish rivers ( $\text{kg day}^{-1}$ ). Absence of bar indicates that all FRs were  $< \text{MDL}$ .

#### 4.3 Perfluoroalkylated substances (PFASs)

All sites had detectable levels of PFASs (Figures 7 and 8; raw data in Table A4, Appendix A). The mean  $\Sigma$ PFAS levels of all sampled rivers was  $9.5 \text{ ng L}^{-1}$  and the median  $4.2 \text{ ng L}^{-1}$ , and the highest mean values were found for PFBS, PFHxS, and PFBA ( $2.1$ ,  $1.9$ , and  $1.4 \text{ ng L}^{-1}$ , respectively). Approximately 80% of the sampled sites had concentrations of  $\leq 10 \text{ ng L}^{-1}$ , and for 11% of the rivers, the levels were  $< 1 \text{ ng L}^{-1}$ . The highest  $\Sigma$ PFAS levels were found in Ångermanälven, Delångersån, Fyrisån, and Emån with values ranging from 27 to  $60 \text{ ng L}^{-1}$ . The levels in the Swedish rivers were in the lower end of those found in other European rivers (Ahrens et al., 2009b; McLachlan et al., 2007), where even single compounds occasionally exceed the  $\Sigma$ PFAS levels in Swedish rivers, e.g. Rhone ( $116 \text{ ng L}^{-1}$  PFOA), Seine ( $97 \text{ ng L}^{-1}$  PFOS) and Po ( $200 \text{ ng L}^{-1}$  PFOA) (McLachlan et al., 2007; Loos et al., 2009).

The nine rivers that showed  $\Sigma$ PFAS concentrations  $> 10 \text{ ng L}^{-1}$  (Ume älv at Gubböle, Ångermanälven, Delångersån, Gavleån, Fyrisån, Norrström, Emån, Helge å and Rönneån) have large variability in catchment size, population density and geographical location. Ångermanälven has the third largest watershed of all rivers screened, whereas Delångersån is one of the smallest catchments. The Norrström sampling site is located in the Stockholm municipality, whereas the Emån watershed is a sparsely populated area. Rönneån is the only river among these nine that is located in the western part of Sweden.

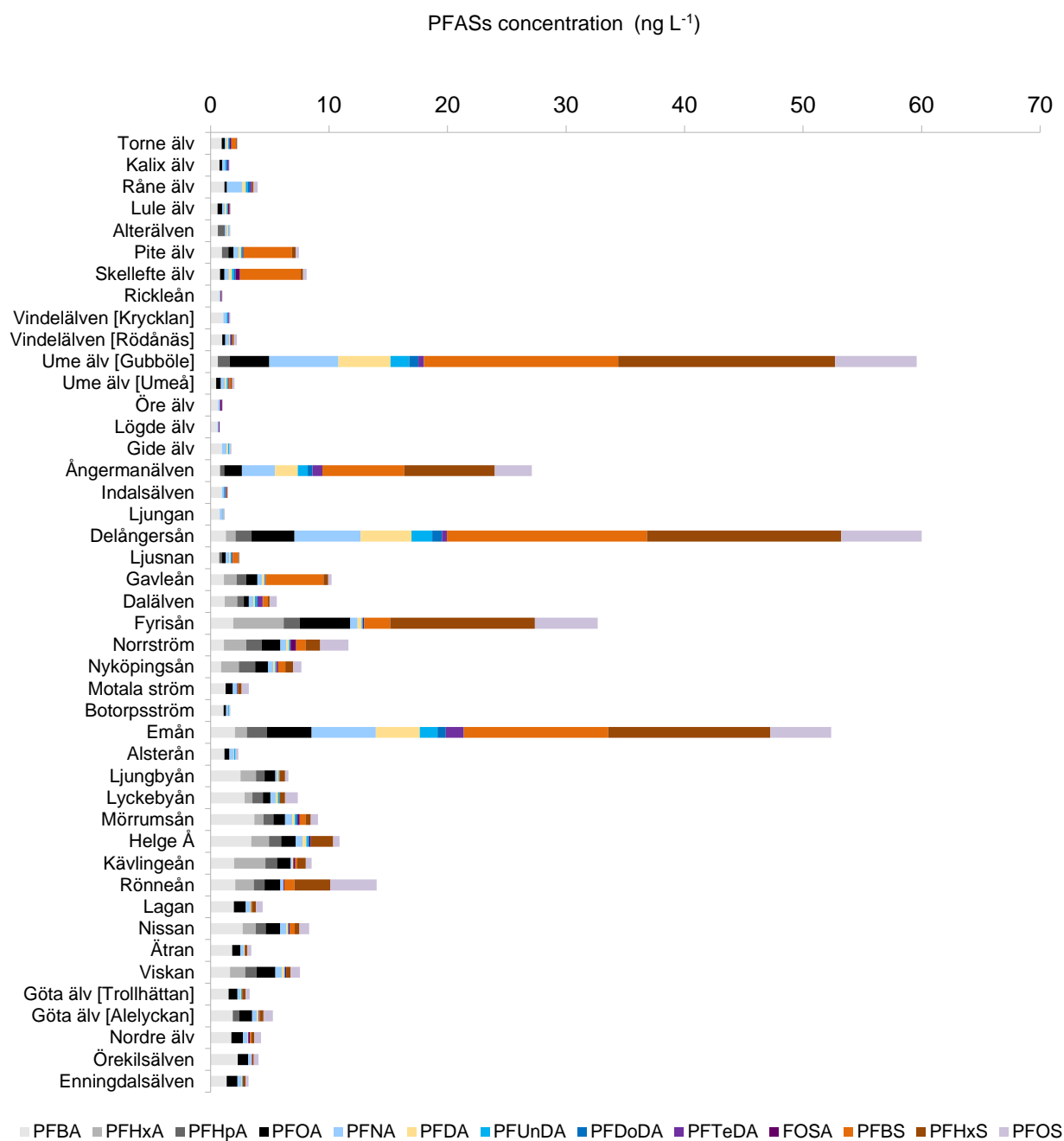
Among the PFASs screened for in this project, PFOS is the only one that is banned from usage in the EU. The maximal average concentration (European quality standards; AA-EQS) for inland surface waters on an annual basis is  $0.65 \text{ ng L}^{-1}$  (Directive 2013/39/EU). This value was exceeded at 12 out of 44 screened sites (representing 41 rivers), both draining small and large watersheds (Figure 9). The maximum allowable concentration environmental quality standard (MAC-EQS) for PFOS in inland surface waters is  $36\,000 \text{ ng L}^{-1}$ .

