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Screening of endocrine disrupting compounds in Swedish rivers

with focus on organic flame retardants and perfluoroalkylated substances

Erik Ribeli

Master thesis

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Abstract

Screening of endocrine disrupting compounds (EDCs) in Swedish rivers, with focus on organic flame retardants (FRs) and perfluoroalkylated substances (PFASs).

Erik Ribeli

The occurrence of chemical contaminants in the environment is one of the key issues the world is facing today. Special effort has been put on the screening of endocrine disrupting compounds (EDCs), substances that have been shown to have adverse effects on the endocrine system. EDCs are mainly found in pharmaceuticals and personal care products (PPCPs), but also other products covering almost all categories of our daily life. EDCs can be both organic, such as the persistent organic pollutants (POPs), and inorganic, e.g. heavy metals. Today, all kinds of EDCs are currently being investigated on a large scale.

Two EDC sub-categories that have gained increased public attention during the last years are organic flame retardants (FRs) and per- and polyfluoroalkylated substances (PFASs). Both categories have shown to be bioaccumulating, persistent and toxic, which has led to banning of several substances in both categories. However, as both FRs and PFASs are considered to be emerging POPs, their fate and behaviour in the environment are still in great need of research. FRs and PFASs often end up in surface waters due to their disinclination of getting removed in waste water treatment plants (WWTPs) and their persistence. Thus, the objective of this project was to provide a snapshot of the current situation of FRs and PFASs in Swedish rivers, including both smaller streams and bigger rivers. Grab water samples were taken at 25 sites for FRs and 44 for PFASs in rivers all over Sweden.

The results showed that sparsely populated areas such as the northern part of Sweden generally showed lower concentrations of PFASs in the water than the southern part did. The summarised concentrations of FRs ranged from 37 ng L^{-1} to 4.6 µg L^{-1}, and from 0.59 ng L^{-1} to 59 ng L^{-1} for the detected PFASs, which was in good comparison to previous studies carried out on surface water in Europe. The percentile composition, the so-called fingerprint, showed significant differences between the southern part and the northern part for both FRs and PFASs, but also great similarities between some of the rivers with the highest measured PFASs concentrations. The highest loads of both FRs and PFASs were detected in Delångersån, which is one of the smaller rivers screened and likely to be affected by a nearby industrial point source. The European environmental quality standard of 0.65 ng L^{-1} of perfluorooctane sulfonic acid (PFOS) was exceeded in 12 of all 44 sampled rivers.

Keywords: EDC, flame retardants, PFAS, PFAA, PFCA, PFSA, screening, rivers, surface water, grab samples, Sweden.

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Referat

Kartläggning av belastningen av hormonstörande ämnen i svenska vattendrag, med fokus på organiska flamskyddsmedel samt perfluoroalkylerade substanser (PFASer).
Erik Ribeli

Under de senaste åren har försämringen av yt- och grundvattenkvalitet på grund av förorening av giftiga substanser blivit en mycket uppmärksammad fråga. Särskilt fokus har riktats mot så kallade hormonstörande substanser, det vill säga ämnen som har en negativ inverkan på det endokrina (hormon-) systemet. Hormonstörande ämnen har hittats i en rad vardagsprodukter såsom exempelvis läkemedel och hygienartiklar. Halterna är oftast mycket låga, men ämnena kan ändå ha negativ inverkan på växt- och djurliv i alla delar av ekosystemet.

Till de hormonstörande ämnena hör bland annat organiska flamskyddsmedel samt per- och polyfluoroalkylerade substanser (PFASer). Det har visat sig att dessa ämnen ofta är bioackumulerande, persistenta och giftiga, vilket har lett att flera av dessa ämnen fasats ut eller förbjudits de senaste årtiondena. På grund av att de är svårnedbrytbara hittas även numera förbjudna ämnen fortfarande förhållandevis ofta i miljön.

Syftet med detta examensarbete har varit att kartlägga halterna av hormonstörande ämnen i olika svenska vattendrag längs hela kusten. Dessutom undersöktes deras fördelning, sammanhang och orsaker till de olika halterna. Vid 25 respektive 44 platser togs därför vattenprover som analyserades för mängden flamskyddsmedel respektive PFASer.

Analysresultaten visade på generellt bra vattenkvalitet i Sverige då halterna var liknande eller något lägre än de som uppmätts i liknande studier på kontinenten. De summerade koncentrationerna av flamskyddsmedel uppmättes till mellan 37 ng L^{-1} och 4,6 µg L^{-1}, medan de summerade koncentrationerna av PFASer uppmättes till mellan 0,59 ng L^{-1} och 59 ng L^{-1}. Vid betraktande av provplatsernas procentuella flammskyddsmedels- respektive PFAS-sammansättningar kunde vissa skillnader mellan de norra och södra delarna av landet påvisas, samtidigt som några av floderna med de högsta PFAS-halterna hade stora likheter. De högsta halterna av såväl flamskyddsmedel som PFASer uppmättes i Delångersån, ett av de mindre vattendragen som undersökts i detta projekt och som vars höga halter tros bero på en närliggande punktkälla. De av den europeiska unionen fastslagna maxvärdena för perfluoroktansulfonat (PFOS) på 0,65 ng L^{-1} överskreds i 12 av 44 analyserade ytvattenprov.

Nyckelord: Hormonstörande ämnen, flammskyddsmedel, PFAS, PFCA, PFSA, PFAA, vattenkvalitet, screening, älvar, åar, floder.

Zusammenfassung

Ermittlung der Belastung von hormonaktiven Substanzen in den schwedischen Flüssen, mit Augenmerk auf organische Flammschutzmittel sowie perfluorierte Stoffe.
Erik Ribeli

In den letzten Jahren ist die Verschlechterung der Wasserqualität in Flüssen und Seen zu einem Thema geworden, dem viel Beachtung geschenkt wurde. Verschiedenste chemische Stoffe gelangen auf unterschiedlichsten Wegen in die Umwelt, was zu unerwünschten Belastungen und in gewissen Fällen sogar zur Gefährdung der Gesundheit von Tieren und Menschen führen kann.

Bei einigen dieser Stoffe besteht die Gefahr, dass sie negative Einwirkungen auf das Hormonsystem haben. Beispiele für solche schädliche Substanzen sind die in diesem Projekt untersuchten Flammschutzmittel sowie die per- und polyfluorierten Stoffe (PFASs). Flammschutzmittel werden verwendet, um die Entzündbarkeit verschiedenster Gegenstände zu verringern. PFASe sind chemische Verbindungen, die verwendet werden, um verschiedenen Produkten fett- und wasserabweisende Eigenschaften zu verleihen. Die Produktion und Verwendung beider Stoffgruppen ist in den letzten fünfzig Jahren stark angestiegen, was dazu geführt hat, dass diese Stoffe heute überall in der Umwelt vorkommen.

Das Ziel dieser Studie bestand darin, einerseits die Belastung Schwedischer Flüsse und andererseits das Vorkommen und die Verteilung der Stoffe über das ganze Land zu untersuchen. Zu diesem Zweck wurden Gewässerproben in allen Teilen in Schweden genommen und untersucht, so aus Flüssen verschiedenster Grösse, Flusseinzugsgebieten und Durchflüssen.

Die Ergebnisse der vorliegenden Studie zeigen, dass die Belastung Schwedens mit Flammschutzmitteln und PFASs generell vergleichbar oder sogar etwas geringer ist als die in anderen europäischen Ländern gemessenen Konzentrationen. Die gemessenen Flammschutzmittelkonzentrationen lagen zwischen 37 ng L^{-1} und 4,6 µg L^{-1}, die PFASs-Konzentrationen zwischen 0,59 ng L^{-1} und 59 ng L^{-1}. Gewisse Unterschiede zwischen den nördlichen und südlichen Teilen des Landes konnten bei Betrachtung der prozentuellen Zusammensetzung festgestellt werden, sowohl für die Flammschutzmittel wie auch für die PFASs. Bei der Analyse der PFASe fiel zudem auf, dass bei den Flüssen mit den höchsten gemessenen Konzentrationen signifikante Ähnlichkeiten bezüglich ihrer prozentualen Verteilung festzustellen waren. Dies lässt vermuten, dass die überdurchschnittlich hohen Konzentrationen auch auf ähnlichen Ursachen beruhen, wobei die Wahrscheinlichkeit für die Verunreinigung der Flüsse durch Punktquellen wie beispielsweise Abwasserreinigungsanlagen am Grössten ist. Die höchsten Konzentrationen an Flammschutzmitteln sowie PFASs wurden im Fluss Delångersån bei Iggesund gemessen, einem der kleineren in diesem Projekt untersuchten Flüsse. Die von der Europäischen Union bestimmten Höchstwerte von für perfluoroctansulfonat (PFOS) von 0,65 ng L^{-1} wurden bei 12 von insgesamt 44 Flussproben überschritten.

Schlüsselbegriffe: Hormonaktive Substanzen, Flammschutzmittel, PFAS, PFCA, PFSA, PFAA, Wasserqualität, Flüsse, Umweltproben.

Acknowledgements

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[1] *"The seriousness makes the man, the diligence the genius"*

Populärvetenskaplig sammanfattning

Kartläggning av hormonstörande substanser i svenska vattendrag, med fokus på organiska flamskyddsmedel samt perfluoroalkylerade substanser.

Erik Ribeli

Kemikalier används idag i stor utsträckning och finns i alla delar av vårt vardagliga liv, från mat och kläder till byggnader och elektronik. Medan de positiva egenskaperna är starkt övervägande så finns det vissa ämnen som är bekymmersamma då de hamnar på platser där de inte hör hemma. De kemiska föreningarna blir då till föroreningar. De mest problematiska ämnena är sådana som är toxiska, persistenta och bioackumulerande, vilket innebär att de är giftiga, svårnedbrytbara samt ansamlas i kroppen. Exempel på välkända miljögifter är insektsbekämpningsmedlet DDT (diklordifenyltrikloretan) och växtbekämpningsmedlet hormoslyr (en blandning av olika fenoxisyror). De visade bra resultat i de tilltänkta användningsområdena, men med tiden upptäckte man att de var mycket giftiga och orsakade fosterskador och cancer hos såväl människor som djur.

Problemet med miljögifter är att det ofta behövs väldigt små mängder för att de ska vara hälsovådliga för djur eller människor. Vissa ämnen är inte heller akuttoxiska utan blir en hälsorisk då man utsätts för ämnena under en längre tid, med exempelvis cancer som följd. Ämnena ansamlas ofta i ett eller ett fåtal kroppsorgan, som på så sätt tar skada på sikt. Speciellt bekymmersamt blir det då föroreningarna påverkar hormonsystemet, som reglerar en mängd kroppsliga funktioner såsom blodtryck, ämnesomsättning och fortplantning. Sådana ämnen kallas för hormonstörande substanser. Många hormonstörande kemikalier har förbjudits och slutat produceras, men i och med att industrin ständigt producerar nya och förbättrade produkter fortgår även den oönskade spridningen till miljön.

Två ämnesklasser som använts under en lång tid men på senare år även upptäckts i miljön samt visat sig vara både långlivade och hormonstörande är flamskyddsmedel och så kallade fluorerade substanser. Flamskyddsmedel är ämnen som ska förhindra att saker och ting tar eld, och den flitiga användningen i alla möjliga produkter såsom textilier, kläder och elektronikprodukter har lett till ett kraftigt minskat antal dödsfall på grund av bränder i västvärlden. Fluorerade ämnen, till exempel perfluorerade ämnen (PFASer) är ytaktiva substanser som används för att minska ytspänningen och finns exempelvis målarfärg, livsmedelsförpackning eller smörjoljor då de har förmågan att vara såväl vara vatten- som fettavvisande.

I det här projektet har fokus varit på organiska flamskyddsmedel och perfluorerade ämnen. Båda dessa har använts under en lång tid med goda resultat, men har på senare år hittats i miljön samt visat sig påverka hormonsystemet negativt. Ämnena sprids ofta via vattnet till miljön, vilket är problematiskt eftersom vatten är förutsättningen för allt liv på jorden. Flera av Sveriges 16 miljömål har vatten som en central del, däribland "Levande sjöar och vattendrag", "Grundvatten av god kvalitet" samt "Hav i balans samt levande kust och skärgård".

Syftet med detta examensarbete har varit att undersöka vilken belastning som flamskyddsmedel och perfluorerade ämnen står för i svenska vattendrag, och vilka problem det innebär för vattenkvaliteten i Sverige. Inga sådana undersökningar på Sveriges vattendrag i helhet har tidigare genomförts med fokus på dessa två ämnesklasser. 40 av Sveriges vattendrag, både stora och små, har provtagits, för att se vilka mängder av dessa föroreningar som finns och för att se fördelningen av ämnena över landet. Examensarbetet är sista momentet på civilingenjörsutbildningen i miljö- och

vattenteknik vid Uppsala universitet och Sveriges lantbruksuniversitet, SLU. Det genomfördes vid Institutionen för vatten och miljö på SLU.

Resultaten av studien visade att svenska vattendrag generellt sett hade låga halter av de undersökta föroreningarna. Flamskyddsmedlen i svenskt ytvatten visade sig ligga mellan 37 ng per liter (det vill säga 37 miljarddelars gram per liter) till 4,6 μg per liter (det vill säga 4,6 miljondelars gram per liter) medan koncentrationerna av de perfluorerade ämnena låg mellan 0,59 ng per liter och 59 ng per liter. Älvarna i norr visade generellt något lägre halter än vad åar och vattendrag i söder gjorde, men i alla delar av landet kunde såväl hög som låg förorening av vissa vatten påvisas.

Orsaken till de delvis rätt höga halterna tros vara utsläpp från punktkällor, exempelvis reningsverk, men möjligheten finns också att ämnena har transporterats via luften och därmed färdats lång väg innan de nått recipienten, i detta fall vattnet. Då man betraktar den procentuella fördelningen av perfluorerade ämnen i de olika proven syns tydliga skillnader mellan vattendrag i norr och i söder, men även vissa likheter mellan de vattendrag med höga. Detta indikerar att föroreningskällan är likartad. De högsta halterna uppmättes i Delångersån i Iggesund, där mängden flamskyddsmedel överskred 4,5 μg per liter och mängden fluorerade ämnen nästan uppgick till 60 ng per liter. Delångersån är i denna jämförelse en av de mindre åarna, både vad avrinningsområde och vattenföringsmängd beträffar och de höga halterna tros vara påverkade av en närliggande punktkälla. De renaste vattendragen var Nyköpingsån (vad mängden flamskyddsmedel beträffar) samt Lögde älv (beträffande mängden perfluorerade ämnen). Totalt överskred 12 av de 44 i Sverige undersökta vattendragen de av den europeiska unionen fastslagna maxhalterna för PFAS-ämnet PFOS (perfluoroktansulfonat) på 0,65 ng per liter.

Contents

1. Introduction

"What kingdom lies under that tossing surface! Numberless animals must be there, hidden from my sight. Its a kingdom close to man, one he can fly above all day and never recognize."

Charles A. Lindbergh

1.1. Endocrine disruptors (EDCs)

Ever since the early 1950's, the amount of chemicals we use has increased rapidly. Today, there are thousands of different compounds on the market, covering all categories of our daily life. Food can be kept fresh for a longer time by adding preservatives to it, undesired weeds can be avoided by applying herbicides to the field, and new pharmaceuticals fight diseases both faster and more effectively than the old ones. However, this intense use of chemicals causes problems as they can enter the environment during or after their usage. This leads to problems due to the bioaccumulative behaviour and the persistency of several EDCs. One of the best known examples hereof is DDT*[1] (dichlorodiphenyltrichloroethane), first famous for its insecticidal effects but later shown to have severe adverse effects on humans, wildlife and the environment (Sterner, 2003). DDT is now banned from most parts of the world (Turusov et al., 2002). However, that wake-up call did not stop the release of substances with similar undesired adverse effects, e.g. bioaccumulating, biomagnifying and persistent against degradation (URL1; Birnbaum, 1995). Some of the chemicals of vital interest for environmental chemistry today are the ones that have been shown to have adverse effects on the endocrine system of humans and wildlife, named endocrine disrupting compounds or simply endocrine disruptors (EDCs*). Many different compounds are classified as EDCs, such as e.g. pharmaceuticals and personal care products (PPCPs*), but also flame retardants (FRs*), per-and polyfluoroalkylated substances (PFASs*) and several agricultural and industry chemicals (Snyder et al., 2002, Falconer et al., 2006).

The human endocrine system consists of glands that regulate several important physiological functions, e.g. blood pressure and temperature, as well as our reproduction and metabolism (Sterner, 2003). Some of the most crucial major endocrine glands are the hypothalamus, the hypophysis and the thyroidal gland. The endocrine system also includes proteins that have the possibility to initialise or disable certain sequences of deoxyribonucleic acid (DNA*) coding, which makes the endocrine system very sensitive even for small levels of EDCs (Mantovani, 2002; Sterner, 2003). Moreover, studies have been able to discover nonmonotonic dose responses (i.e. dose exposure and responses show no significant correlations) and observed adverse effects at low but not high doses of different EDCs, indicating that small amounts of EDCs in the environment might be a bigger problem than expected (Welshons et al., 2006; Vandenberg et al., 2012; Angle et al., 2013). There are three different categories of adverse effects on the endocrine system, namely estrogenic (e-EDC*), androgenic (a-EDC*), and thyroidal (t-EDC*) (Snyder et al., 2003). Estrogenic endocrine disruptors often originate from PPCPs, and they have been found widespread in the environment despite their disinclination of getting dissolved in water and their facilitated transport when bound to organic matter (Campbell et al., 2006). However, more research is still needed in order to clarify categories as e.g. effects, transport behaviours, environmental degradation and mixture toxicity of these substances (Schwarzenbach et al., 2006; Kannan, 2011; Rydh Stenström, 2013).