**Daily discharges of PFASs:** Estimates of daily loads of PFASs using the snapshot PFAS concentrations and river water discharges (SMHI) are shown in Figure 10. In these calculations, upstream sampling sites (e.g. Vindelälven, Fyrisån and Göta älv near Trollhättan) are not included. Ångermanälven showed the highest loads with >1 kg PFASs per day. Sites with higher PFAS concentrations, such as Delångersån and Emån, showed lower loads due to their lower water discharge. The total riverine input of all PFASs into recipient seas was calculated to 3.2 kg day<sup>-1</sup> in the current study (1150 kg yr<sup>-1</sup>).

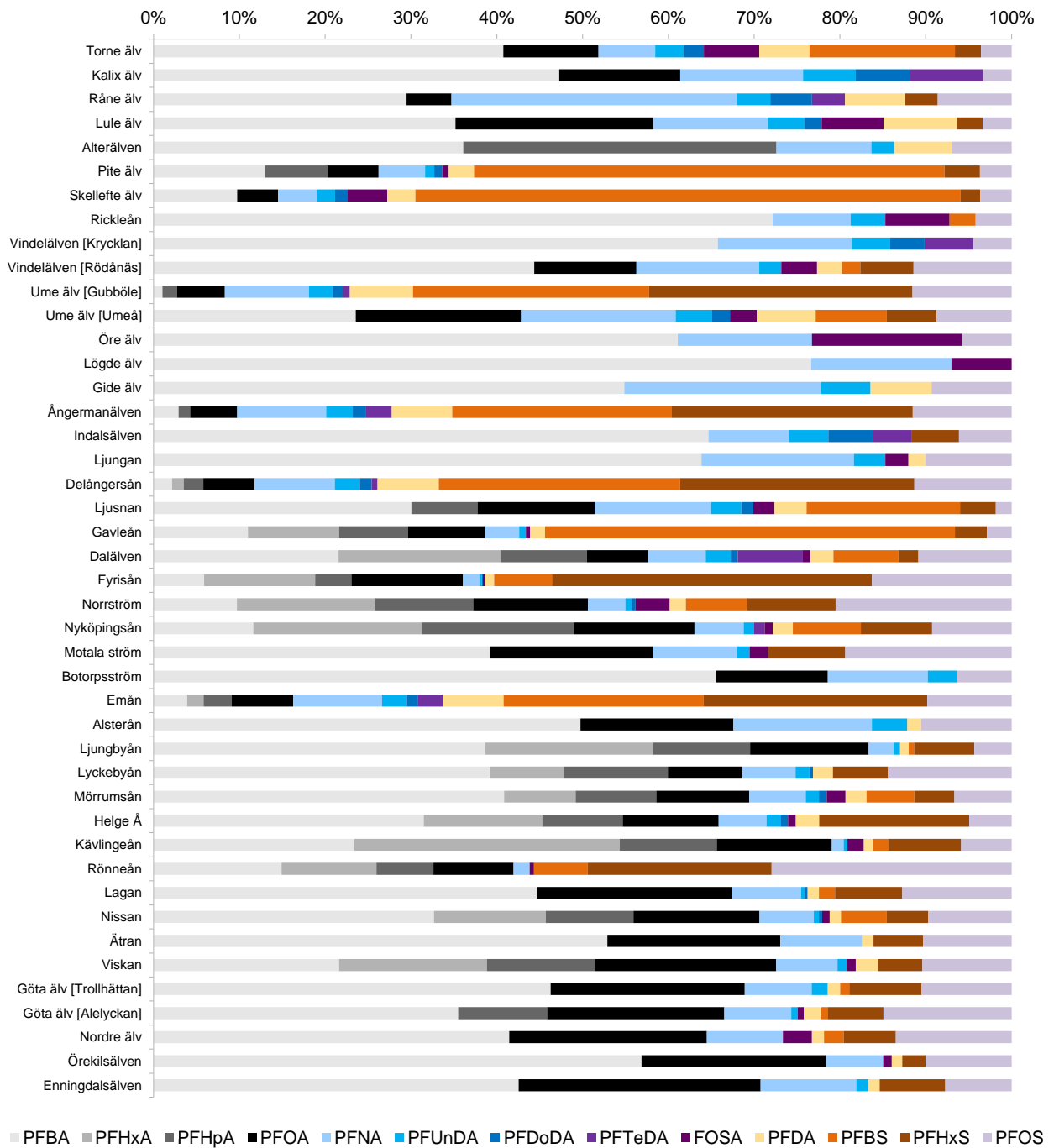
**PFASs composition:** Streams in the north (e.g. Alterälven, Öre älv, Gide älv, Lögde älv and Ljungan) showed in general higher fractions of the longer chained PFCAs (i.e. PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA) whereas in the south the fractions of PFHpA and PFOA were higher. Almost all sites on the west coast had a contribution of PFOA and PFOS that was >20% and >30% of the ΣPFASs, respectively, whereas corresponding values on the east coast were both <20%.

**Sources of PFASs:** The rivers with the highest ΣPFAS levels were Ume älv at Gubböle, Ångermanälven, Delångersån, Fyrisån and Emån. All of these except Fyrisån showed close resemblance in PFASs composition (Figure 11) indicating a common source type. The fraction of PFOS was ~10%, PFHxS ~30%, PFOA ~8%, and the sum of long-chained PFCAs (PFNA, PFDA, PFUnDA and PFDoDA) ~20%, whereas the fraction of short-chained PFCAs also was similar but increased towards the south.

The reasons for these similarities and dissimilarities are not fully understood. It could be due to influence by a common type of point source, such as a WWTP. Ume älv (Gubböle) and Delångersån were sampled downstream a nearby WWTPs, although the WWTP just upstream Gubböle is a small plant (Figure 12). For the other two rivers, WWTPs cannot explain the high levels and similar patterns. Moreover, Fyrisån that was sampled just downstream the Uppsala WWTP, showed a different PFAS composition than the others (Figure 11) with higher fractions of short-chained PFCAs and longer-chained PFCAs (high fractions of PFHxA, PFOA, PFHxS and PFOS) than the other sites. Emån has had several issues with its water quality. Upstream the sampling site, the former paper mill of Emsfors (closed down in 1989) and a military training area are located. However, no ongoing industrial activities are found on-site today. In summary, the explanation for the similarities and dissimilarities seen among the rivers with high levels is complex and need more detailed studies to get further insight.