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[1] * indicates that the abbreviation can also be found in the list of abbreviations in the end (chapter 7).

1.2. Production and release

The most common pathways for the release of EDCs into the environment are production and usage of the products (Ahrens, 2010). Indirect pathways such as landfill leachates, atmospheric deposition and waste water treatment plant (WWTP*) discharges are also considered to be of great importance, but as knowledge on these secondary sources is still very limited, making predictions and risk assessment difficult (Vollmuth and Niessner, 1995; de Wit, 2002; Loos et al., 2009). Once released to the environment, EDCs are hard to degrade and remove; simulated water treatment processes (WTP*) have also shown that the conventionally used techniques remove less than 25% of the known EDCs, a value that might be increased by several new techniques (Westerhoff et al., 2005). As EDCs comprise of many different kinds of substances, their fates and behaviours in the environment need to be investigated more in detail.

1.3. Regulations

Chemicals are produced in considerable quantities today. Some compounds are known to have adverse endocrine disrupting effects, and so they get phased out, replaced or banned. Regulations are often discussed lively as different opinions are prevalent, and there are different legislations on international, multinational, national and even regional levels (e.g. seen by the debate on EDC regulations by Bergman et al., 2013; Dietrich et al., 2013; Gore, 2013; Gore et al., 2013; Grandjean and Onzoff, 2013). However, the effects of EDCs do not end simultaneously with the end of manufacturing; many EDCs are persistent and bioaccumulative, and can reach temporary or even long-lasting sinks such as agricultural soil or sediments, respectively. Outdoor studies have been able to demonstrate that pesticides applied to agricultural fields can be stuck in soil pores for a long time (Bergström and Stenström, 1998; Gevao and Jones, 2002). As this fact was observed for both ionic and non-ionic pesticides, there is thus reason to presume that a similar behaviour is to expect for EDCs.

Substances of great environmental concern, i.e. toxic, bioaccumulative, persistent against natural degradation and with potential for long-range transport, are added to the Stockholm Convention, leading to restrictions in the 179 countries that so far have signed the convention (URL2, Vierke et al., 2012).

1.4. EDCs in the aquatic environment

The release of so-called "emerging" organic contaminants (EOCs*) to ground- and surface waters is one of the key issues environmental chemistry is facing today. Emerging pollutants do not need to be new; it simply indicates that these substances have not previously been monitored, but the ongoing introduction to the environment suggests them to be included in future national or international monitoring programs (Reemtsma et al., 2008). In the aquatic environment, the EOCs can often cause adverse effects on several levels such as water-living organisms, predator fish or even wildlife that consumes surface water. These waters are crucial, as they are one of the first places for gathering and further transport in the ecosystem. Several studies have shown that EDCs get accumulated in surface waters due to their physical-chemical properties, eventually accumulating in lake and ocean sediments when they are bound to particles and the water flow is decelerated, compared to the rivers (Petrovic et al., 2002, Prevedouros et al., 2006; Ko et al., 2007).

PFASs and FRs are two examples of anthropogenic substance groups whose public attention has increased substantially during the last decades. PFASs have been detected in blood serum sam-

ples from different places all over the world (Giesy and Kannan 2002; Jensen, 2008; Meironyté, 2010). Although they do not occur naturally in the aquatic environment, they have been detected in fish, peregrine falcon eggs and even polar bear blood (Sellström et al., 2001; Boon et al. 2002; Giesy and Kannan, 2002; Smithwick et al., 2006; Kannan, 2011). Some of the main pathways of EDCs into the aquatic environment are atmospheric deposition, as well as riverine discharges and point sources such as WWTP (Westerhoff et al., 2005; Ahrens et al.,, 2009b; Ahrens, 2010; Kannan, 2011).

1.5. Objectives and hypotheses

Emerging EDCs were the substances of interest for this thesis, as the knowledge on these substances, their behaviour and fate is still quite limited. Since EDCs comprise a large group of chemicals, this study focuses on two of its sub-categories. No studies have yet been carried out in order to screen the amount and distribution of these compounds in Sweden in its entirety, resulting in a lack of knowledge at this point. Information on EDCs in the Nordic environment is thus urgently needed.

The overall aim of the study was to identify which substances that are found in rivers in Sweden, as well as to map their occurrence and distribution. Grab samples were collected at 25 and 44 sites, for FRs and PFASs, respectively, all over the country.

In order to get a good understanding of EDCs and their behaviour and fate in the environment, a literature study was carried out. Several articles and reports were perused, focusing mainly on FRs and PFASs but also PPCPs and other EDCs. Moreover, the literature study was also needed in order to get a better understanding of the detected pollutants and their effects when released to the environment. Based on the results found in earlier studies, the hypotheses of the thesis were:

- ☑ Rivers passing areas with high population density have higher levels of EDCs than rivers in more sparely populated areas.
- ☑ Sampling sites downstream of point sources such as WWTPs or industrial activities will show higher levels of EDCs than remote and unaffected sites.
- ☑ Upstream samples are less polluted than samples taken further down the watershed.
- ☑ Sites with high loads of EDCs show similarities in the distribution of the different compounds when similar sources are expected.
- ☑ The total loads of FRs are higher than the PFASs loads, as the total production and usage of FRs is several orders of magnitudes higher than for PFASs.

In the following chapter, the two substance categories (FRs and PFASs) are characterised and discussed more in detail. Also, an overview on all screened compounds and their properties is given.

2. Literature study of flame retardants (FRs) and per- and polyfluoroalkyl substances (PFASs)

2.1. Flame retardants (FRs)

Ever since the 1973 Michigan PBB disaster, the chemical contamination of the environment by FRs is of vital public interest. Back then, an accidental mix-up of the highly toxic FR "FireMaster BP-6" (a mixture of different commercial polybrominated biphenyls, PBBs*) with the livestock fodder additive "NutriMaster" lead to a severe feed contamination (Kay, 1977; Safe et al., 1978). PBB levels as high as 13 500 ppm (i.e. ng g^{-1}) were measured in cattle feed, which impacted the livestock with symptoms as illnesses and weight loss, and while getting exposed to PBB contaminated fodder over time also more severe health effects and even deaths were observed (Kay, 1977; Safe et al., 1978; Hoque et al., 1998; Blanck et al., 2000). As much as 30 000 cattle, 6 000 pigs and 1.5 million chicken needed to be emergency slaughtered (Reich, 1983). However, as the mistake was not discovered until 1974, it has been stated that approximately 1000 farms received toxic fodder, resulting in direct and long-lasting exposure of 8 000 Michigan residents with PBB contaminated meat, eggs and milk (Kay, 1977; Reich, 1983; Hoque et al, 1998). As much as 9 million inhabitants of Michigan state are expected to have consumed PBB contaminated animal products at least once (de Wit, 2002).

Today, FRs are used in a large and still increasing number of our daily life products, reaching from diverse categories as carpets and textiles to furniture and IT products (Papachlimotzou et al., 2011). More than 175 different kinds of FRs are known today, and their increased use has led to a significantly reduced amount 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 (URL3). The FRs used today are of two different types: additive or reactive (Schlabach et al., 2011). Additive FRs are normally added to the product, mainly thermoplastics, after polymerisation; they are not chemically bound to the plastic and can therefore easily be released from the product (Schlabach et al., 2011). The so-called reactive FRs are less probable of getting released to the environment as they react chemically with the termoplastic, and therefore are bound chemically into the product (Papachlimitzou, 2011; Schlabach et al., 2011).

2.1.1. Properties and uses of FRs

Today, halogenated (primarily chlorinated flame retardants, CFRs*, and brominated flame retardants, BFRs*) and phosphorous flame retardants (PFRs*) are the most frequently used FRs, but others without halogens or phosphorous do also exist (Bergman et al., 2012). BFRs usually consist of one or two phenyl rings with some of the hydrogens substituted by bromine. Polybrominated diphenyl ethers (PBDEs*) consist of two phenyl rings with one to ten bromine atoms, so that the sum of hydrogen plus bromine always is equal to ten (Birnbaum and Cohen Hubal, 2006). They were

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[2] *"You cannot vote on how nature works"*

among the first additive FRs invented and had their palmy days with peaked production and usage 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).

PFRs are defined as FRs with phosphorous as the central atom, with possibilities of different types of functional groups, e.g. halogenated or phenylic ones. PFRs belong to the group of organophosphates, which can also be found in lubricants, concrete and hydraulic fluids (Andresen et al., 2004; US EPA*, 1985). Furthermore, PFRs have the ability of being covalently bound to halogenated functional groups (as e.g. Tri(1-chloro-2-propyl) phosphate, TCIPP).

All BFRs have low water solubility (although for some it is pH-dependent) and high values for the log octanol-water partitioning coefficient (log $K_{OW} \geq 4.4$), as shown in Table 1 (Birnbaum and Staskal, 2004; Birnbaum and Cohen Hubal, 2009). The corresponding values for PFRs are distinctly different (log $K_{OW} < 5$), as shown in Table 2 (Bergman et al., 2012). Moreover, phosphorous flame retardants as well as brominated ones are known to have a boiling point above 250°C, making them important in environmental research due to their semivolatile behaviour (Bytingsvik et al., 2004; Araki et al, 2013).

Halogenated FRs inhibit fires by reacting with the radicals, formed during the initial combustion, instead of letting the oxygen molecules react (Kolic et al., 2009). PFRs are acting in a similar way, in the solid phase of fires (van der Veen and de Boer, 2012). Other FRs mechanisms work by acting in the gaseous phase (in order to inhibit smoke development), or by liquefying the material (resulting in a withdrawal of burnable materials from the flame).

Table 1: Name, structure and properties of BFRs analysed in this project. Abbreviations: Molecular weight (MW*, displayed in [g mol⁻¹]), Chemical abbreviation standard (CAS*) number, log water-octanol coefficient (log K_{OW})*, soil organic carbon-water partitioning coefficient (K_{OC}*), vapour pressure, given in Pascal (Vp [Pa])*. The acid dissociation coefficient (pK_a = $-\log_{10} K_a$)* only relevant for phenolic FRs, namely 2,4,6-TBP, PBP and TBBPA, was 6.32±0.23, 4.43±0.33 and 7.7 or 8.5±0.10, respectively (Values from Birnbaum and Staskal, 2004; Kolic et al., 2009; Schlabach et al., 2011; Bergman et al., 2012 and URL4).

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	5.22	pH-dep.	2.55E-03
TBBPA	Tetrabromobisphenol A		$C_{15}H_{12}Br_4O_2$	79-94-7	543,87	9.69	4.47E+06	1.88E-05
HBB	Hexabromobenzene		C_6Br_6	87-82-1	551,42	6.11	50300	1.14E-04
BEHTBP	Bis(2-ethyl-1-hexyl)tetrabromophthalate		$C_{24}H_{34}Br_4O_4$	706.14	706.15	9.34	2.88E+06	1.55E-11
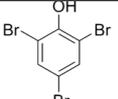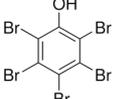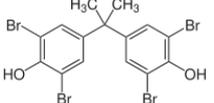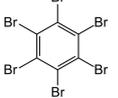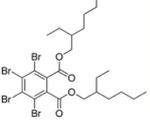
Compound	Name	Structure	Molecular formula	CAS no.	MW	log K_{OW}	K_{OC}	Vp (Pa)
DBDPE	1,2-Bis(2,3,4,5,6-pentabromophe-nyl)ethane		$C_{14}H_4Br_{10}$	84852-53-9	971.22	11.1	1.00E+07	n.a.
EHTBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate		$C_{15}H_{18}Br_4O_2$	183658-27-7	549.92	7.73	3.82E+05	3.71E-07
PBT	Pentabromotoluene		$C_7H_3Br_5$	87-83-2	486.62	5.22	60 200	6.00E-04
DBE-DBCH	1,2-Dibromo-4-(1,2-dibromoethyl) cyclo-hexane		$C_8H_4Br_4$	3322-93-8	427.8	4.82	10 000	2.97E-03
HBCDD	Hexabromocyclo-dodecane		$C_{12}H_{18}Br_6$	3194-55-6	641,73	7.92	4.86E+05	1.04E-07
PBDE	Polybrominated diphenyl ether		$C_{12}H_{(9-0)}Br_{(1-10)}O$	n.a.	n.a.	>5	n.a.	n.a.
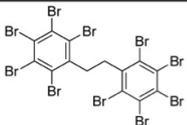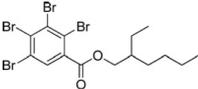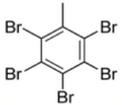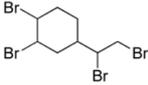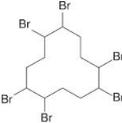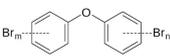
Table 2: Name, structure and properties of PFRs analysed in this project. Abbreviations: Molecular weight (MW, displayed in [g mol^{-1}]), log octanol-water partitioning coefficient (log K_{OW}), vapour pressure, given in Pascal (Vp [Pa]). (Values from Bergman et al., 2012).

Compound	Name	Structure	Molecular formula	CAS no.	MW	log K_{OW}	K_{OC}	Vp (Pa)
TPP	Tripropylphosphate		$C_8H_{21}O_4P$	513-08-6	224.24	1.87	676	5.77E-01
TCIPP	Tri(1-chloro-2-propyl) phosphate		$C_9H_{12}O_4Cl_3P$	13674-84-5	327,56	2.59	275	2.69E-03
TPHP	Triphenyl phosphate		$C_{18}H_{15}O_4P$	115-86-6	326,28	4.59	2630	8.37E-04
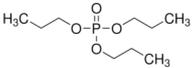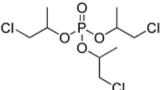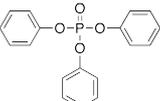
2.1.2. Transport processes and fate in the environment

FRs are a topic of vital interest for research today, but the mechanisms and reasons for their release to the environment are still hard to clarify. PBBs (mainly due to the Michigan accident) and PBDEs (due to their considerable production quantities) are among the most thoroughly investigated (Darnerud, 2003). Highly brominated PBDEs have shown to be able to degrade to lower brominated derivatives, although with a higher toxicity (Darnerud, 2003). PBBs and PBDEs have been detected globally, both close to point sources as well as far from their production mills, suggesting that the risks for long-range transport (LRT*) are of significant importance (Birnbaum and Staskal, 2004; Kolic et al., 2009). Most frequently detected FRs are, apart from those mentioned above, also tetrabromobisphenol A (TBBPA) and HBCDD (Birnbaum and Staskal, 2004). Studies have primarily been carried out in Northern America, the European Union (EU*) and in Japan, showing that BFRs are not only ubiquitously found, but also being detected at increasing levels in the environment (de Wit, 2002). PBDEs are known to be persistent, lipophilic and bioaccumulative

(Sellström et al., 2001; de Wit, 2002). Unlike other EDCs, the short half-life time of PBDEs in the atmosphere is an additional issue of concern, as less brominated PBDEs are known to be more toxic (de Wit, 2002; Harju et al., 2009). There are suspicions of possible debromination under LRT in the atmosphere, e.g. due to UV radiation or ozone (Vollmuth and Niessner, 1995; Harju et al., 2009).

The amounts of FRs in the environment are varying over time as well as geographically (Schlabach et al., 2011). A study carried out by Sellström et al. (2001) on eggs of peregrine falcons *(Falco peregrinus)* showed increasing levels of PBDEs. On the other hand, a later study in the Baltic Sea area showed decreasing levels of PBDEs in the environment; however, the levels in pike are almost stable since the 1980s (Julander and Georgellis, 2008). Although PBDEs are not produced in the Baltic Sea region, they have been detected in air samples, indicating that LRT is likely to occur (Julander and Georgellis, 2008; Schlabach et al., 2011). A similar study done by Covaci et al. (2006) showed high concentrations of HBCDD in predators such as birds of prey that were in the range of the Michigan PBB contamination (up to 19 200 ng g⁻¹).

Figure 1 highlights some of the main pathways for the release of FRs to the environment; as an example are FRs in textiles shown. FRs can reach the surface water by WWTP effluents as well as from landfill leachates and groundwater. However, there might be other pathways, such as atmospheric deposition and agricultural fields, that are still in great need of research.

Figure 1: Possible transport processes of FRs in the environment, when released from furniture and textiles.

The sources of FRs in the environment are mainly use and release directly from the products as well as sewage treatment plants (STPs*) (de Wit, 2002; Andresen et al., 2004). Also fire fighting training areas and airports are known to be areas with elevated FR levels (Harju et al., 2008).