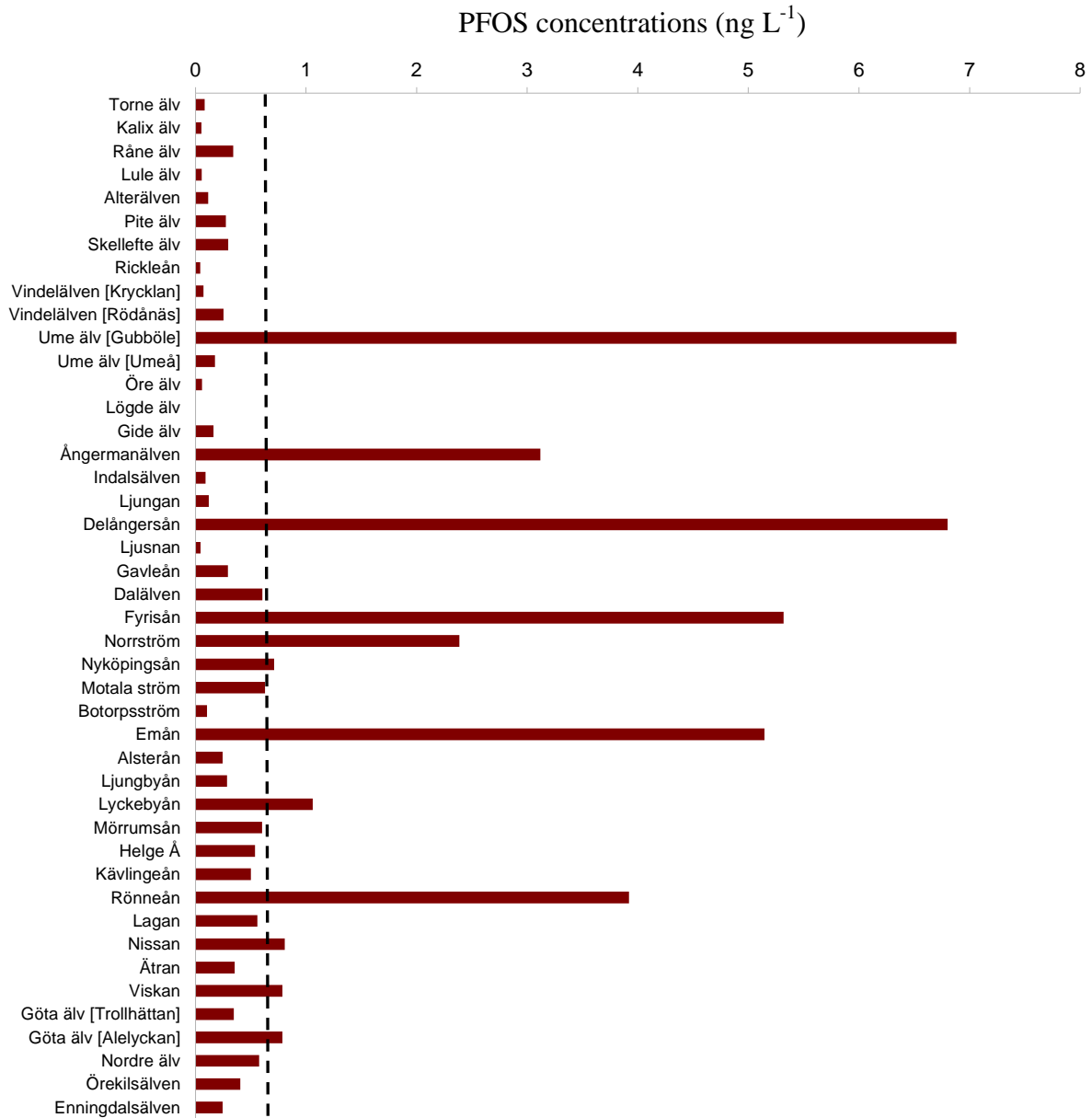


**Figure 7:** Levels of PFASs at the 44 sampling sites (ng L<sup>-1</sup>; representing 41 rivers) from north (upper) to south (lower) until Helge å, then going to the west coast from south to north.