2.1.3. Exposure and health aspects of FRs

The knowledge available for exposure and health effects varies greatly between the different compounds. PBBs and PBDEs have, as mentioned earlier, been investigated more thoroughly than other FRs. Not unlike other persistent organic pollutants (POPs*), FRs usually are sparingly soluble in water but do accumulate in fatty tissues and upward in the food chain (e.g. de Wit, 2002). Due to this fact, the amounts found in predators such as pike and falcons, as well as in humans, are significantly higher than in biota at lower trophic levels. The Michigan PBB accident is a queasy example of how fast FRs (and EDCs) can migrate up the food chain (Safe et al., 1978).

Despite the public attention, the health effects of FRs are still in vital need of research. On directly exposed livestock, symptoms as lowered milk production occurred after a few weeks (Kay, 1977). The continuous exposure to toxic fodder lead to visible deteriorated health of the cattle, namely lethargy, difficulties while walking, malformations such as growth of bigger hoofs and miscarriages, and finally even deaths (Kay, 1977; Chanda et al., 1981). Thus, it needs to be clarified that these effects originate from extremely high PBB values of up to 13 500 parts per million (ppm) (Kay, 1977). The mechanisms of skin toxicity are still not fully understood and examined (Chanda et al., 1981). A carcinogenicity study performed by Hoque et al. (1998) stated that no strong relation existed between the exposure of PBB contaminated food in 1973-1974 and the risk for development of cancer in humans. On the other hand, long-term animal studies showed that most BFRs have a low acute toxicity in rats, rodents and mice, but health issues such as reduced growth and body weight as well as reduced thyroid size or aborted pregnancies could be observed (Darnerud, 2003). Carcinogenicity on PFRs has only been observed for chloride-containing substances (van der Veen and de Boer, 2012). Research is still ongoing, and recent studies have shown significant relationships between e.g. PFRs in indoor dust and asthma (Araki et al., 2013).

Areas where health effects are not completely understood but with vital ongoing research are the ones of FRs in human milk, human blood and blood serum as well as in blood and organs of animals (e.g. Meironyté et al., 1999; Darnerud, 2003; van der Veen and de Boer, 2012).

2.2. PFASs

The second group of chemical substances this thesis' focus has been on is the one of perfluoroalkyl- and polyfluoroalkyl substances (PFASs). PFASs are purely anthropogenic substances and have been used widely since the early 1950s due to their unique properties of lowering surface tension and repelling both water and grease, e.g. being both hydrophobic and lipophobic (Kissa, 2001; Giesy and Kannan, 2002). However, PFASs are also known to have several similarities to POPs in endocrine disruption and environmental behaviour, such as persistency in surface waters, toxicity, subject to LRT, et cetera (Jensen and Leffers, 2008; Vierke et al., 2012). Two of the most studied PFASs are perfluorooctanoic acid and perfluorooctane sulfonic acid (PFOA and PFOS, respectively) of whom PFOS now is classified as substance of very high concern (SVHC*) under REACH*, and its use was prohibited in the EU by June 28, 2008 and added to the Stockholm Convention list in May 2009 (KemI, 2009; Ahrens, 2010; Vierke et al., 2012). PFASs are known to be among the most persistent substances ever discovered in environment, and have even been found in wildlife of remote areas of the world such as minks, otters and polar bears (Giesy and Kannan, 2002; Kannan et al., 2002).

Despite the long usage time, little attention was paid to their environmental aspects prior to the last decade (Kannan, 2011). Since then, more than 2500 research articles on their properties,

fate and occurrence have been published, making PFASs a major science topic (Kannan, 2011). Although numerous studies have been carried out in order to clarify the distribution of PFASs in different parts of our environment (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 are still several parts of the world where screening has not taken place yet. In the case of Sweden, several of the rivers included in this project were not investigated for FRs and PFASs earlier.

2.2.1. Properties and uses

Due to the fact that PFASs are sparsely soluble in both water and organic solvents, they are used in a big variety of industry- and consumer products (Jensen and Leffers, 2008). Some of their main uses are as surfactants in paint, leather and textile coating, clothes, shoes and carpets, as lubricants in floor- and car waxes, and in aqueous fire fighting foams (AFFFs*) at airports and oil platforms (Kissa, 2001; Jensen and Leffers, 2008).

The general formula of PFASs screened in this project is $C_nF_{2n+1}R$, determining that they consist of a fully fluorinated carbon chain and a carboxylic functional group (-CO_2H, for perfluoro-alkylated carboxylic acids, PFCAs*), a sulfonic functional group (-SO_3H when regarding perfluorinated sulfonic acids, PFSAs*) or simply an alkyl group (PFAAs*). n is equal to the number of carbon (C)-atoms in the molecule. On the other hand, the so-called polyfluoroalkylated substances have at least one C atom in the chain that is not fully flourinated, i.e. still being bound to a hydrogen (H) atom. Experiments have shown that both the number of F atoms as well as their location are important for the physiochemical properties of the substance (Kissa, 2001). However, in this study, focus has been on fully (per-)fluorinated compounds and not on polyfluorinated substances.

The fluorine atoms (F) are attached to the carbon chain by strong covalent bounds. 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. Moreover, studies have been able to show that PFASs can resist to e.g. heat and hydrolysis, although some degradation from longer to shorter C-chains have been shown when exposed to UV light (Taniyasu et al., 2013). However, most PFASs have low or even negligible vapour pressure, i.e. low volatility (Prevedouros et al., 2006; Ahrens et al., 2010).

PFASs can be ionic (cationic or anionic), amphoteric (i.e. both anionic and cationic) or neutral (Kissa, 2001; Ahrens, 2010). Anionic and cationic surfactants can dissociate in water and have been shown to be sensitive to changes in pH, whereas nonionic PFASs are insoluble in water (Kissa, 2001). Substances screened in this project were PFCAs, perfluorosulfonamides (FOSAs) and PFSAs, all non-polymeric compounds. They are listed in Table 3, 4 and 5, respectively.

Table 3: PFCAs screened in the project. Not detected substances are listed below the table. Abbreviations: Molecular weight (MW, displayed in [g mol^{-1}]), log octanol-water partitioning coefficient (log K_{OW}), vapour pressure, given in Pascal (Vp [Pa]). n.a. = not available. Vp was calculated from experimental data. Values from Wang et al. (2011).

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow, dry}$	Vp [Pa]
PFBA	Perfluoro-butanoate		$C_3F_7CO_2H$	45048-62-2	213.04	2.82	3890
PFPeA	Perfluoropen-tanoate		$C_4F_9CO_2H$	2706-90-3	263.05	3.43	1349
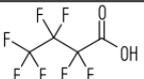
Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow, dry}$	Vp [Pa]
PFHxA	Perfluoro-hexanoate		$C_5F_{11}CO_2H$	92612-52-7	313.06	4.06	457
PFHpA	Perfluoro-hepanoate		$C_6F_{13}CO_2H$	120885-29-2	363.07	4.67	158
PFOA	Perfluoro-octanoate		$C_7F_{15}CO_2H$	45285-51-6	413.08	5.30	53.7
PFNA	Perfluoro-nonanoate		$C_8F_{17}CO_2H$	72007-68-2	463.09	5.92	18.6
PFDA	Perfluoro-decanoate		$C_9F_{19}CO_2H$	73829-36-4	513.10	6.50	6.61
PFUnDA	Perfluoro-undecanoate		$C_{10}F_{21}CO_2H$	196859-54-8	563.11	7.15	2.19
PFDoDA	Perfluoro-dodecanoate		$C_{11}F_{23}CO_2H$	171978-95-3	613.12	7.77	0.741
PFTrDA	Perfluorotri-decanoate		$C_{12}F_{25}CO_2H$	72629-94-8	663.13	–0.57	n.a.
PFTeDA	Perfluorotetra-decanoate		$C_{13}F_{27}CO_2H$	376-06-7	713.14	–0.99	n.a.
PFHxDA	Perfluoro-hexadecanoate		$C_{15}F_{31}CO_2H$	n.a.	813.16	n.a.	n.a.
PFOcDA	Perfluoroocta-decanoate		$C_{17}F_{35}CO_2H$	n.a.	913.18	n.a.	n.a.
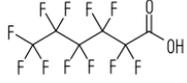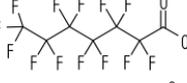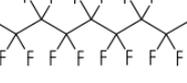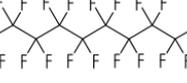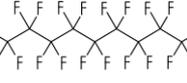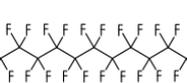
The following PFAAs were investigated, but found at concentrations below method detection limit (MDL): PFPeA, PFTrDA, PFTeDA, PFHxDA and PFOcDA.

Table 4: FOSAs screened for in the project. Not detected substances are listed below the table. Abbreviations: Molecular weight (MW, displayed in [g mol⁻¹]), log octanol-water partitioning coefficient (log K_{OW}), vapour pressure, given in Pascal (Vp [Pa]). n.a. = not available. Vp was calculated from experimental data. Values from Wang et al. (2011).

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow,dry}$	Vp [Pa]
FOSA	Perfluorooctane sulfo-namide		$C_8F_{17}SO_2NH_2$	754-91-6	499.18	5.62	0.245
FOSAA	perfluorooctane sulfo-namidoacetic acid		$C_8F_{17}SO_2NHCH_2CO_2$	n.a.	559.23	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-octanesulfonamidoace-tic acid		$C_8F_{17}SO_2N(CH_2)_2CH_3$ CO_2	n.a.	584.26	n.a.	n.a.
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-etha nol		$C_8F_{17}SO_2N(CH_2)_3CH_3$ OH	1691-99-2	571.25	n.a.	n.a.
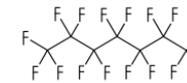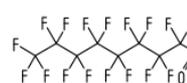
Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow,dry}$	Vp [Pa]
MeFOSA	N-methylperfluoro-1-octansulfonamide		$C_8F_{17}SO_2NHCH_3$	31506-32-8	513.20	n.a.	n.a.
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid		$C_8F_{17}SO_2N$-$CH_3CH_2CO_2$	n.a.	570.23	n.a.	n.a.
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol		$C_8F_{17}SO_2N(CH_2)_2CH_3$ OH	24448-09-7	557.22	n.a.	n.a.
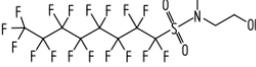
The following FOSAs were investigated, but found at concentrations below MDL: N-EtFOSA, N-EtFOSAA, Et-FOSEE, N-EtFOSE, FOSAA, N-MeFOSA, N-MeFOSAA and MeFOSE.

Table 5: PFSAs screened for in the project. Not detected substances are listed below the table. Abbreviations: Molecular weight (MW), log octanol-water coefficient (log K_{OW}), vapour pressure, given in Pascal (Vp [Pa]). n.a. = not available. Vp was calculated from experimental data. Values from Wang et al. (2011).

Compound	Name	Structure	Molecular formula	CAS no.	MW	log $K_{ow,dry}$	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
PFOS	Perfluorooctane sulfonic acid		$C_8F_{17}SO_3H$	1763-23-1	500.16	6.43	6.76
PFDS	Perfluorodecane-sulfonic acid		$C_{10}F_{21}SO_3H$	335-77-3	600.18	7.66	n.a.
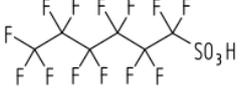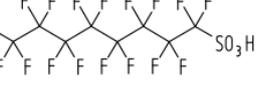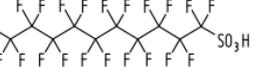
The following PFSA was investigated, but found at concentrations below MDL: PFDS.

2.2.2. Transport and fate in the environment

Researchers have been able to show that the fluxes of PFASs are present in all parts of the ecosystem – water, air, soil et cetera. Due to their sensitivity and crucial importance, surface water bodies such as oceans, lakes and rivers have been and are still being widely studied. An investigation done by Ahrens et al. (2009a) on the Atlantic ocean showed that the northern part of the ocean had moderate PFASs concentrations in the surface water, whereas the samples from the Southern Hemisphere could be classified as "clean" when considering PFASs contamination. On a smaller scale, studies done by Loos et al. (2009 and 2010, respectively) and Möller et al. (2010) showed that PFASs were found in more than 90% of the European rivers, at concentrations ranging between 3 to 1371 ng L^{-1}. As little as 10% of the rivers included in the EU-wide screening of 2008 could be denoted as clean with respect to chemical contaminants (Loos et al., 2009). PFASs have also been found in treated waste water, tap water, and bottled drinking water (Llorca et al., 2012).

The origin and sources of PFASs in the environment are of many different types. In addition to the sources listed in section 2.2., discharges from WWTPs and atmospheric deposition are supposed to be the major PFASs contributors to the environment (Filipovic et al., 2013; Loos et al., 2010). However, there are uncertainties when discussing which pathways that are the dominant ones; atmospheric deposition is supposed to be a major (e.g. McLachlan et al., 2007; Loos et al.,

2010) as well as a minor source (e.g. Murakami et al., 2008; Filipovic et al., 2013). Therefore, focus in this project was limited to the aqueous pathways.

Water is the worlds most used natural solvent, making its ongoing contamination with chemical pollutants a severe problem. Pollutants such as e.g. WWTPs, industries and landfill leach-ates are some of the sources of increased PFASs concentrations in the aqueous system. However, the behaviour of PFASs in the environment is still not fully understood. There are indications that PFASs can vary with temporal trends, temperature or pH, although the reason for the variability is unknown (Myers et al., 2012). A compilation of a number of possible PFASs sources for the release into the environment and the aqueous system is displayed in Figure 2.
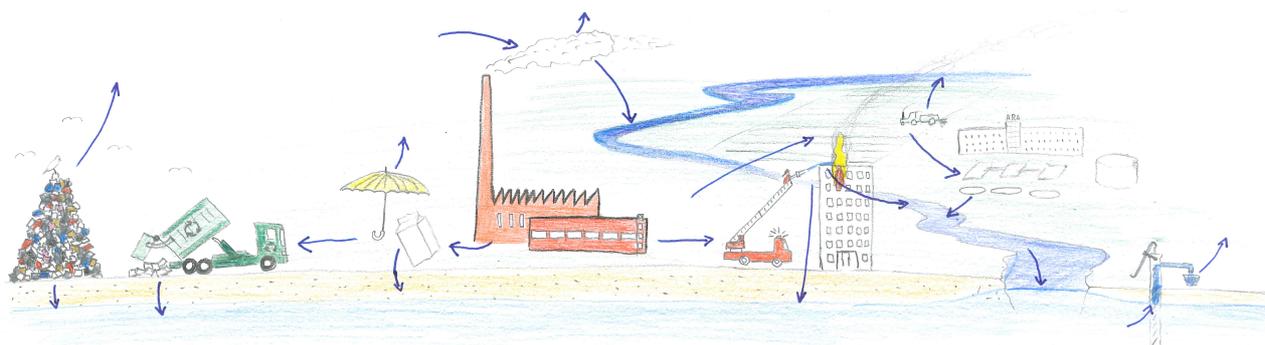
Figure 2: Fluxes of PFASs in the environment. Some of the main pathways for PFASs to reach the environment are by fire fighting foams, landfill leachates and ef-fluents from WWTPs. More pathways than the ones displayed might exist.

Other contributors to PFASs in surface waters are contaminated sediments and landfill leachates. Landfill leachates can be an important contributor to PFASs in the environment as there are possibilities for very high levels (up to and above 8000 ng L^{-1}) even in treated water (Busch et al., 2010). A lake sediment study performed by Myers et al. (2012) showed predominance of shorter-chained PFASs near urban or industrial areas, reaching peak concentrations of 1.1 ng L^{-1}. Moreover, the high values detected in sediments and treated waste water, illustrate in combination with their detection in bottled water (Llorca et al., 2012) the difficulties in the removal of PFASs from water.

In addition to the possibility of being transported in the dissolved form, PFASs can also bind to particles and be transported with them in the aqueous systems. Particles are believed to en-hance the transport of PFASs when the velocity is moderate or high, but simultaneously increase the sedimentation rate when transported at a low pace; studies done on lake and sea sediments point in that direction (Myers et al., 2012).

2.2.3. Exposure and health aspects

The use of PFASs is variegated, and so is our exposure to them. Drinking water, food packaging and even the food itself have traces of fluorinated compounds inside, making them our key exposure pathways (e.g. Boon et al., 2002; KemI, 2009; Thompson et al., 2011; Llorca et al., 2012). Emissions calculations and extrapolations estimate that almost 80% of the PFCAs historically produced have

been emitted to the environment, suggesting that all mankind have grains of PFASs in their bodies (Prevedouros et al., 2006; Loos et al., 2009; Ahrens et al., 2009b).

PFASs have shown several adverse effects on both humans and wildlife. Today, PFASs are known to be toxic, bioaccumulative, biomagnifying, carcinogenic and endocrine disrupting (Jensen and Leffers, 2008; Ahrens, 2010; Kannan, 2011). Hence, different studies have been able to elucidate that both carbon chain length and the functional group are of great importance for the toxicity of a PFASs; toxicity is known to increase with increased chain length, and sulfonic perfluoroalkyl acids (PFAAs) are more toxic than carboxylic PFAAs (Ahrens, 2010; Ulhaq et al., 2013a; Ulhaq et al., 2013b).