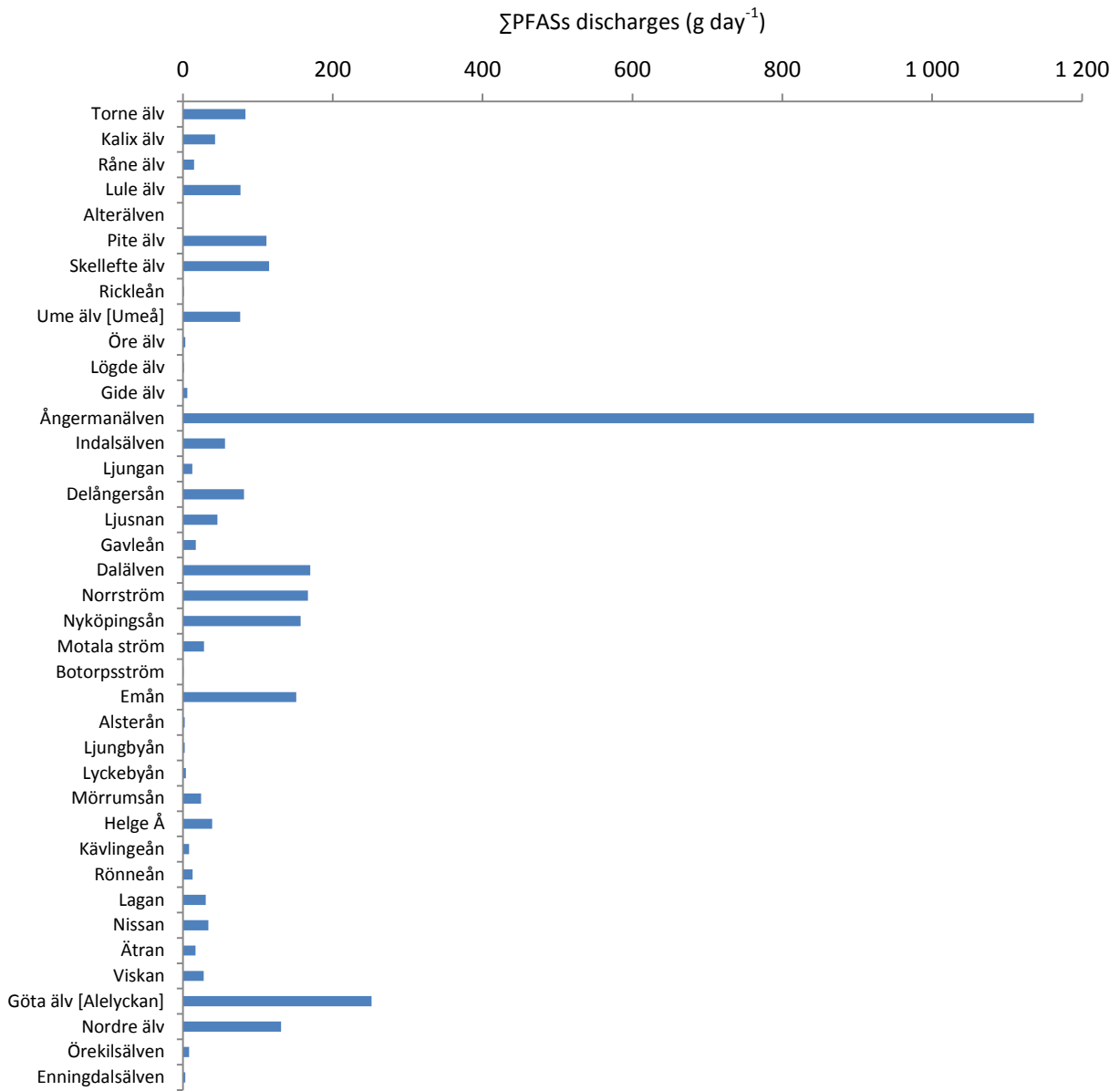


**Figure 8:** Composition of the detected PFASs at the various sampling sites (%)

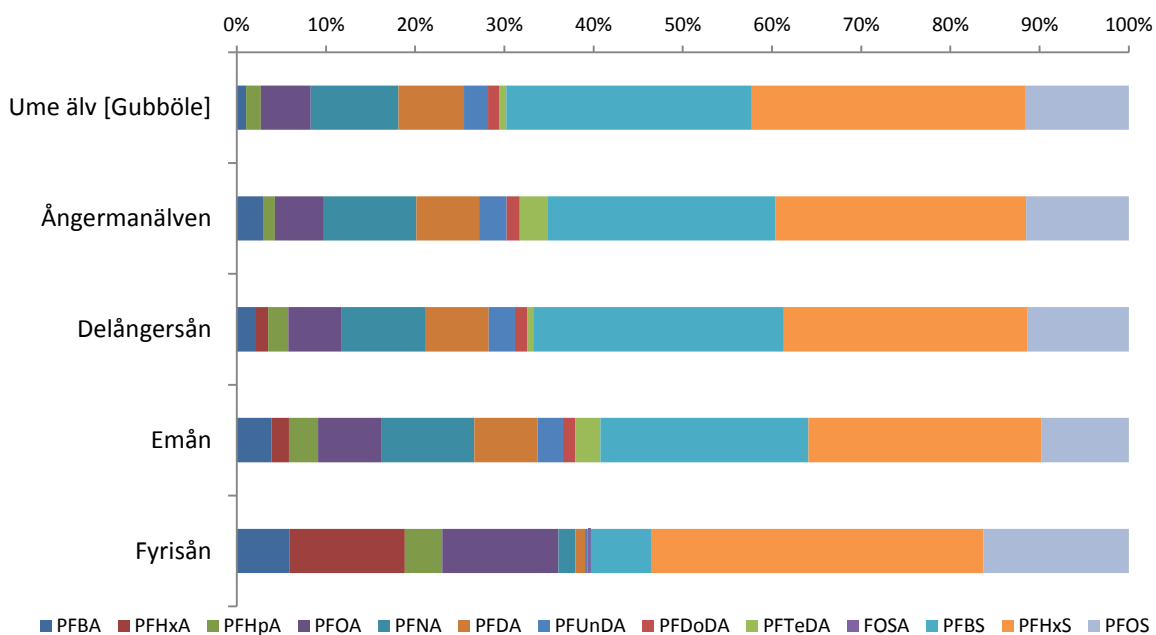




**Figure 9:** Levels of PFOS in Swedish rivers (ng L<sup>-1</sup>) from north (upper) to south (lower) until Helge å, then going to the west coast from south to north. The EQS of 0.65 ng L<sup>-1</sup> is indicated with a dashed line.



**Figure 10:** Discharge of  $\Sigma$ PFASs from Swedish rivers ( $\text{g day}^{-1}$ )



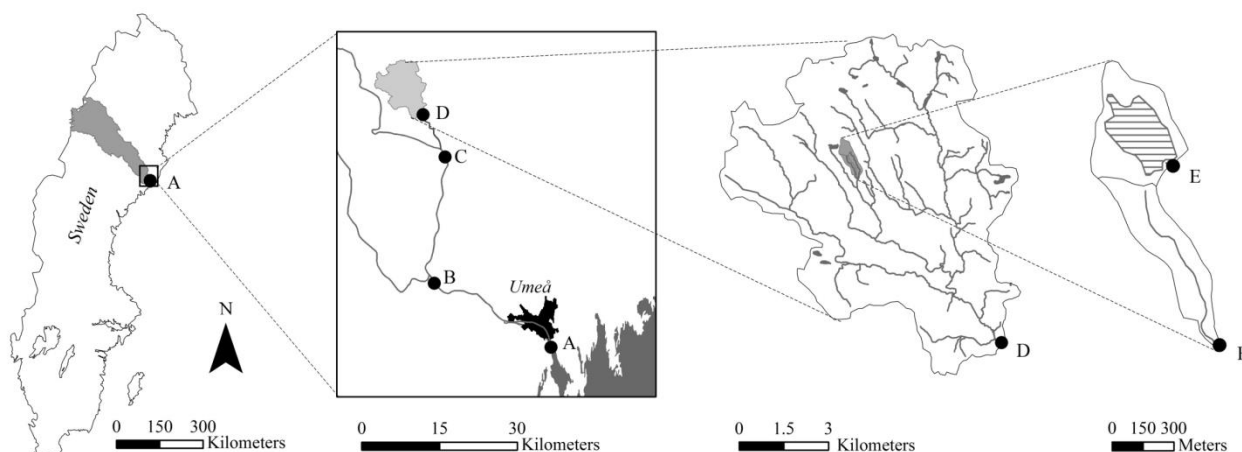
**Figure 11:** Composition of PFASs (%) in the five rivers with highest levels of  $\Sigma$ PFASs



**Figure 12:** Sampling site in Ume älv (indicated with red arrow) and the location of the WWTP (blue circle)

In the Ume älv/Vindelälven river system, samples were taken at four different sites in order to check for variation of PFASs levels following a water path approaching more densely populated areas downstream (Figure 13). The two most remote sites (C and D) showed low levels of  $\Sigma$ PFASs, well below the average value obtained for Sweden and with PFOA below the MDL. As the river was approaching slightly more urbanised areas (C), longer-chained PFCAs and PFSA were detected at increasing concentrations, along with detectable levels of PFOA. Continuing downstream, the sample from Gubböle (B) showed unexpectedly high values representing the second highest PFAS levels of all samples. As the Umeå sample (A) again showed low values even

though it was downstream the city of Umeå and its main WWPT, the high values near Gubböle need verification.



**Figure 13:** Sampling sites (A-D) in the Ume älv/Vindelälven river system

## 5. Conclusions and future perspectives

From the current study, it can be concluded that FRs and PFASs are ubiquitously present in Swedish rivers, and that some rivers have elevated pollution. A screening study like the current may reveal hot spots. However, as it provides a snapshot of the current situation with few sampling replicates, some results may need verification. For example, in the Vindelälven/Ume älv river system, two of three upstream (i.e. remote area) samples showed low PFAS levels, while the third was elevated for PFASs as well as for FRs. The reason for the extreme values may be one or several point sources near the sampling site, but repeated and detailed studies are needed to confirm and further explore the situation.

Some general pollution patterns of the FRs and PFASs in the Swedish rivers were found. For the FRs, 2,4,6-TBP was frequently detected in rivers draining southern areas. Streams in the north (e.g. Alterälven, Öre älv, Gide älv, Lögde älv and Ljungan) showed generally higher fractions of the longer chained PFCAs (i.e. PFNA, PFDA, PFUnDA, PFDoDA) whereas in the south, the fractions of PFHpA and PFOA were distinctly higher. Almost all sites on the west coast had a contribution of PFOA and PFOS that was >20% and >30% of the  $\Sigma$ PFASs, respectively, whereas corresponding values on the east coast were both <20%.

Four of the five sites with the highest concentrations showed similar PFASs composition although they were collected at sites from very different regions of Sweden (Ume älv at Gubböle, Ångermanälven in central Sollefteå, Delångersån in Iggesund and Emån near Emsfors), indicating a common source type. The results from the current study could not reveal which source type(s) are

the most important.

For PFOS, an annual average EQS of 0.65 ng L<sup>-1</sup> is set in the priority substance directive (2013/39/EU). In total, 12 out of 44 sampling sites located in all parts of the country exceeded this value (Ume älv at Gubböle, Ångermanälven, Delångersån, Fyrisån, Norrström, Nyköpingsån, Emån, Lyckebyån, Rönneån, Nissan, Viskan and Göta älv at Alelyckan).

The calculated fluxes of PFASs into recipient seas showed that the Swedish rivers contributed with approx. 3.2 kg day<sup>-1</sup>, and there appear to be needs for reducing high concentrations on a local and regional scale. The daily total load of FRs into the Baltic Sea was estimated to 38 kg day<sup>-1</sup>. It should be noted, that the targeted FRs represent novel FRs and do not include e.g. the historically heavily used PBDEs. Therefore, these values are not representative for all FRs emitted in Sweden.

As this study was a one-time grab sampling campaign for screening purposes, all values should be interpreted with great care. Verification and more detailed studies are recommended for sites with elevated levels. Our study also suggests that upstream monitoring is necessary to reveal hotspots.

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**Table A1:** Sampling details for the FR sampling sites. The ID numbers correspond to the locations given in Figure 1.

ID no.	Site	Date	Time	POP-can no.	TOC-bottle	TOC (mg/L)	T(air) (°C)	T(water) (°C)	pH	U (mV)	Coordinates (RT90)	
											X	Y
FR01	Torne älv	2013-10-01	10:15	6	8	4.1	3.0	5.7	7.0	-0.8	7 330 503	1 880 556
FR02	Kalix älv	2013-10-01	11:15	1	10	5.8	6.0	7.6	7.2	-7.6	7 325 285	1 833 885
FR03	Råne älv	2013-10-01	14:00	5	4	8.1	5.0	10.2	7.1	-5.5	7 338 361	1 779 226
FR04	Lule älv	2013-10-01	16:30	3	21	3.1	6.0	9.4	7.3	-16.2	7 290 561	1 786 921
FR05	Pite älv	2013-10-02	09:30	4	3	4.4	8.0	6.8	6.5	12.3	7 264 163	1 755 232
FR06	Skellefte älv	2013-10-02	12:11	8	22	3.8	10.0	10.3	7.1	-5.2	7 190 964	1 736 256
FR06	Skellefte älv DUPL	2013-10-02	12:11	9	23	3.8	10.0	10.3	7.1	-3.4	7 190 964	1 736 256
FR07	Ume älv	2013-10-03	08:02	7	19	4.7	2.0	7.9	7.9	-3.4	7 087 353	1 718 699
FR07B	Ume älv [Gubböle]	2013-10-02	18:50	15	9	4.5	8.0	8.2	8.2	-3.4	7 092 989	1 701 914
FR07C	Vindelälven [Rödånäs]	2013-10-02	16:15	11	12	4.2	11.0	9.1	9.1	-18	7 115 827	1 701 376
FR07D	Vindelälven [Krycklan, 16]	2013-10-02	15:23	14	11	13.4	11.0	7.2	7.2	-11.8	7 127 639	1 697 343
FR08	Öre älv	2013-10-03	09:30	10	25	16.3	3.0	8.5	6.4	26.2	7 061 011	1 691 347
FR09	Ångermanälven	2013-10-03	13:55	2	13	6.5	13.0	9.6	6.7	4.2	7 007 585	1 573 842
FR010	Indalsälven	2013-10-03	16:55	12	2	5.9	12.0	10.3	7.3	-13.2	6 934 786	1 580 851
FR011	Ljungan	2013-10-09	13:45	25	317	7.2	12.0	10.7	6.9	-4.2	6 917 403	1 559 911
	Ljungan BLANK	2013-10-09	13:45	30	N/A	N/A	12.0	N/A	N/A	N/A	6 917 403	1 559 911
FR012	Delångersån	2013-10-04	11:45	13	1	6.7	11.0	10.2	6.8	3.2	6 836 677	1 567 893
FR013	Ljusnan	2013-10-09	17:45	26	337	7.4	13.0	11.6	6.9	1.5	6 789 337	1 568 698
FR014	Gavleån	2013-10-09	19:50	28	333	11.8	12.0	9.8	6.8	-2.6	6 729 091	1 572 721
FR015	Dalälven	2013-10-09	21:10	29	334	6.3	10.0	10.3	6.8	8.3	6 717 372	1 589 704
FR016	Norrström	2013-10-06	18:50	22	15	9.5	12.0	13.1	7.4	-28.0	6 580 773	1 628 741
FR016A	Fyrisån	2013-10-25	11:00	31	340	10.5	10.0	11.1	7.0	-0.3	6 636 135	1 604 086
FR016A	Fyrisån DUPL	2013-10-25	11:00	32	441	10.4	10.0	11.1	7.0	-0.3	6 636 135	1 604 086
FR017	Nyköpingsån	2013-10-06	17:00	21	5	13.6	14.0	9.9	7.5	-32.2	6 523 002	1 564 896
FR018	Motala Ström	2013-10-06	15:35	20	18	8.0	14.0	11.8	7.4	-27.2	6 496 919	1 518 441