Concerning toxicity, little is known on the risks environmentally released PFASs cause to human health. There are several studies done on mice, fish, birds and different top predators, showing that, firstly, bioaccumulation is occurring due to the fact that predators had much higher PFASs concentrations than the environment and their feed, and secondly, PFASs were accumulated in liver, brain, gallbladder and intestines of zebrafish, indicating that there is an in-body recirculation of PFASs (Thompson et al., 2012; Ulhaq et al., 2014). Giesy and Kannan (2001) were able to state that there were differences between the exposure of animals in terms of distance to urban or industrial areas, as well as differences between the northern and southern hemisphere. Although results assuming little exposure of animals in remote regions of the world were partly contradicted by Smithwick et al. (2006), the fact that proximity to cities result in higher PFASs concentrations is still deemed to be valid. Bioaccumulation and bioconcentration was also found to be present in humans; PFOS and PFOA analysed in human blood was found to be bound to blood serum proteins (Jensen and Leffers, 2008).

3. Materials and methods

3.1. Experiment design

The goal of this project was to screen of FR and PFAS levels in rivers all over Sweden, in order to provide information on their contribution to the FRs and PFASs found in the Baltic Sea. Sampling was performed as proposed by Loos et al. (2009 and 2010). The plan was not to provide long-time sampling, but to give a snapshot of the situation in a small interval of time. Due to that reason, the decision was made to take grab samples.

3.2. Chemicals and equipment

In this chapter, chemicals and reagents used throughout the laboratory work of project are listed. Solvents used were: Acetone (SupraSolv®), dichloromethane (DCM*) (SupraSolv®), isooctane (SupraSolv®), methanol (LiChrosolv®) and toluene (SupraSolv®), all purchased from Merck KGaA, Darmstadt, Germany. Acetic acid solution (≥99.7%), ethyl acetate, 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 (filtered with Milli-Pak® 0.22 μm filter) was available at the laboratory.

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

The following laboratory equipment and machinery was used: 2 ml amber glass vials (from Agilent Technologies), 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 μm (from Waters, Wexford, Ireland), peristaltic pump MasterFlex® (model 77800-62 Cole-Parmer easyload®3 from Barnant Company, Barrington, USA), pH-meter VWR pHenomenal™ (and calibration solutions pH 4.01 and 7.00, also from VWR, Germany), 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 Ø, GE Healthcare UK Limited, Buckinghamshire, United Kingdom).

The FRs samples were collected in POP-cans (volume 3 US gallons/12 litres, from Sharpsville container/NSF Component®). Samples for PFASs and SPM were collected in polypropylene (PP*) bottles (volume 1 L, fromVWR International, Radnor, India).

3.2.1. Chemicals used for FRs

The FR screening part of the project contained 13 different compounds. Native compounds used in the calibration samples were in the range of 0.25 pg μL^{-1} to 450 pg μL^{-1}. The compounds included in the calibration batch were 2,4,6-TBP, PBP, TBBPA, HBB, BEHTBP, DBDPE, EHTBB, PBT,

DBE-DBCH, α-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 mass-labeled (^{13}C) internal standards (IS*) of the screened FRs. This was done in order to be able to identify and correct for losses during extraction and concentration. The spike solution contained BTBPE, γ-HBCDD, TNBP and a PBDE surrogate stock, including BDE28, BDE47, BDE99, BDE100, BDE153, BDE154 and BDE183 (URL5). Lastly, the injection standard (InjS*) Mirex was added to all samples prior to analysis. All IS, InjS and Mirex were purchased from Wellington laboratories, Ontario, Canada.

3.2.2. Chemicals used for PFASs

The screening of PFASs contained 16 different fluorinated compounds. Native compounds were used in the calibration samples and set to concentrations between 0.05 pg μL^{-1} to 40 pg μL^{-1}. The compounds included in the calibration batch were PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, EtFOSA, EtFOSAA, EtFOSE, FOSA, MeFOSA, MeFOSAA, MeFOSE, PFHxS and PFOS. More information on these compounds as well as chemical formulas and full names can be found in Tables 3, 4 and 5 in the literature study part. The samples were spiked with mass-labeled (^{13}C) IS, including the compounds PFBA, PFHxA, PFOA (^{13}C$_4$ PFOA was used as IS and ^{13}C$_8$ PFOA was used as InjS), PFNA, PFDA, PFUnDA, PFDoDA, PFHxS, EtFOSE, EtFOSAA, FOSA, MeFOSAA and MeFOSE. Both IS and InjS were purchased from Wellington laboratories, Ontario, Canada.

3.2.3. Chemicals used for analysis of total organic carbon content (TOC)

For analysis of the amount of total organic carbon (TOC*) in the samples, 1000 ppm KH-phthalate, EDTA and 2 M hydrogen chloride (HCl) was used for the standard solutions. TOC was analysed using a Shimadzu TOC-VCPH and an ASI Autosampler. Each sample was spiked with 1000 ppm KH-phthalate and 2 M HCl prior to analysis. No analysis of dissolved organic carbon (DOC*) were carried out in this project.

3.3. Site selection

In order to provide a comprehensive view of the pollutant situation due to FRs and PFASs in Sweden, sites were selected on the basis of several criteria. Firstly, catchment size and riverine discharge were of vital importance. All rivers with a catchment of 4000 km^2 or more were directly included in the project. Secondly, rivers of densely populated parts of Sweden were chosen, as urban areas are supposed to have higher levels of both FRs and PFASs. Eventually, some rivers where high values could be expected (due to, e.g. large-scale industrial activities) but that did not fit into the criteria of large discharge areas or populations were added to the screening sites. However, the goal was to screen a big variety of different water bodies, big and small as well as from urban and remote areas. Thus, rivers included in the project are of manifold characteristics.

For the FRs, 25 sampling sites were chosen between Haparanda (Torne älv) in northern Sweden and Kristianstad (Helge Å) in the southern part, all on the east coast of Sweden. There were also four extra sites (Vindelälven at Krycklan and at Rödånäs, Ume älv at Gubböle and Fyrisån in Uppsala) sampled in order to compare FR variations at different places in the river. Although these rivers did not drain to the sea surrounding Sweden (i.e. the Baltic Sea, Skagerrak and Kattegat), the main focus was to sample rivers that had a direct impact on its water quality. An overview of the

sampling sites is presented in Figure 3. A more detailed map of sampling sites, rivers and watersheds, river maps and sampling sites are displayed in Figure A1 in the appendix. Moreover, GPS coordinates of all exact locations can be seen in Table B2 in the appendix.

The screening of PFASs included 44 sites between Haparanda (Torne älv) and Kristianstad (Helge Å) on the east coast as well as samples from the west coast between Löddeköpinge (Kävlingeån, partly also called Lödde Å) and Östad (Enningdalsälven). All rivers screened for FRs were also included in the PFASs screening. However, some sites not included in the FR screening of the east coast were added for the PFASs screening. The reasons for this were logistical circumstances and the fact that the extremely hydrophobic FR compounds (see Tables 1 and 2) needed larger volumes for the laboratory work. Sampling was performed by the author and by people involved in the Project "Flodmynningar" by the Swedish University of Agricultural Sciences. However, all samples were taken within a short time period in the first weeks of October, 2013. Catchments, river maps and PFASs sampling sites are displayed in Figure A2 in the appendix.
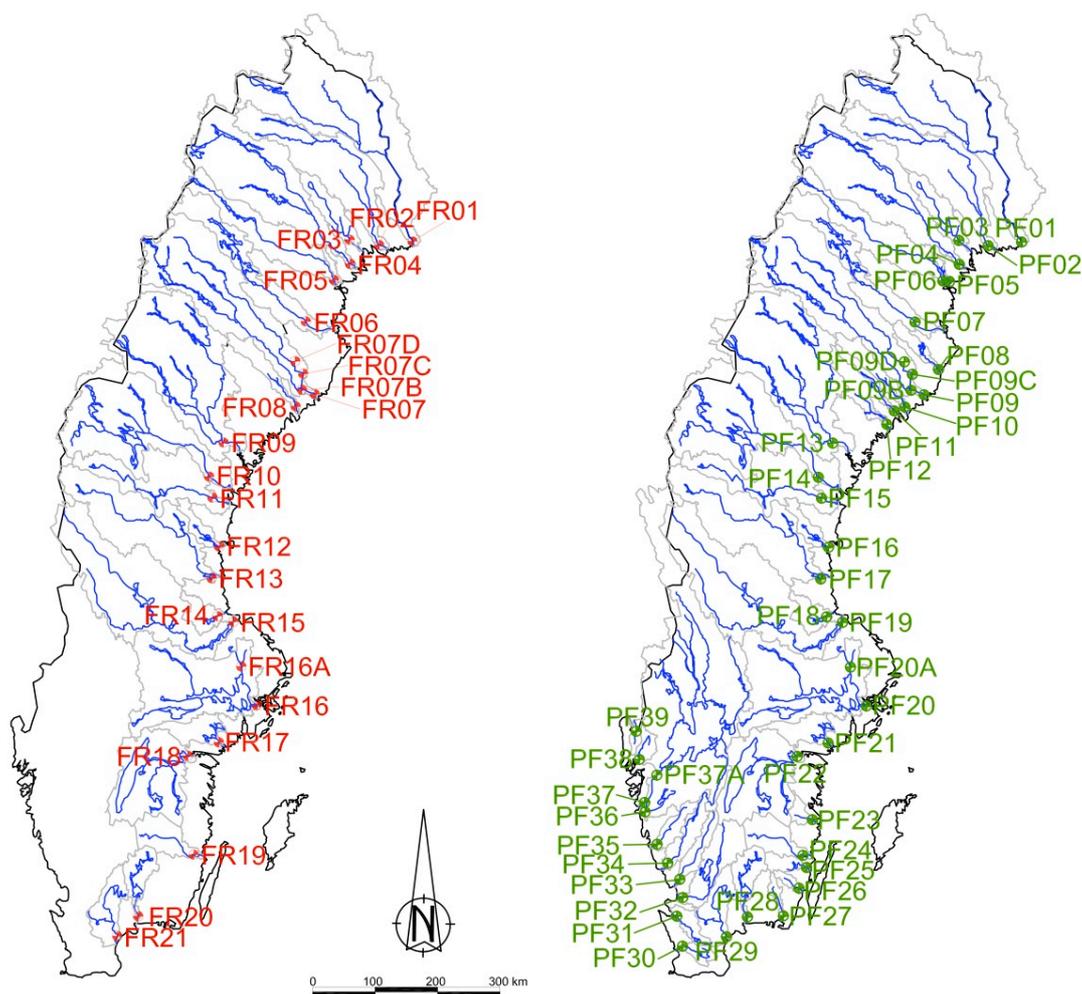
Figure 3: Sampling sites for FRs (on the left) and PFASs (on the right). Rivers are displayed in blue, watersheds in grey. More detailed maps are attached in the appendix part A, Figures A1 and A2, respectively. Maps drawn by the author.

The extra (upstream) sites sampled in Ume älv/Vindelälven catchment (Sites FR07-FR07D for FRs and PF09-PF09D for PFASs), Fyrisån (Site FR16A and PF20A) and Göta älv (Sites PF37 and

PF37A) were chosen to be included in the study due to several reasons. *Pro primo,* they have all been thoroughly investigated in previous studies, and, *pro secundo,* they do either allow us to draw conclusions on background values and water quality of remote and sparsely populated areas, or of densely populated areas, respectively. The Fyrisån ends up in the lake Mälaren, whose discharged water was also sampled in Stockholm (Norrström). Göta älv was sampled upstreams at Trollhättan and further downstreams at Gothenburg, however just for PFASs and not for FRs. These extra sites are denoted with capital letters, in order to clarify that they are not from different rivers. Their locations can be seen in Figure 4; GPS coordinates are displayed in Table B2 in the appendix.
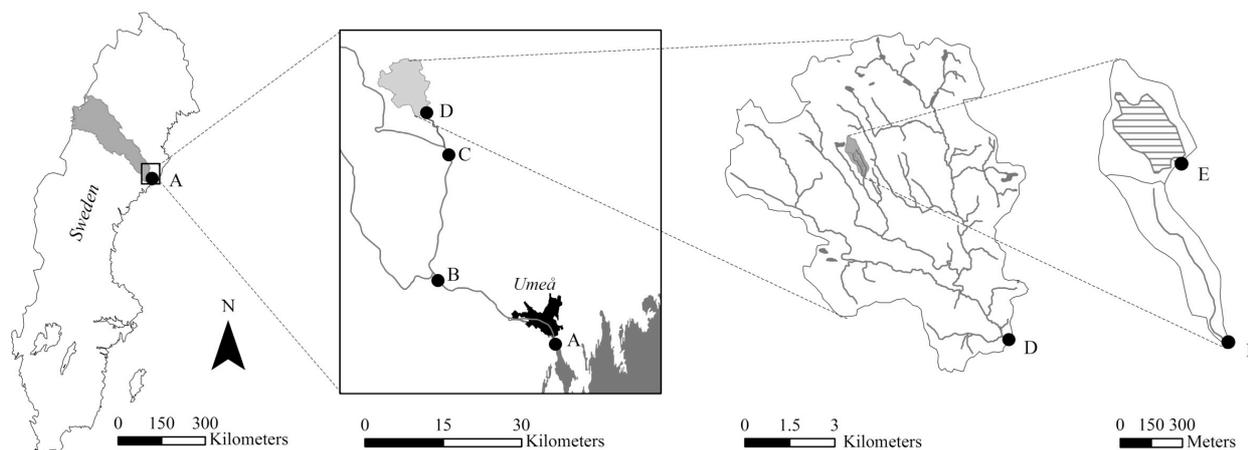
Figure 4: Sampling sites of the Krycklan catchment study. Sites A, E and F were not used in this project. Figure from Bergknut et al. (2012).

3.4. Sample collection

In order to provide a snapshot of the situation of new, possibly emerging EDCs all over the Swedish area, all samples except the Fyrisån sample were collected within a 10-day period, from October 1st to October 9th, 2013. The Fyrisån sampling was scheduled later due to practical reasons and was performed on October 25th.

All samples were collected according to techniques used in previous screening (Loos et al., 2009; Loos et al., 2010). A stainless steel bucket was connected to a 30 m polypropylene (PP) rope and lowered into from the rivers. All sampling was performed in the middle of the stream (from the upstream side of a bridge), or from the shore when no useful bridges were available. 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 sampling was performed from a jetty in both cases. Pictures of sampling Råne älv (near Niemisel) are shown in Figures 5 and 6 in order to illustrate the sample collection. All FR sites were also sampled for total organic carbon (TOC*) and suspended particulate matter (SPM*). After sampling, measurements of pH and water temperature were done at each site, using the electric pH-meter mentioned earlier.

For the FR sampling, the samples were collected in 12 L stainless steel POP-cans. PFASs and SPM samples were collected in 1 L PP-bottles. Water for TOC analysis was collected in 250 ml PP bottles. All stainless steel sampling equipment was rinsed prior to sampling with three times ethanol, Millipore water and acetone, respectively. Moreover, a second rinsing (of i.e. bucket, sample

bottles and POP-cans) with three times river water was done prior to the sample collection at each site. The PFASs, SPM and TOC bottles were purchased from VWR International and did not undergo a pre-cleaning step with solvents. However, they were also rinsed three times at site with local river water. Bottles for PFASs, SPM and TOC were wrapped in aluminium foil after sampling in order to prevent exposure to direct sunlight or UV radiation and stockpiled in at upright position. TOC bottles were stored in a cooling box. All samples were brought to the laboratory within at most 3 days and then stored in a refrigerator at +4 °C. All FR extractions were performed within one month after sample collection, whereas the extractions for PFAS were done within two months from sample collection.
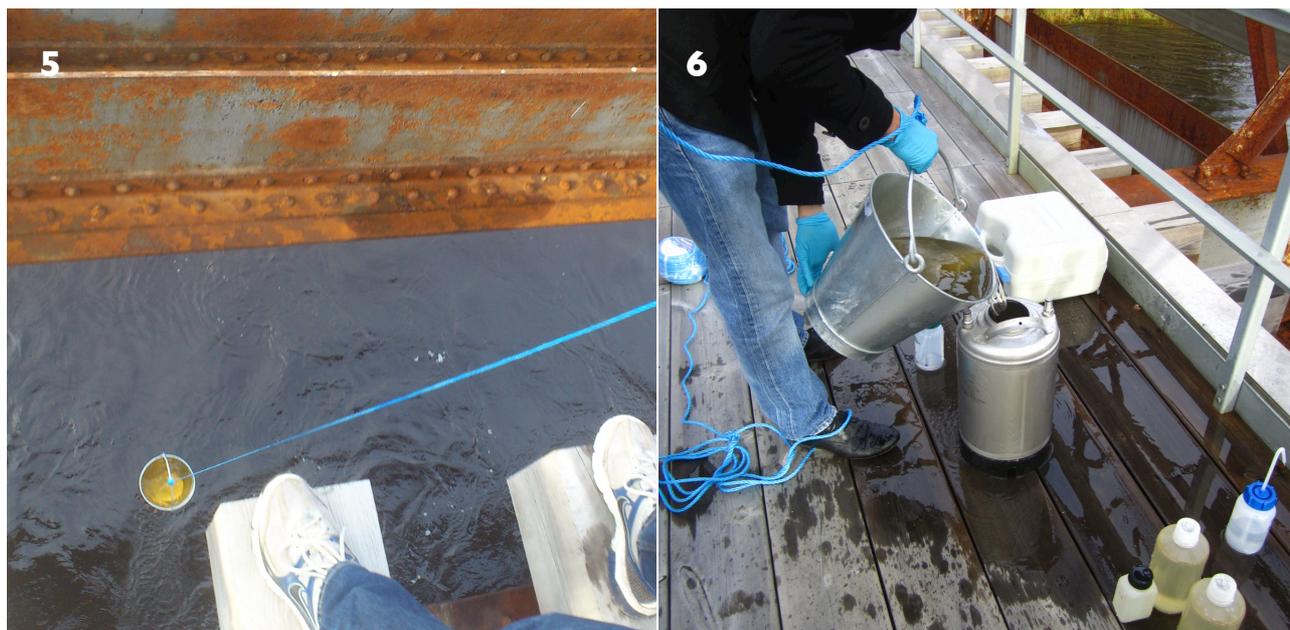
Figures 5 and 6: Bucket sampling at Råne älv, Niemisel. All sampling equipment was rinsed on site with river water prior to using or filling.