ID no.	Site	Date	Time	POP- can no.	TOC- bottle	TOC (mg/L)	T(air) (°C)	T(water) (°C)	pH	U (mV)	Coordinates (RT90)	
											X	Y
	Motala Ström BLANK	2013-10-06	15:35	17	N/A	N/A	14.0	N/A	N/A	N/A	6 496 919	1 518 441
FR019	Emån	2013-10-06	12:30	23	14	11.0	13.0	11.0	7.3	-15.3	6 335 205	1 539 225
FR019	Emån DUPL	2013-10-06	12:30	24	24	10.8	13.0	11.0	7.3	-15.3	6 335 205	1 539 225
FR020	Mörrumsån	2013-10-06	09:50	19	6	12.0	13.0	10.6	7.1	-7.2	6 230 020	1 434 417
FR021	Helge å	2013-10-06	07:20	18	7	11.2	11.0	11.2	7.6	-32.2	6 202 819	1 400 869
	Helge å BLANK	2013-10-06	07:20	16	N/A	N/A	11.0	N/A	N/A	N/A	6 202 819	1 400 869

N/A: Data not available or not applicable

**Table A2:** Sampling details for the PFASs sampling sites. The ID numbers correspond to the locations given in Figure 1.

ID no.	Site	Date	Coordinates X	(RT90) Y	Flow	T(air) °C	pH	TOC mg/l	SLU site code	Sampler no.
PF01	Torne älv Mattila	2013-10-17	7334720	1878815		2.0	7.3	4.6	BD0001	122
PF02	Kalix älv Karlsborg	2013-10-14	7324070	1836040		5.2	6.9	5.0	BD0004	37
PF03	Råne älv Niemisel	2013-10-12	7338356	1779202	Normal	7.2	6.8	8.6	BD0006	83
PF04	Lule älv Luleå	2013-10-21	7291860	1785750		7.1	7.0	2.8	BD1008	54
PF05	Alterälven Norrfjärden	2013-10-12	7269363	1763502	Low	6.0	7.0	10.5	BD0009	46
PF06	Pite älv Bölebyn	2013-10-12	7264178	1755197	Low	6.0	6.9	3.3	BD1010	46
PF07	Skellefte älv. Kvistforsen	2013-10-23	7190950	1736220	Normal	3.4	7.0	3.4	AC0012	55
PF08	Rickleån Ut	2013-10-14	7119026	1750187	Normal	6.7	6.8	12.3	AC1015	90
PF09A	Ume älv [Stornorrfors]	2013-10-14	7089729	1708725	Normal	6.7	7.1	3.8	AC1017	66
PF09B	Ume älv [Gubböle]	2013-10-02	7092989	1701914		8.0	8.2	4.5	N/A	N/A
PF09C	Vidälven [Rödånäs]	2013-10-02	7115827	1701376		11.0	9.1	4.2	N/A	N/A
PF09D	Vidälven [Krycklan]	2013-10-02	7127639	1 697343		11.0	7.2	13.4	N/A	N/A
PF10	Öre älv Torrböle	2013-10-14	7071637	1687280	Normal	7.5	6.7	15.2	AC0019	133
PF11	Lögde älv Lögdeå	2013-10-16	7054406	1679440	Low	6.1	6.7	9.8	AC0020	59
PF12	Gide älv Gideåbacka	2013-10-14	7031312	1665106		N/A	6.5	12.6	Y0021	91
PF13	Ångermanälven Sollefteå	2013-10-15	7007746	1573568	Normal	8.61	6.9	6.0	Y0022	40
PF14	Indalsälven Bergeforsen	2013-10-15	6935369	1581644	Normal	8.8	7.4	5.2	Y0023	33
PF15	Ljungan Skallböleforsen	2013-10-14	6917356	1559809	Normal	9.5	7.3	6.5	Y0026	39
PF16	Delångersån Iggesund	2013-10-14	6836610	1567930	Normal	9.9	7.1	6.4	X0027	50
PF17	Ljusnan Ljusne Strömmar	2013-10-15	6789328	1568670		10.1	7.0	7.0	X0028	58
PF18	Gavleån Gävle	2013-10-15	6729240	1572240	Low	8.5	7.1	11.6	X0030	5
PF19	Dalälven Älvkarleby	2013-10-16	6717115	1589769	Low	8.9	7.2	5.6	C0031	31
PF20	Norrström Stockholm	2013-10-14	6580657	1628573		12.1	7.5	8.9	AB0037	65
PF20A	Fyrisån	2013-10-25	6636135	1604086		10.0	7.0	10.5	N/A	N/A
PF21	Nyköpingsån Spånga	2013-10-15	6521803	1565424	Low	10.1	7.3	13.2	D0040	15
PF22	Motala Ström Norrköping	2013-10-17	6496730	1518380		12.3	7.5	7.1	E0041	67
PF23	Botorpström Brunnösö	2013-10-15	6393358	1541228	Low	10.9	7.2	11.4	H0043	94
PF24	Emån Emsfors	2013-10-14	6335434	1539139		9.0	7.3	10.3	H0044	93
PF25	Alsterån	2013-10-13	6320320	1521687		10.2	6.9	13.0	H0070	92
PF26	Ljungbyån Ljungbyholm	2013-10-15	6278353	1522508	Low	9.5	6.9	11.1	H0045	107