3.5. Analysis of suspended particulate matter and total organic carbon

Being considered potentially important parameters for pollutant transport in rivers, gravimetrical measurements of SPM and TOC were performed, using a Whatman™ glass microfibre filters (diameter 47 mm) and the filtration glassware (Werner Glas). Depending on the amount of particles in the water, between one and three filters were used per litre water. These filters were then dried and weighted. SPM is defined as fine and insoluble organic or inorganic particles that are transported in the water phase (URL6). SPM gives an indication of the amount of particles that are transported with the river, while TOC shows the amount of organic carbon. Hydrophobic POPs tend to bind to organic carbon, but a previous study has demonstrated that SPM is a better proxy for the levels of very hydrophobic POPs in rivers (Josefsson, 2011). The analysis of both SPM and TOC was thus done in order to characterise the pathways for the transport of PFASs and FRs in the aquatic system.

3.6. Extractions of EDCs

All water samples were extracted and analysed at the POP laboratory of the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences SLU in Uppsala, Sweden.

3.6.1. Solid-phase extraction for FRs

For the FR, Amberlite XAD-2 Polymeric Adsorbent was used. XAD-2 was pre-cleaned in a Soxhlet apparatus in two steps (firstly methanol for 48 hours, secondly ethyl acetate for 48 hours), then dried in nitrogen gas (N_2) for 1 hour and finally stored in a freezer at -20 °C until usage.

Glass columns used for the extraction were prepared as follows: firstly, 0.5 g glass wool (GW*) was placed at the bottom of the glass column in order to prevent the adsorbent from entering the piping system. Secondly, 20.0 g XAD-2 was added to the column and sealed with another 0.5 g GW. Finally, 34 g glass beads were added to the column in order to keep adsorbent and GW in place. Each sample was spiked with 100 μL (80 pg μL^{-1}) of internal standard (IS*), directly into the POP-can. The IS contained the masslabeled compounds mentioned earlier. After spiking, the POP-cans were manually shaken 3x30 seconds in order to distribute the internal standards evenly.

The piping system consisted of rubber tubes, PP tubes and silicone tubing. Rubber tubes were connected directly to the POP-cans on the one hand and to the glass columns on the other hand, as shown in Figures 7 and 8. A peristaltic pump with a three-rollers rotor was used to pump the fluid through the glass column at a speed of 10 (during start-up) to 25 rpm, which corresponds to a flow rate of 6.53E^{-4} L s^{-1}. Silicone tubing was used in the rotor part of the pump due to its flexibility and low chemical reactivity. All pipes were pre-cleaned with 2.5 L MilliPore water prior to connecting it to the glass column, in order to ensure that possible left-over pollutants were removed; the possible sorption of analytes to the piping system was also accounted for by the use of internal standards that were considered to stick to the piping system in the same way as the screened compounds. The cleaning was carried out at considerably higher water flow. However, no MilliPore water was pumped through glass column or adsorbent.

The SPE was followed by drying the XAD-2 adsorbent with N_2-gas flow for 45 minutes. It was then eluted using 2x70 mL dichloromethane (DCM*). The eluted samples were collected in round-bottom flasks, sealed and stored in the freezer at -20 °C until concentration of the samples by volume reduction. Elution was performed the same day as the extraction occurred.
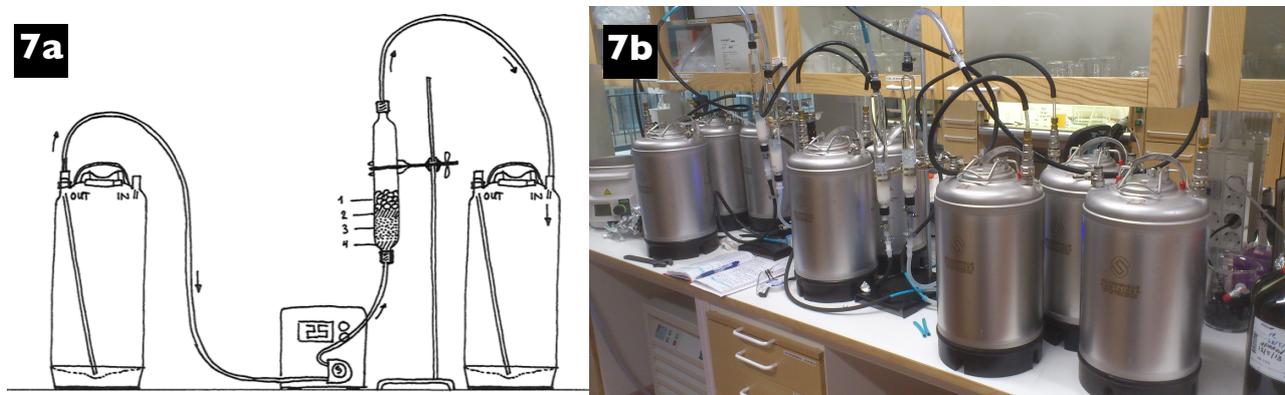
Figures 7a and 7b: The FR SPE. *Figure 7a* shows the extraction process schematically. Numbering: 1: glass beads, 2 and 4: GW, 3: XAD-2. *Figure 7b* is a picture of the extraction process with four extractions running in parallel.

While storing in the freezer, water still present in the sample congealed at the surface or along the side walls. The first step in further concentrating the samples was done by pouring them into TurboVap™-flasks, leaving the ice in the round-bottom flask. They were then concentrated from 140 ml to 1 ml in the Biotage TurboVap™ machine by evaporation of the DCM solvent (water temperature was set to 40 °C, N_2-pressure 8 bar). DCM has a higher vapour pressure than water (47 kPa at 20 °C for DCM compared to 2.3 kPa at 20 °C for H_2O) and therefore evaporates faster, while the FR were left in the sample concentrates (Aylward and Finley, 2007). In order to ensure complete water removal, the sample was poured through a second extraction column, prepared with 1 g sodium sulphate (Na_2SO_4). This second extraction column was pre-cleaned with DCM, and also eluted with 6 mL DCM afterwards. The sample in DCM was collected in a 10 ml glass vial and stored at -20 °C until the final concentration. The final concentration step was done by reducing the sample volume to 1 ml under N_2-stream in a nitrogen evaporator N-Evap™112. The samples were hereafter transferred to 1 ml amber glass vials. The injection standard (Mirex) was added and the samples were stored in freezer at -20 °C until instrumental analysis.

3.6.2. Solid-phase extraction for PFASs

PFASs were filtrated prior to the SPE. Filtration was done using a glass microfibre filter (GF*), Werner Glas filtration equipment and vacuum. All glass material was burnt at 400 °C for four hours and carefully cleaned using methanol prior to use. After the filtration, the GFF were packed in aluminium foil and stored in a desiccator in order to remove water from the filter. GFFs were weighted and before and after drying, but not analysed for PFASs bound to suspended particle matter. The weight results are displayed in Table B1 in the appendix. After the filtration, the samples were divided into 2x0.5 L, as only 0.5 L was needed for the extraction and clean-up. The bottles were stored in the refrigerator 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. A schematic drawing of the extraction set-up for PFASs is shown in Figure 8a, and a picture of the used workstation is displayed in Figure 8b. Prior to the SPE, each water sample was spiked with 100 μL internal standard (20 pg μL^{-1}) in order to correct for possible losses during extraction and concentration. Cartridges and extraction materials were preconditioned in three steps, using 4 mL ammonium hydroxide buffer, 4 mL methanol and 4 mL MilliPore water. After preconditioning, the extraction was started and the water flow was regulated to one drop per second by using vacuum.
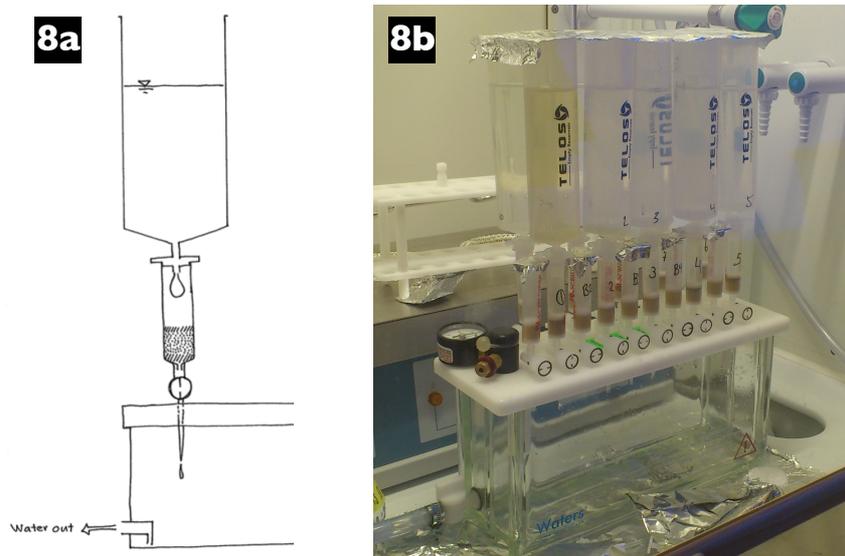
Figures 8a and 8b PFASs SPE. *Figure 8a* shows a schematically drawn set-up of the SPE for PFASs. The water samples are loaded into the upper reservoirs. *Figure 8b* is a picture of the SPE.

After the extraction, the cartridges were washed with a ammonium acetate buffer, and left-over water was removed using a centrifuge prior to the elution. The water extracts were eluted using 4 mL methanol (for FOSAs) and 4 mL 0.1% ammonium hydroxide buffer (for PFCAs, PFSAs et cetera). They were collected in 15 mL PP tubes and stored in freezer until further concentration. The extracts were further concentrated, again using the nitrogen evaporator N-Evap™112, to 1 mL. Having reached a final volume of 1 mL, they were transferred to 2 mL amber glass vial. 10 μL InjS was added (200 pg μL^{-1}) and the samples were stored in the freezer until instrumental analysis.

3.7. Instrumental analysis of FRs and PFASs

All analyses were done according to the standard procedures at the POP laboratory of the Swedish University of Agricultural Sciences SLU. Laboratory blanks were used and showed that no significant site-external contamination occurred. All sample concentrations were corrected for concentrations in corresponding blanks.

3.8. Gas chromatography tandem mass spectrometry

All FR extracts were analysed for the FRs mentioned in Tables 1 and 2, using gas chromatography coupled with tandem mass spectrometry (GC-MS^2)*, according to NIVA (2010) and Papachlimitzou et al. (2011). The GC-MS^2 used was the GC system 7890A and the GC/MS Triple Quad 7000 from Agilent Technologies, shown in Figure 9. The analysis was performed in two runs, where the second was for PBDE analysis only. Internal quantification was used. A calibration curve was set up using seven FR calibration solutions with native compounds at concentrations of 0.25, 1.25, 6, 30, 150, 300 and 450 ng mL^{-1}. For peak identification, retention time (RT*) and quantifier/qualifier ratio of the target compounds was used.
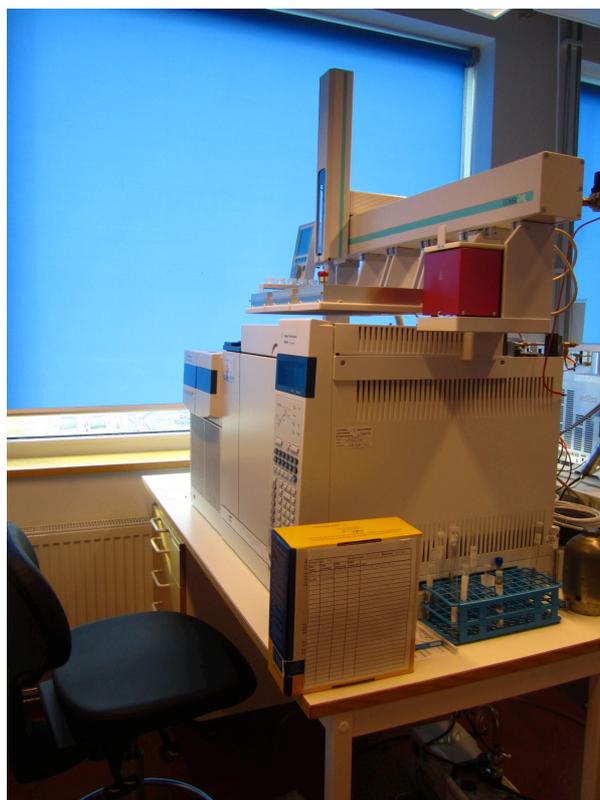
Figure 9: The GC-MS² used for the analysis of FRs.

3.9.   Liquid chromatography tandem mass spectrometry

All PFASs extracts were analysed for the compounds mentioned in Tables 3, 4 and 5, using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS²)*, according to the methods suggested by van Leeuwen and de Boer (2007) and Ahrens et al. (2009). Identical to the FR analysis, internal quantification was used. The LC used was the 1200 series from Agilent Technologies and the 6460 TripleQuad, also from Agilent. The calibration curve was set up a series of six PFAS calibration solutions of native compounds, at concentrations of 0.05, 0.25, 1.0, 4.0, 8.0 and 40 ng mL⁻¹. For peak identification, RT and quantifier/qualifier ratio of the target compounds was used. The LC-MS² used is shown in Figure 10.
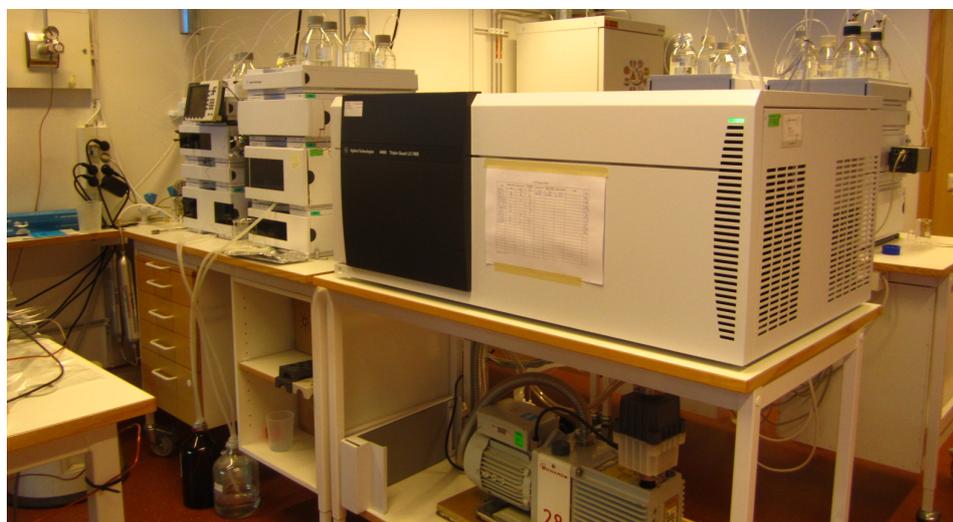
Figure 10: The LC-MS² used for the analysation of PFASs.

3.10. Chromatogram analysis

Compounds of both substance categories were identified by using the Agilent QQQ MassHunter and Oracle™ OpenOffice. Quality assurance and quality control was performed by integrating the peaks from the chromatogram and eventually comparing the areas of calibration standards with known concentrations with the areas of the extracts. Retention times given by the calibration standards were used as setpoint values. Peaks at correct retention times were used if the signal to noise ratio was ≥3. Hereafter, the sample peak areas were compared with the peaks from the calibration standards in order to determine the recovery of the substances. This was done in an identical way for both substance classes.

3.11. Quality Assurance/Quality control

Due to the wide-spread presence of FRs and PFASs and their common use in daily life products, care was taken in order to avoid contamination from site-external objects and materials, by use of and correction for several blanks such as field blank, elution blank, laboratory blanks et cetera. For the FRs, two field blanks and one elution blank was used for calculating the method detection limit (MDL*) and method quantification limit (MQL*). For the PFASs, a total of five blanks were used, namely laboratory blanks.

MDL and MQL were determined as described by Simonsen (2005). A mean value concentration of the blanks was used together with the following formula in order to get the MDL:

$$MDL = mean_{\text{blanks}} + 3 \cdot SD_{\text{blanks}} \tag{1}$$

where $mean_{\text{blanks}}$ is the mean value of the blanks, SD_{blanks} is their standard deviation. If the substance was not detected in the blanks, the MDL was calculated from the lowest calibration standard detected. The MDL was calculated both as an absolute value [ng] as well as a value adjusted to its corresponding value, displayed in [ng L^{-1}]. MQL was calculated from the MDL, using formula (2):

$$MQL = \frac{10 \cdot MDL}{3} \tag{2}$$

4. Results

4.1. Quality assurance and quality control

In order to provide reliable and satisfactory results, quality assurance and quality control (QA/QC) was carried out by analysing both laboratory and field blanks. The recovery was calculated by relating peak areas of internal standards to peak areas of injection standards added to the samples prior to extraction and prior to instrumental analysis, respectively, and is displayed in Table 6 for the PFASs. For the FRs, only one compound was used as a standard (namely M-BDE99), and its recovery was calculated to 72 ±0.43%. All substances (FRs and PFASs) were in the range of 50–150% recovery, which is considered to be acceptable.

Table 6: Recovery for PFASs. Compilation of peak areas of the native compounds with the investigated PFASs and their corresponding recovery.

Internal Standard:	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Recovery [%]	105 ±4.8	91 ±19	110 ±21	106 ±20	106 ±32	101 ±32	89 ±38

Internal Standard:	FOSA	MeFOSAA	MeFOSE	EtFOSAA	EtFOSE	PFHxS	PFOS
Recovery [%]	94 ±31	117 ±28	59 ±10	109 ±28	53 ±10	94 ±2.6	110 ±21

For all target substances, the method detection limit was calculated using the results achieved by the blanks. For the FRs, two fieldblanks were used, consisting of POP-cans filled with Millipore water at the lab and opened on site (Helge Å near Kristianstad and Motala ström near Norrköping) for 30 seconds. Also, elution blanks (consisting of clean DCM and clean XAD-2) and laboratory blanks/GC blanks (IS spiked directly into the analysis vials) were used. For PFASs, blanks consisted of spiking directly into the cartridges. No field blanks with Millipore water from the lab were used for the PFASs samples as Uppsala has had issues with PFASs pollution of its drinking water earlier (Kärrman et al., 2007). The MDL and MQL for the FR and PFAS target substances are listed below in Tables 7 and 8, respectively.

Table 7: Method detection limit for FRs, calculated from the blanks. The mean values of the blanks are displayed in ng absolute. Formulas for the calculations of MDL and MQL can be found in part 3.11. Quality assurance/Quality control.

Substance	Blank concentration [ng]	MDL [ng]	MDL [ng L⁻¹]	MQL [ng]	MQL [ng L⁻¹]
2,4,6-TBP	n.d.	9.00	0.75	30.00	2.50
PBP	0.56	2.82	0.24	9.41	0.78
TBBPA	n.d.	1.80	0.15	6.00	0.50
HBB	n.d.	0.38	0.03	1.25	0.10
BEHTBP	3.92	24.31	2.03	81.03	6.75
DBDPE	702	2600	220	8600	720

Substance	Blank concentration [ng]	MDL [ng]	MDL [ng L⁻¹]	MQL [ng]	MQL [ng L⁻¹]
EHTBB	6.3	39	3.3	130	11
PBT	n.d.	0.38	0.03	1.3	0.10
HBCDD	20	120	9.9	390	33
TCIPP	310	1000	86	3400	290
TPHP	38	190	16	630	53
BTBPE	n.d.	9.0	0.75	30	2.5
DBE_DBCH	1.8	11	0.91	37	3.0
Sum DBE-DBCH	n.d.	1.8	0.15	6.0	0.50

n.d. = not detected.

Table 8: Method detection limit, calculated from the blank. The mean values of the blanks are displayed in ng absolute. Formulas for the calculations of MDL and MQL can be found in part 3.11. Quality assurance/Quality control.

Substance	Blank concentration [ng]	MDL [ng]	MDL [ng L⁻¹]	MQL [ng]	MQL [ng L⁻¹]
PFBA	0.029	0.12	0.23	0.38	0.77
PFHxA	0.058	0.32	0.64	1.06	2.1
PFOA	0.051	0.087	0.17	0.29	0.580
PFNA	0.012	0.032	0.064	0.11	0.21
PFDA	0.015	0.015	0.030	0.050	0.10
PFUnDA	0.014	0.018	0.036	0.060	0.12
PFDoDA	0.015	0.015	0.030	0.050	0.10
FOSA	0.015	0.015	0.030	0.050	0.10
MeFOSAA	0.012	0.030	0.060	0.10	0.20
MeFOSE	0.061	0.15	0.31	0.51	1.02
EtFOSAA	0.015	0.015	0.030	0.050	0.10
EtFOSE	0.058	0.17	0.35	0.58	1.2
PFHxS	0.015	0.015	0.030	0.050	0.10
PFOS	0.015	0.015	0.030	0.050	0.10

The levels of FRs and PFASs showed great dissimilarities. While the PFASs blanks had rather low concentrations (below 1 ng L⁻¹), some compounds of the FRs were found at concentrations of up to 310 ng L⁻¹. TCIPP was the substance showing the highest amounts in the blanks. Combined with a rather high standard deviation between the elution blank and the field blanks, the MDL and MQL ended up being 86 and 290 ng L⁻¹, respectively.

The blank analysis for the PFASs showed detectable traces of most short-chained compounds, but the values were generally low. The MDL values were in the range of 0.030 ng L⁻¹ (i.e. not detected in the blanks at all) to 0.64 ng L⁻¹, the MQL values found between 0.10 ng L⁻¹ and 2.1 ng L⁻¹.

4.2. FR results

The target compounds screened for in this project were selected due to their ubiquitous presence in the environment, as literature of previous research stated. The investigation of the samples showed that almost all rivers had low to very low overall levels of FR. Out of the 14 compounds of interest, only 8 were actually found. However, six rivers (Delångersån, Ljusnan, Fyrisån and Helge Å) showed FR levels well above the mean values, with TCIPP as the main compound. The observed levels as well as the percentage composition of FRs are shown in Figures 11 and 12.
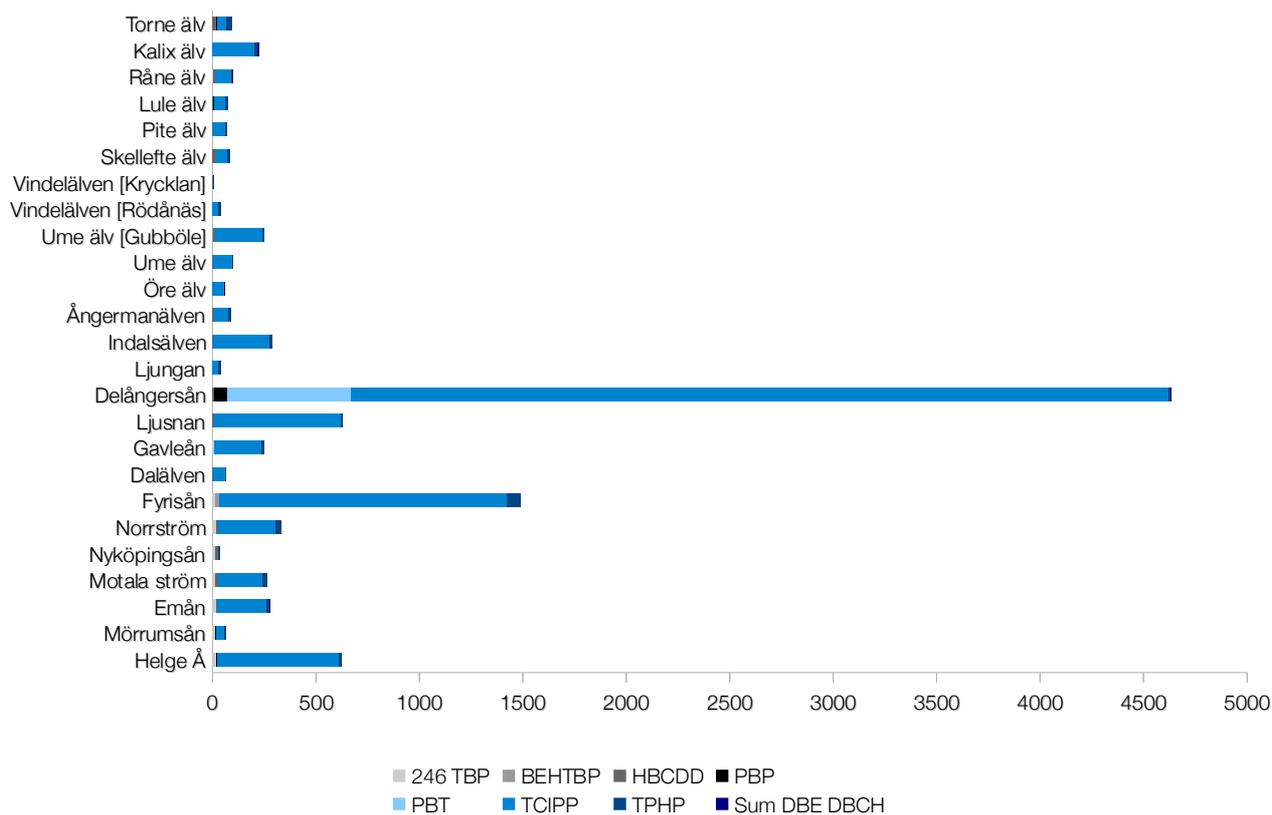
Figure 11: Summarised comparison of the FR loads at the different sampling stations, from north to south, displayed in [ng L^{-1}]. Values have been blank corrected but not adjusted to MDL.

A first major observation was that the water quality of Swedish rivers in terms of pollution by FRs in general is low. Concentrations of FRs in Swedish rivers were generally lower compared to other studies in Europe (Xie and Ebinghaus, 2008; van der Veen and de Boer, 2012). The highest values were observed in Delångersån (almost 4 μg L^{-1}), which is in the range of values found in other studies, between 0.6-24 ng L^{-1} (e.g. by Marklund et al., 2005, Reemtsma et al., 2006 and Martínez-Carballo et al., 2007). However, as these high values were measured from WWTP effluents, this suggests that similar activities are the reason for the Delångersån, Fyrisån and possibly Helge Å river samples, as they had the highest concentrations. For the sites where duplicate samples were taken (Skellefte älv, Fyrisån and Emån), similar concentrations were expected. However, as there was always some time passing between gathering the first sample and its duplicate, the expected similarities of the samples were not always obtained, and thus their mean values are displayed.
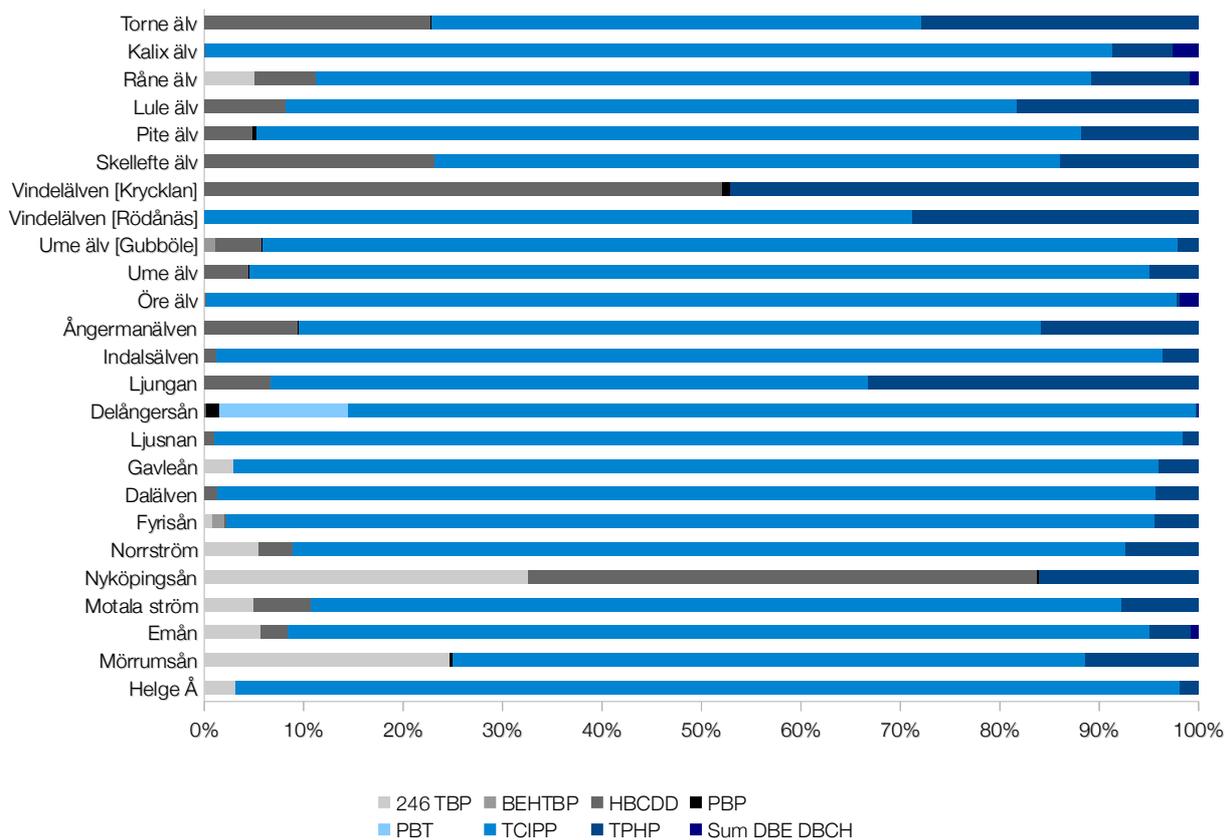
Figure 12: Percentage comparison of the detected FR loads.

A second major observation is that smaller streams near industrial activity or urban areas have a tendency to be very contaminated with just one or two major components. This is the case for Delångersån (Site FR12, near the city of Iggesund), Fyrisån (Site FR16A, taken in Uppsala) and Helge Å (Site FR21, near Kristianstad). Delångersån has the highest levels of PBT as well as TCIPP of all investigated sites. The analysis of the chromatograms for Gavleån and Mörrumsån showed high peak contaminations of HBCDD, but these values were way above the previously observed values for both environmental detection and experimental solubility (Sternbeck et al., 2001). The samples were not filtrated prior to sampling, which makes both influences by particulate bound HBCDD as well as matrix effects (i.e. effects that were caused by interactions between the screened pollutants, interference by solids, et cetera) possible explanations. In conclusion, these results are considered to have high uncertainties and were therefore excluded from the compilation in Figures 11 and 12.

Field blanks showed partly very high values for several compounds (e.g. DBDPE, TCIPP and TPHP) while the elution blank showed significantly lower values. For DBDPE, the field blank from Motala ström showed a two orders of magnitude higher value than the original sample from the site, making the calculated MDL very high. None of the 11 sites where DBDPE was found were above the MDL or MQL value.

Using the blank corrected values, only TCIPP was detected at all sites. TPHP was detected in 97% of all extracts and PBP in 87%. BTBPE and TBBPA were not detected at all. BTBPE showed almost no peaks at all in the chromatogram, whereas TBBPA, today's most widely used BFR since the ban of the PBDEs (e.g. Birnbaum and Staskal, 2004), were observed below the detection limit (0.15 ng L^{-1}). Other substances with low detection frequency were PBT (detected in

one sample), EHTBB (detected in two samples) and BEHTBP (found in four samples). However, these emerging FRs are only slowly replacing the older ones (such as PBDEs), and in a recent study carried out by Geens et al. (2010) on indoor dust, most of the emerging FRs had a very low detection frequency although indoor dust is considered to have higher concentrations of FRs than natural waters. Comparing with Figure 14, it can be seen that all samples are clearly dominated by TCIPP. TCIPP had the highest MDL of all screened substances and has been thoroughly investigated in other studies screening surface waters and WWTP effluents.