ID no.	Site	Date	Coordinates X	(RT90) Y	Flow	T(air) °C	pH	TOC mg/l	SLU site code	Sampler no.
PF27	Lyckebyån Lyckeby	2013-10-14	6229911	1491022	Low	11.2	6.8	14.1	K0046	52
PF28	Mörrumsån Mörrum	2013-10-17	6229702	1434540	Low	11.3	7.2	11.2	K0047	72
PF29	Helgeån Hammarsjön	2013-10-17	6202532	1400797	Normal	10.7	7.6	9.0	M0048	53
PF30	Kävlingeån Högsmölla	2013-10-21	6186780	1328810	Normal	9.7	7.8	8.6	M0073	56
PF31	Rönneån Klippan	2013-10-17	6224672	1334520	Normal	10.6	7.5	10.1	M0053	53
PF32	Lagan Laholm	2013-10-15	6268702	1330473	Low	10.2	7.0	10.0	N0054	6
PF33	Nissan Halmstad	2013-10-14	6288723	1320412	Low	10.6	7.2	10.4	N0056	6
PF34	Ätran Falkenberg	2013-10-14	6313335	1298307	Low	11.7	7.3	9.2	N0057	6
PF35	Viskan Åsbro	2013-10-21	6351360	1288950	Normal	7.9	7.1	7.3	N0059	38
PF36	Nordre älv. Ormo Skärarna	2013-10-15	6420229	1268735		11.2	7.4	4.7	O0075	42
PF37A	Göta älv. Alelyckan	2013-10-15	6410965	1273888		11.5	7.2	4.7	O0069	42
PF37B	Göta Älv Trollhättan	2013-10-15	6467704	1293498		11.0	7.3	4.9	O0060	42
PF38	Örekilsälven Munkedal	2013-10-08	6489459	1259609	Low	12.0	7.0	11.7	O0063	47
PF39	Enningdalsälv N.Bullaren	2013-10-14	6536199	1253913		11.5	6.8	9.0	O0064	73

N/A: Data not available or not applicable

**Table A3:** Levels of targeted flame retardants (FRs) in Swedish rivers (ng L<sup>-1</sup>)<sup>a</sup>

ID		2,4,6-TBP	TCIPP	TPHP	ΣFRs
FR01	Torne älv	<MDL	<MDL	<MDL	<MDL
FR02	Kalix älv	<MDL	231	<MDL	231
FR03	Råne älv	<MDL	<MDL	<MDL	<MDL
FR04	Lule älv	<MDL	<MDL	<MDL	<MDL
FR05	Pite älv	<MDL	<MDL	<MDL	<MDL
FR06	Skellefte älv	<MDL	<MDL	<MDL	<MDL
FR07	Ume älv [Umeå]	<MDL	<MDL	<MDL	<MDL
FR07B	Ume älv [Gubböle]	<MDL	287	<MDL	287
FR07C	Vindelälven [Rödånäs]	<MDL	<MDL	<MDL	<MDL
FR07D	Vindelälven [Krycklan]	<MDL	<MDL	<MDL	<MDL
FR08	Öre älv	<MDL	<MDL	<MDL	<MDL
FR09	Ångermanälven	<MDL	267	<MDL	267
FR010	Indalsälven	<MDL	<MDL	<MDL	<MDL
FR011	Ljungan	<MDL	<MDL	<MDL	<MDL
FR012	Delångersån	<MDL	<MDL	<MDL	<MDL
FR013	Ljusnan	<MDL	<MDL	<MDL	<MDL
FR014	Gavleån	<MDL	307	<MDL	307
FR015	Dalälven	<MDL	<MDL	<MDL	<MDL
FR016A	Fyrisån	19	3909	66	3993
FR016	Norrström	18	629	<MDL	647
FR017	Nyköpingsån	12	250	<MDL	262
FR018	Motala ström	13	240	<MDL	253
FR019	Emån	16	267	<MDL	283
FR020	Mörrumsån	16	<MDL	<MDL	16
FR021	Helge å	20	621	<MDL	641

<sup>a</sup>MDL = method detection limit, levels for MDL and MQL are given in Table 7; Levels of BEHTBP, EHTBB, HBCDD BTBPE, PBP, PBT, DBDPE, HBB, and TBBPA were also targeted, but were all <MDL (or not quantified due to interfering chromatographic peak); The mean of targeted ΣFRs of all rivers was 288 ng L<sup>-1</sup>.

**Table A4:** Levels of targeted PFASs in Swedish rivers (ng L<sup>-1</sup>)<sup>a</sup>

ID		PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	FOSA	PFBS	PFHxS	PFOS	ΣPFASs
PF01	Torne älv	0.94	<MDL	<MDL	0.26	0.15	0.13	0.077	0.053	<MDL	0.15	0.39	0.069	0.082	2.3
PF02	Kalix älv	0.76	<MDL	<MDL	0.22	0.23	<MDL	0.098	0.10	0.14	<MDL	<MDL	<MDL	0.053	1.6
PF03	Råne älv	1.2	<MDL	<MDL	0.21	1.3	0.28	0.16	0.19	0.15	<MDL	<MDL	0.15	0.34	4.0
PF04	Lule älv	0.60	<MDL	<MDL	0.39	0.23	0.15	0.073	0.033	<MDL	0.12	<MDL	0.051	0.058	1.7
PF05	Alterälven	0.60	<MDL	0.61	<MDL	0.18	0.11	0.044	<MDL	<MDL	<MDL	<MDL	<MDL	0.12	1.7
PF06	Pite älv	0.97	<MDL	0.54	0.44	0.40	0.22	0.081	0.069	<MDL	0.056	4.1	0.31	0.28	7.5
PF07	Skellefte älv	0.79	<MDL	<MDL	0.39	0.37	0.27	0.17	0.12	<MDL	0.37	5.2	0.19	0.30	8.1
PF08	Rickleån	0.72	<MDL	<MDL	<MDL	0.091	<MDL	0.041	<MDL	<MDL	0.075	0.030	<MDL	0.042	1.0
PF09	Ume älv [Umeå]	1.1	<MDL	<MDL	0.39	0.36	0.14	0.084	0.043	0.094	0.064	0.17	0.12	0.18	2.0
PF09B	Ume älv [Gubböle]	0.99	<MDL	1.0	3.3	5.8	4.4	1.6	0.77	<MDL	<MDL	16	18	6.9	60
PF09C	Vindelälven [Rödånäs]	0.62	<MDL	<MDL	0.26	0.32	0.064	0.058	<MDL	0.46	0.093	0.048	0.14	0.25	2.2
PF09D	Vindelälven [Krycklan]	0.47	<MDL	<MDL	<MDL	0.26	<MDL	0.074	0.067	<MDL	<MDL	<MDL	<MDL	0.074	1.7
PF10	Öre älv	0.63	<MDL	<MDL	<MDL	0.16	<MDL	<MDL	<MDL	<MDL	0.18	<MDL	<MDL	0.060	1.0
PF11	Lögde älv	0.57	<MDL	<MDL	<MDL	0.12	<MDL	<MDL	<MDL	<MDL	0.052	<MDL	<MDL	<MDL	0.7
PF12	Gide älv	0.96	<MDL	<MDL	<MDL	0.40	0.12	0.10	<MDL	<MDL	<MDL	<MDL	<MDL	0.16	1.8
PF13	Ångermanälven	0.79	<MDL	0.36	1.5	2.8	1.9	0.84	0.40	0.84	<MDL	6.9	7.63	3.1	27
PF14	Indalsälven	0.96	<MDL	<MDL	<MDL	0.14	<MDL	0.068	0.077	0.07	<MDL	<MDL	0.081	0.091	1.5
PF15	Ljungan	0.77	<MDL	<MDL	<MDL	0.21	0.024	0.044	<MDL	<MDL	0.032	<MDL	<MDL	0.12	1.2
PF16	Delångersån	1.3	0.82	1.4	3.6	5.6	4.3	1.8	0.82	0.41	<MDL	17	16	6.8	60
PF17	Ljusnan	0.74	<MDL	0.19	0.34	0.33	0.092	0.087	0.035	<MDL	0.061	0.44	0.10	0.046	2.5
PF18	Gavleån	1.1	1.1	0.82	0.92	0.41	0.17	0.078	<MDL	<MDL	0.052	4.9	0.38	0.29	10
PF19	Dalälven	1.2	1.1	0.56	0.40	0.37	0.15	0.162	0.046	0.42	0.053	0.42	0.13	0.61	5.6
PF20	Norrström	1.9	1.9	1.3	1.6	0.51	0.22	0.075	0.061	<MDL	0.46	0.83	1.2	2.4	33
PF20A	Fyrisån	1.1	4.2	1.4	4.2	0.63	0.34	0.092	0.034	<MDL	0.094	2.2	12	5.3	12
PF21	Nyköpingsån	0.89	1.5	1.4	1.1	0.44	0.18	0.093	<MDL	0.09	0.076	0.61	0.64	0.71	7.7
PF22	Motala ström	1.3	<MDL	<MDL	0.61	0.32	<MDL	0.047	<MDL	<MDL	0.070	<MDL	0.29	0.63	3.2

ID		PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	FOSA	PFBS	PFHxS	PFOS	ΣPFASs
PF23	Botorpsström	1.1	<MDL	<MDL	0.22	0.19	<MDL	0.057	<MDL	<MDL	<MDL	<MDL	<MDL	0.11	1.7
PF24	Emån	2.1	1.0	1.7	3.8	5.4	3.7	1.5	0.70	<MDL	<MDL	12	14	5.1	52
PF25	Alsterån	1.2	<MDL	<MDL	0.42	0.38	0.038	0.097	<MDL	<MDL	<MDL	<MDL	<MDL	0.25	2.3
PF26	Ljungbyån	2.5	1.3	0.74	0.91	0.19	0.065	0.051	<MDL	<MDL	<MDL	0.042	0.46	0.29	6.6
PF27	Lyckebyån	2.9	0.64	0.89	0.64	0.45	0.17	0.12	0.031	<MDL	<MDL	<MDL	0.47	1.1	7.4
PF28	Mörrumsån	3.7	0.76	0.85	0.98	0.60	0.22	0.14	0.080	<MDL	0.20	0.51	0.42	0.60	9.1
PF29	Helge å	3.4	1.5	1.0	1.2	0.61	0.30	0.18	0.095	<MDL	0.10	<MDL	1.9	0.54	11
PF30	Kävlingeån	2.0	2.6	0.96	1.1	0.12	0.088	0.037	<MDL	<MDL	0.16	0.15	0.73	0.50	8.5
PF31	Rönneån	2.1	1.6	0.93	1.3	0.26	<MDL	<MDL	<MDL	<MDL	0.072	0.87	3.0	3.9	14
PF32	Lagan	2.0	<MDL	<MDL	1.0	0.36	0.058	0.018	0.016	<MDL	<MDL	0.083	0.35	0.56	4.4
PF33	Nissan	2.7	1.1	0.85	1.2	0.53	0.11	0.050	0.030	<MDL	0.072	0.440	0.41	0.81	8.3
PF34	Ätran	1.8	<MDL	<MDL	0.69	0.33	0.045	<MDL	<MDL	<MDL	<MDL	<MDL	0.20	0.36	3.4
PF35	Viskan	1.6	1.3	0.95	1.6	0.54	0.20	0.081	<MDL	<MDL	0.079	<MDL	0.39	0.79	7.5
PF36	Nordre älv	1.5	<MDL	<MDL	0.98	0.38	0.060	<MDL	<MDL	<MDL	0.14	0.098	0.26	0.58	3.3
PF37	Göta älv [Alelyckan]	1.9	<MDL	0.55	1.1	0.41	0.11	0.039	<MDL	<MDL	0.037	0.041	0.34	0.79	5.3
PF37A	Göta älv [Trollhättan]	1.8	<MDL	<MDL	0.75	0.26	0.047	0.062	<MDL	<MDL	<MDL	0.035	0.28	0.35	4.3
PF38	Örekilsälven	2.3	<MDL	<MDL	0.87	0.27	0.049	<MDL	<MDL	<MDL	0.041	<MDL	0.11	0.41	4.0
PF39	Enningdalsälven	1.4	<MDL	<MDL	0.90	0.36	0.042	0.046	<MDL	<MDL	<MDL	<MDL	0.24	0.25	3.2

\*MDL = method detection limit; levels for MDL and MQL are given in Table 8; Levels of PFPeA, PFTeDA, PFHxDA, PFOcDA, FOSAA, EtFOSA, EtFOSAA, EtFOSE, MeFOSA, MeFOSAA, MeFOSE, and PFDS were also targeted, but were all <MDL. The mean of targeted ΣPFASs of all rivers was 9.5 ng L<sup>-1</sup> and median 4.2 ng L<sup>-1</sup>.