When combining the results of the measured FR concentrations with the daily riverine water discharge (calculated from the yearly mean water flow) to the sea, the results appear slightly different (Figure 13 and Table 9). Streams from smaller watersheds may have high amounts of FRs but their contribution to the total loads to the sea are less important than the contribution of less polluted rivers with a higher flow rate.
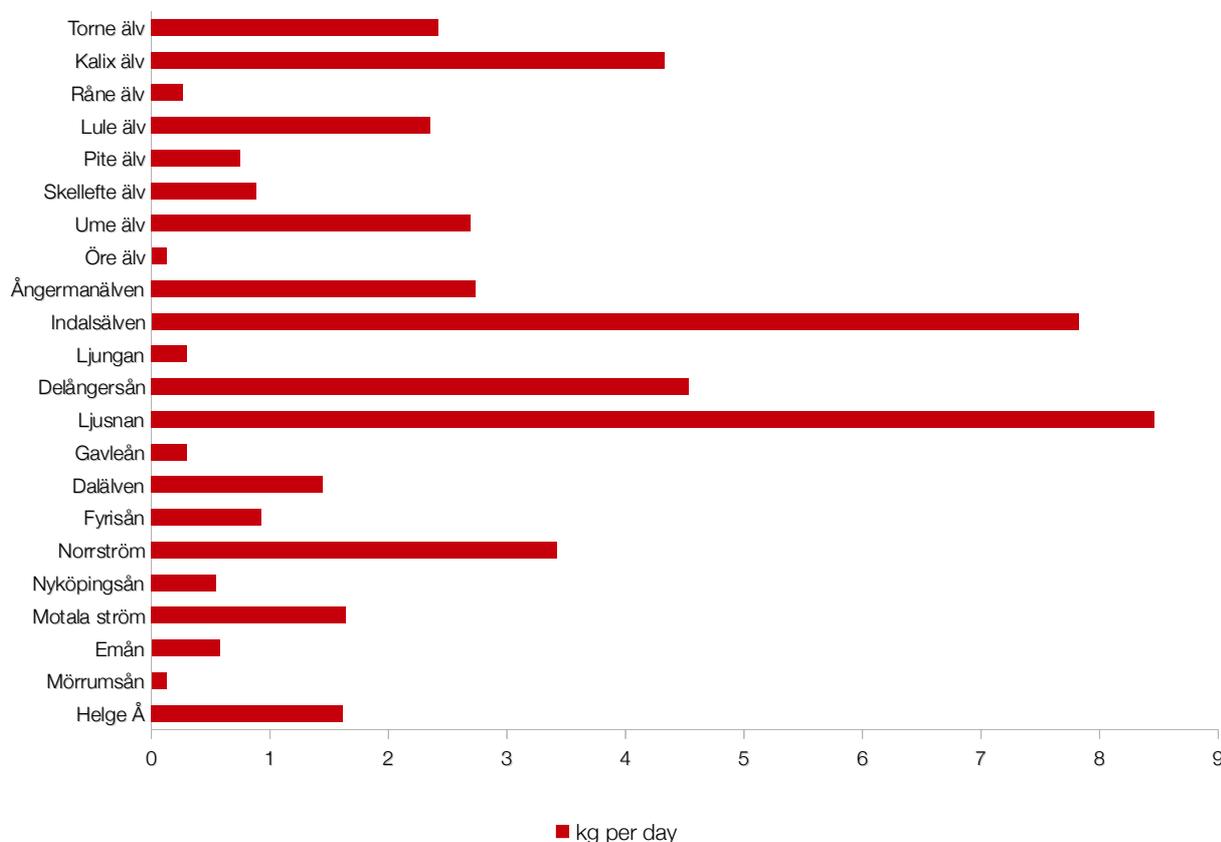
Figure 13: Discharge of ΣFR from Swedish rivers, in kg per day, into the Baltic Sea and the Gulf of Bothnia.

Table 9: Contribution of ΣFR from the east-coast rivers investigated. All values are displayed in kg per day.

Torne älv	Kalix älv	Råne älv	Lule älv	Pite älv	Skellefte älv	Ume älv	Öre älv
2.4	4.3	0.26	2.4	0.75	0.88	2.7	0.13

Ångermanälven	Indalsälven	Ljungan	Delångersån	Ljusnan	Gavleån	Dalälven	Fyrisån
2.7	7.8	0.30	4.5	8.5	0.30	1.5	0.93

Norrström	Nyköpingsån	Motala ström	Emån	Mörrumsån	Helge Å
3.4	0.55	1.6	0.57	0.13	1.6

The Ljusnan river was found to be the most notable source of FRs to the Baltic Sea, with a daily amount of over 8 kg day^{-1}. Ljusnan has a catchment area of 19 282 km^2 and a mean water flow rate of 216 m^3 s^{-1}, whereas Torne älv with a more than double-sized catchment area (40 157 km^2) and an almost doubled water flow rate of 419 m^3 s^{-1} has less than half of its load. The loads of Norrström and Helge Å, rivers situated in densely most populated areas and with medium FR concentrations, are in the middle field of FR loads despite their dense population. Nevertheless, it needs to be pointed out that the sampling was a one-time snapshot for screening purposes, implying that these results do not necessarily reflect a true picture over time.

Summarising the results of the FR screening, the general values were comparable to other studies carried out on European rivers. Literature on this topic, especially on riverine water samples is rarely found. Moreover, low detection frequencies and analysis difficulties deteriorated the results both due to noise interference and high MDL/MQL, problems that studies done by Schlabach et al. (2011) and NIVA (2011) also encountered. Several of the screened substances were previously only detected in WWTP effluents at levels above the MDL.

4.3. PFASs results

While the FR screening suffered from high MDL/MQL and low detection frequency, the PFASs screening gave more exhaustive results. 44 sites were sampled in total, of which 39 were rivers discharging into the Gulf of Bothnia, the Baltic Sea or Kattegatt. All sites had detectable PFASs-concentrations, and most sites also showed detectable concentrations of both PFCAs and PFSAs. The results of the PFASs-sampling are displayed in Figures 14 and 15. PFAS compounds where less than 50% of all sampled sites had values above the MQL were excluded in the figures, namely 6:2 FTS, PFTrDA, PFTeDA, PFHxDA, PFOcDA, FOSAA, EtFOSA, EtFOSAA, EtFOSE, Me-FOSA, MeFOSAA, MeFOSE and PFDS.

The summarised PFASs concentrations for each site was generally lower than the summarised concentration of the FRs. Six rivers had moderate levels (Ume älv at Gubböle, Ångermanälven at Sollefteå, Delångersån at Iggesund, Fyrisån downstream of Uppsala, Emån near Emsfors and Helge Å near Kristianstad), whereas the other rivers showed low PFASs-levels compared with recent European studies (Ahrens et al., 2009b; McLachlan et al., 2007).

Interestingly, the rivers with the highest concentrations showed all almost identical distributions of the different PFASs. Dominated by the PFSAs, mainly the short-chained PFBS and PFHxS were found. The similarities of the two most polluted samples, from Ume älv near Gubböle and Delångersån near Iggesund, were striking as they were not only similar in percentual comparison but also had almost identical concentrations of PFSAs and long-chained PFCAs.

Three rivers (Ume älv/Vindelälven, Fyrisån/Norrström and Göta älv) were sampled at different locations, often showing similar but both increasing and decreasing amounts of PFASs when approaching the sea. For example, a sharp increase was found when moving from Umeå upstream to Gubböle.

Lastly, calculations were also made considering the rivers' contribution to the PFASs load to the Baltic Sea (Figure 16). Ångermanälven showed the highest loads of all measured sites and considering this grab sample being part of a medium value (which does not need to be the case), more than 1 kg PFASs are released from Ångermanälven to the Baltic Sea every day. On the other hand, sites with high PFASs concentrations such as Delångersån and Emån were less important due to their lower rate of water discharge. Upstream sampling sites (e.g. Vindelälven, Göta älv near Trollhättan) were not included in the calculations of loads to the sea as sampling points further downstream were used instead. However, since Fyrisån is ending up in Lake Mälaren, which can be seen as a temporary sink, it was included in the diagram.

Of all substances screened for and analysed in this project, only PFOS is actually banned from usage in the European Union and therefore also in Sweden. Considering the PFOS levels (compiled in Figure 17), the maximal annual average concentration for inland surface waters (of 0.65 ng L^{-1}, Directive 2013/39/EU) is exceeded in 12 of 44 screened rivers. Rivers from both small as well as from large watersheds did exceed the European quality standards (EQS) for the PFOS load.
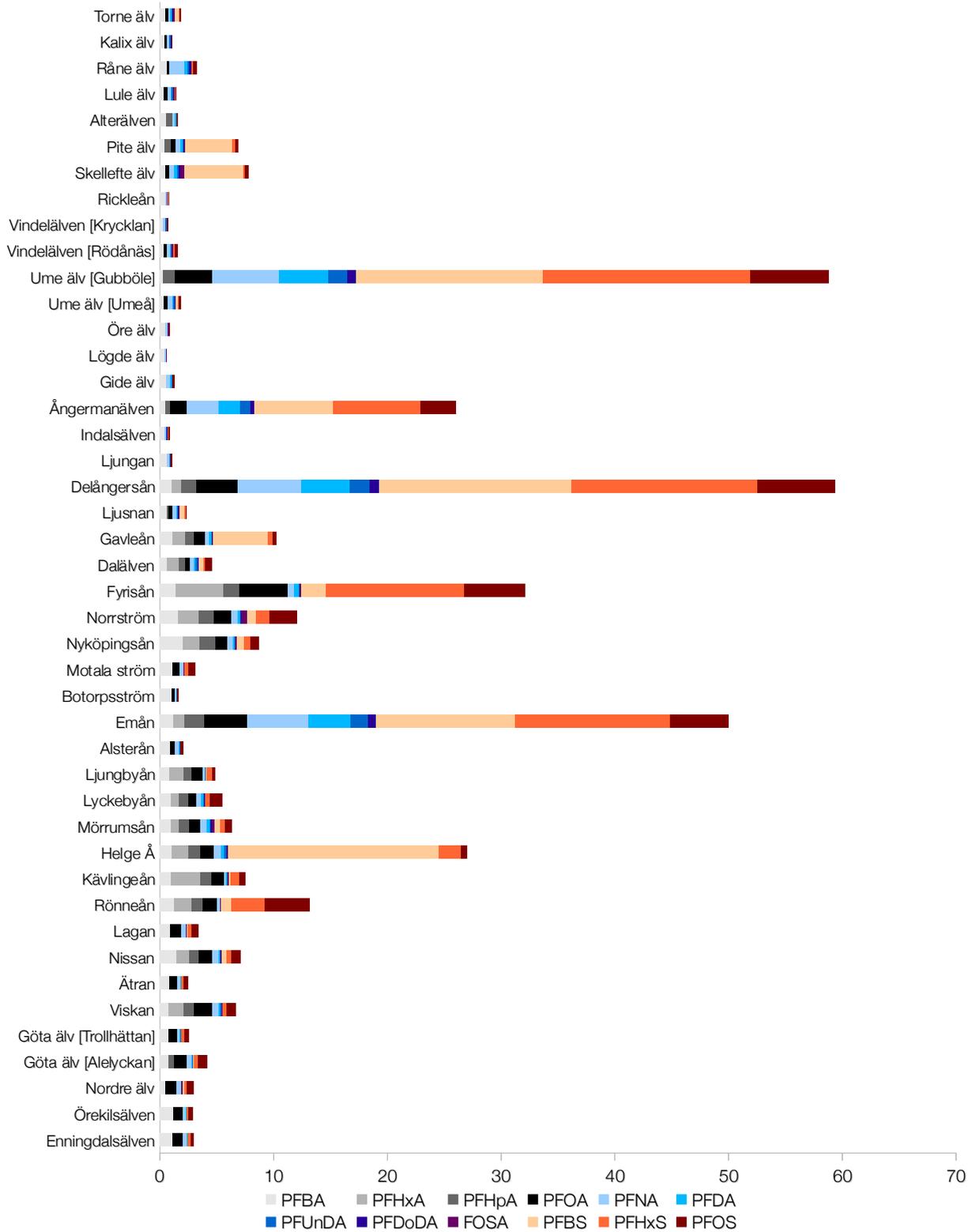
Figure 14: Detected PFASs at all 44 sampling sites. Values displayed are in [ng L⁻¹].
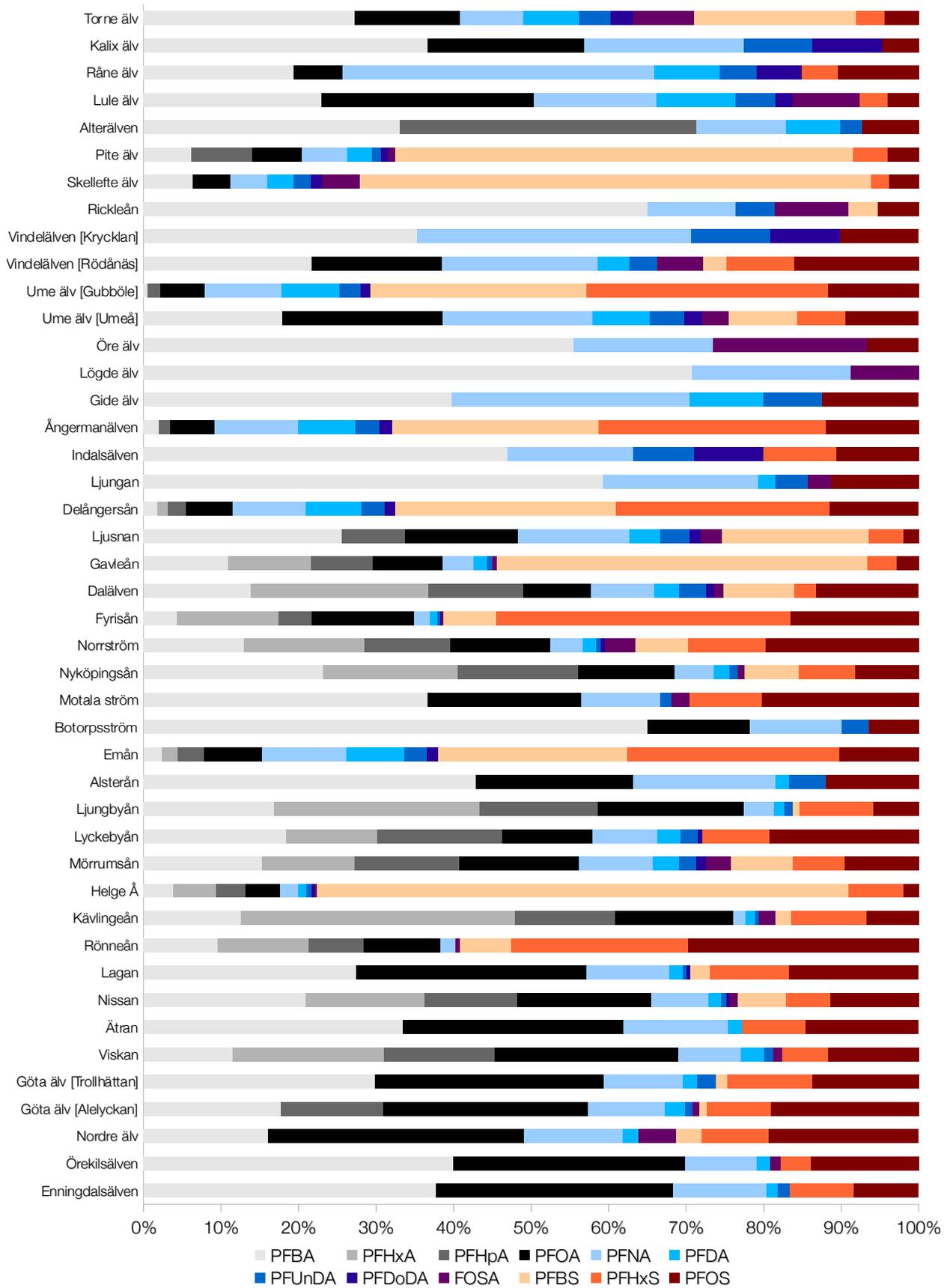
Figure 15: Overview of the PFASs patterns, the so-called "fingerprint".
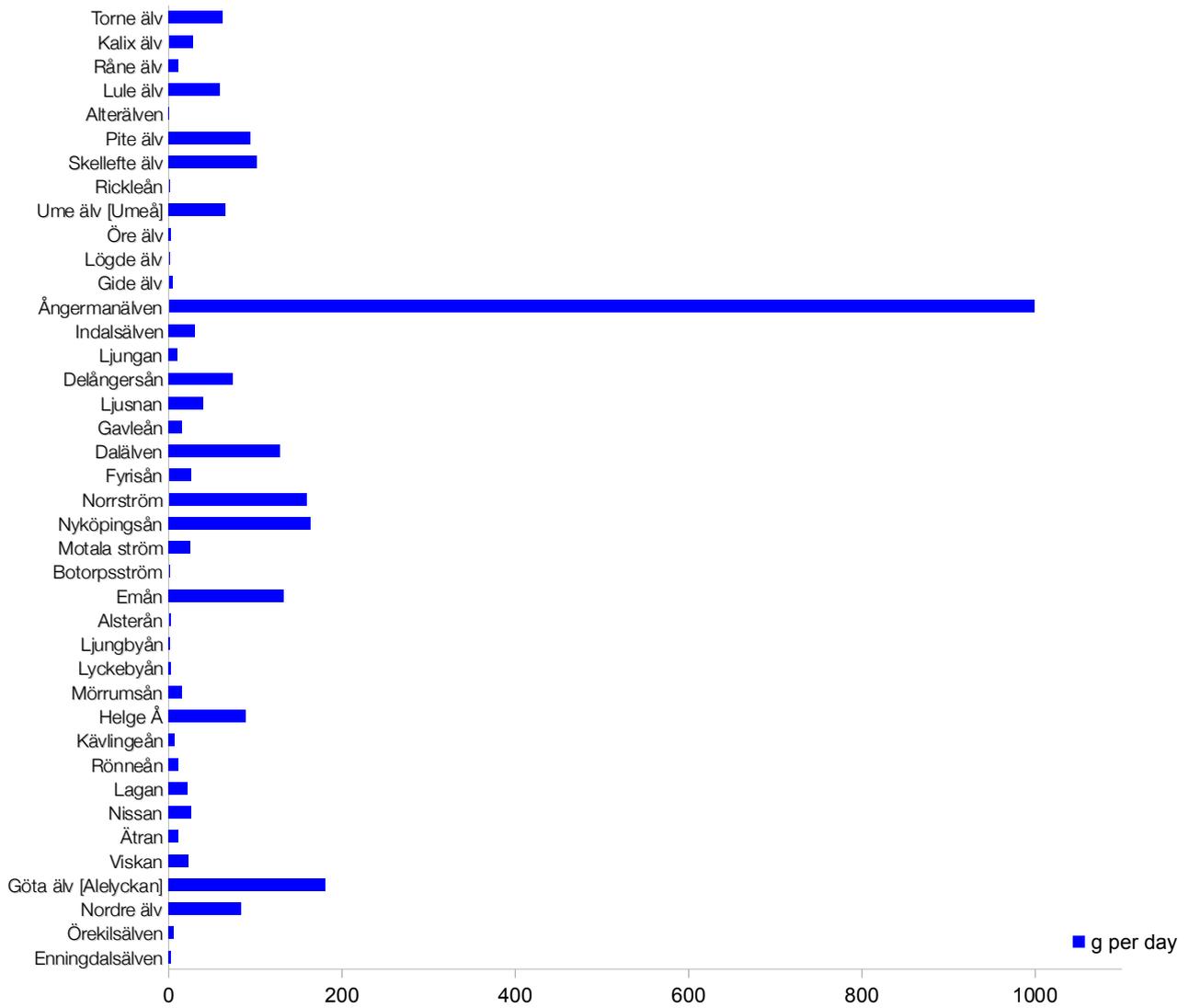
Figure 16: Discharge of PFASs into the Gulf of Bothnia, the Baltic Sea, Kattegat and Skagerrak (in g per day). The values origin from the measured concentrations shown in Figure 14, multiplied with the medium daily riverine discharge.
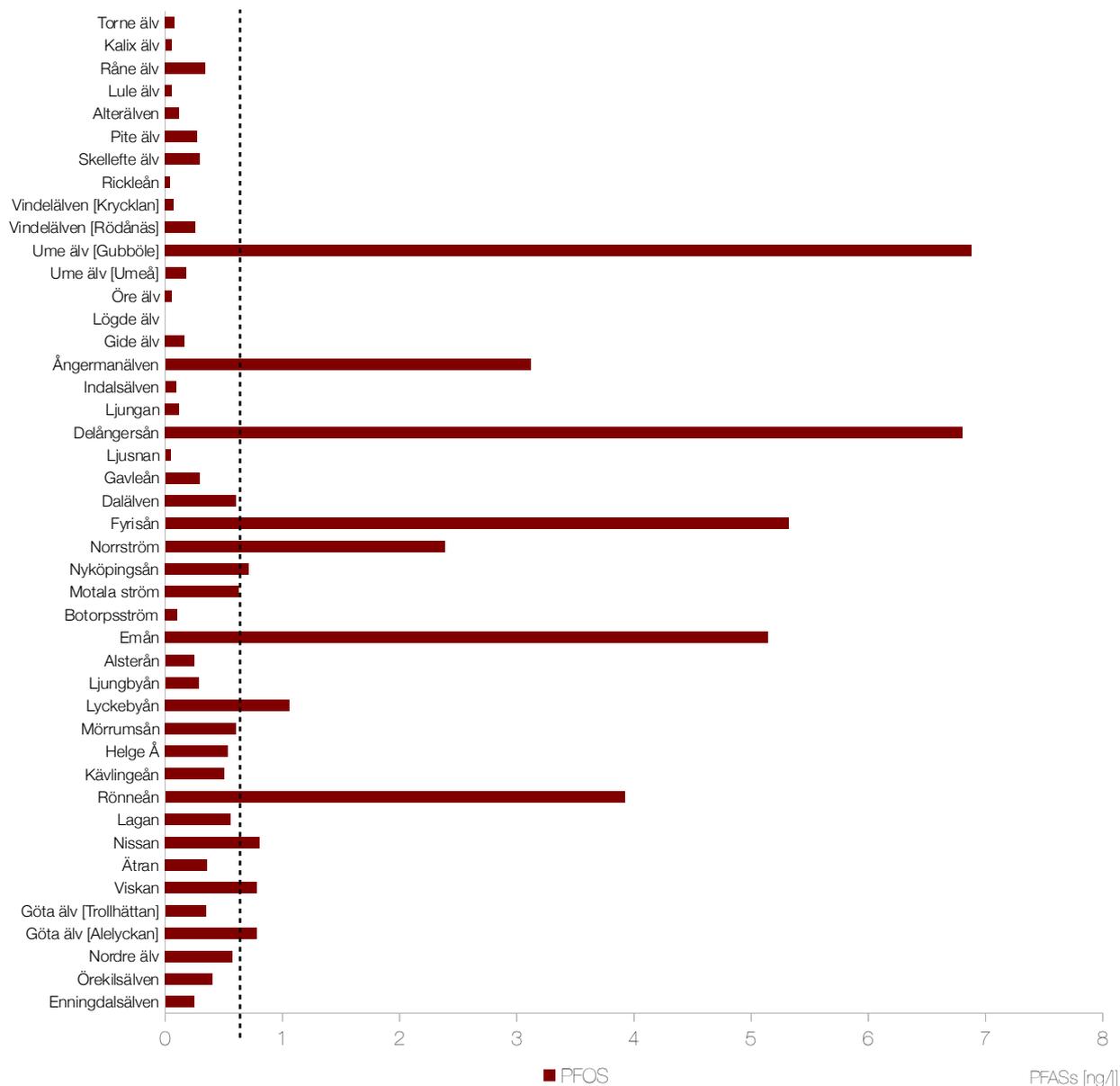
Figure 17: Concentrations of PFOS in Swedish rivers in ng per litre. The environmental quality standards (Directive 2013/39/EU) of 0.65 ng L^{-1} are shown with a dashed line. 12 of the screened 44 sites showed concentrations above the allowed values, namely Ume älv at Gubböle, Ångermanälven, Delångersån, Fyrisån, Norrström, Nyköpingsån, Emån, Lyckebyån, Rönneån, Nissan, Viskan and Göta älv at Alelyckan.

5. Discussion

When discussing the results of this sampling, it is important to bear in mind that it was done in a short period of time and does therefore not consider temporal, seasonal or other variations. The goal was, as mentioned earlier, to screen the pollution situation in Swedish rivers in terms of emerging EDCs such as FRs and PFASs at the time when sampling was performed.

5.1. FRs in Swedish rivers

The FR values in riverine systems in Sweden were generally comparable to values detected by previous studies. The main FR discovered was TCIPP, which was detected in all samples and accounted for around 40% of the total FR load. The range of detected brominated compounds in this study was significantly lower and found at ratios between non detected (n.d.) to 9.8 ng L^{-1} 2,4,6-TBP, and n.d. to 15 ng L^{-1} for HBCDD, just to mention a few. Other studies done on environmental surface water samples from northern Europe and Asia showed 2,4,6-TBP-values between n.d. to 6 ng L^{-1} and HBCDD values of n.d. to 100 μg L^{-1} (Schlabach et al., 2011; Zhao et al., 2011). All rivers except the Delångersån and Fyrisån had concentrations below comparable studies, carried out in Europe. Overall, studies on European river water are hard to find as most studies focus on concentrations in sediments, sewage sludge or biota (Kohler et al., 2008; NIVA, 2010; Schlabach et al., 2011), partly due to difficulties in analysing these hydrophobic compounds in water. The most pristine river was found to be Nyköpingsån (i.e. when regarding rivers that do actually contribute to the FR load of the Baltic Sea and the Gulf of Bothnia) with a summarised FR value of 35.9 ng L^{-1}. Of all 21 rivers investigated, 11 showed FR concentrations below 100 ng L^{-1} even prior to the correction for the values measured in the blanks.

The blank correction step was problematic as some compounds showed very different concentrations between the blanks. The largest discrepancy was, as mentioned earlier, found for the field blank concentrations from Motala ström and Helge Å, where DBDPE was found to be at 105.8 ng L^{-1} and 1.04 ng L^{-1}, respectively. The reason for this may be that some contamination did occur somewhere in between sampling and the laboratory work. A rather big incongruity was also observed for HBCDD (4.79 ng L^{-1} and 0.09 ng L^{-1}, respectively), while the blanks for TCIPP was found to have very similar values (59.1 ng L^{-1} and 63.6 ng L^{-1}, respectively). However, the actual origin of the suspected contamination has not been determined, resulting in the need for using these high values for blank correction.

PBDEs, until their ban in 2004 the most commonly used additive FR (Birnbaum and Cohen Hubal, 2006), were also screened (BDE15, BDE17, BDE28, BDE71, BDE100, BDE119, BDE126, BDE138, BDE153, BDE154, BDE156, BDE183, BDE184, BDE191, BDE196, BDE197 and BDE207), as they are among the most ubiquitously detected when analysing environmental samples. However, noise interference and indistinct chromatogram peaks complicated the interpretation of the results, and they are therefore not displayed in neither results nor discussion as justified conclusions cannot be drawn from their results. In the NIVA RiverPOP study

(2010), all BDEs were found in the pg L^{-1} range or below, which was well below the MDL of this study.

Delångersån near Iggesund was found to have the highest concentrations of FR (namely PBT, PBP as well as TCIPP) of all rivers sampled. Summarising all compounds, the total FR concentration was found to be almost 5 µg L^{-1}. Iggesund has been an industrial area for centuries, with mainly steel industry, sawmills, surface treatment plants and paper industry. Highly toxic chemicals were used for many years, often disposed without any further treatment. In more recent years and after several insolvency closures, the county administration has identified several objects in vital need of remediation due to the risk of contaminating ground- and surface waters in the area (Länsstyrelsen i Gävleborgs län, 2012). The pollutants at these sites consist mainly of heavy metals and not of FRs, but as complete information on the pollutant situation is not available, contamination of FRs might also be part of the problem. In addition, site-specific influences might be one explanation for these high loads. Firstly, the Iggesund sampling site was done from a bridge right next to the Iggesund paperboard mill. Secondly, the mill has its own WWTP a just few meters downstream, and as the water flow rate was rather low when sampling Delångersån, pollutants discharged from the WWTP might have reached the sampling site. These two circumstances combined with the fact that the sampling was performed in the possibly sea breeze-influenced forenoon might be one part of the explanation. Either way, the industrial activities close to the site as well as further upstream are suspected be the largest contributors to the high FR load. The sampling site and a downstream view are provided in Figures 18 and 19, respectively.
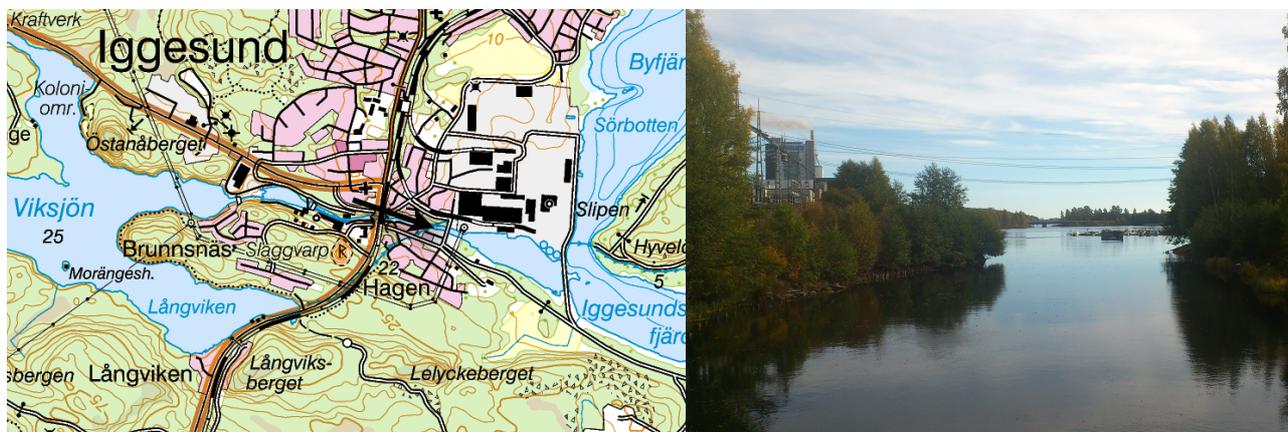
Figures 18 and 19: The Delångersån sampling site location (shown with a black arrow in Figure 18) and the downstream view of the site, illustrating the low water velocity. Water flow direction is from left towards the right in Figure 18. Map downloaded from the SLU Geodata Extraction Tool.

Influences of a WWTP are also the most probable explanation for the FR loads of Fyrisån. BFRs such as 2,4,6-TBP and BEHTBP as well as PFRs such as TCIPP and TPHP were detected at considerable concentrations, even though the PFRs were pronouncedly dominating. The samples of Fyrisån were taken downstream of the Uppsala WWTP, as shown in Figures 20 and 21. Similar to Delångersån, the water velocity was rather slow, which can contribute to the high concentrations observed if the FRs originate from point sources such as WWTPs.

Figure 20 and 21: Fyrisån sampling site. The Uppsala WWTP (blue circle) and the sampling site location (black arrow) are shown in Figure 20 (map downloaded from the SLU Geodata Extraction Tool). The upstream view of the site is displayed in Figure 21. Water flow direction is from top to bottom in Figure 20.

No great similarities were detected when comparing of the so-called fingerprint of the samples, i.e. the percentage distribution of the detected FRs. Only two of the smaller rivers, Gavleån and Helge Å, showed some resemblance: Gavleån has the city of Sandviken as an upstream contributor, Helge Å the city of Kristianstad, both with around 30 000 inhabitants. Also, both Sandviken and Kristianstad have their own WWTP that discharges their waste water into a site-upstream lake (Storsjön and Hammarsjön, respectively). However, their upstream parts and geographical locations are considerably different; Gavleån is a winding river located in the middle of Sweden, discharging into the Bothnian Bay. Helge Å is a river with a more even coarse, located in southern part of Sweden.

5.2. PFASs in Swedish rivers

The measured concentrations of PFASs in the aquatic environment were in good correlation to previous studies carried out on surface water in Europe and Asia (e.g. Murakami et al., 2008; Loos et al., 2009) but considerably lower than the values measured for the FRs. The mean concentration of all sampled rivers was 0.77 ng L^{-1}, the median at 0.43 ng L^{-1}. Also, a summarised compilation of all sites showed that almost 80% of the sampled sites had concentrations of 10 ng L^{-1} or below, and in 11% of all cases the concentrations were below 1 ng L^{-1}.

Sweden is geographically divided in three parts, of which the northern part (named Norrland) is the largest with an area of 261 292 km^2 (59% of Swedens total area) but only 12% of Swedens total population (URL7). Some of the largest rivers and catchments are found here, with mostly low PFASs concentrations. When regarding the different PFASs compounds, a geographical comparison showed that small streams in the northern part of Sweden, namely Alterälven, Öre älv, Gide älv, Lögde älv and Ljungan, partly had no detected PFOA at all, whereas southern rivers all had some amount of PFOA. Furthermore, Lögde älv (sampled near Lögdeå/Nordmaling) was the only river screened that showed no quantifiable amounts of PFOS. As the total PFASs concentration was low as well, Lögde älv can therefore be seen as the most pristine river screened in this study.

Regression analysis of the PFASs load to several other measured parameters was made (including TOC, salinity, temperature, SPM, pH et cetera) and showed low correlation, both for the sum of PFASs and the different compounds. Murakami et al. (2008) showed that there was some correlation between population density and PFOS, PFHpA and PFNA, but these observations could not be confirmed as population data was hard to find and no accurate data was available for all sites. Moreover, there are both urban areas with low PFASs concentrations as well as sparsely populated areas with high concentrations.

Geographical differences could be observed, both for the actual concentrations as well as for the fingerprint. Generally, the northern part of Sweden has less contaminated rivers when speaking of PFASs loads than the southern part. This might be both due to the higher population density as well as due to airborne contamination from continental Europe. Despite a more dense population, pristine rivers exist also in the southern part of Sweden, namely the smaller streams Botorpsström and Alsterån. A previous study showed that PFHxA, PFOA and PFNA were at values below the MDL for Kalix älv and Dalälven, which was no longer the case in this screening due more accurate analysis techniques and the possibilities of detecting lower levels (<0.94 ng L^{-1} compared to 0.63 ng L^{-1} detected in this study) (McLachlan et al., 2007).

The total fluxes of PFASs from Swedish rivers to the surrounding seas are in good agreement with previous studies as performed by Filipovic et al. (2013). The total riverine input of all PFASs info the Baltic Sea was in this study calculated to 2930 g day^{-1}, i.e. 1070 kg per year, compared amounts between 1350 to 2300 kg year^{-1} calculated by Filipovic et al. (2013). However, the 2013 determined limit concentration of PFOS (0.65 ng L^{-1}, for inland surface waters) (Directive 2013/39/EU) was exceeded in 12 of all 44 screened river samples. This is of major concern, as this directive clearly states that both PFOS as well as its derivatives are supposed to be at concentrations lower than 0.65 ng L^{-1}; even more sites do exceed these EQS when including the shorter chained PFSAs as possible derivatives of PFOS.

5.2.1. PFASs concentrations

When regarding the concentrations of PFASs in the screened rivers, nine rivers showed concentrations of over 10 ng L^{-1} for the sum of all detected PFASs. These rivers were Ume älv at Gubböle, Ångermanälven, Delångersån, Gavleån, Fyrisån, Norrström, Emån, Helge Å and Rönneån. Interestingly, these rivers have great variabilities in catchment size, population density and geographical location; Ångermanälven has the third largest watershed of all rivers screened, whereas Delångersån in comparison had one of the smallest catchments. The Norrström sampling site was located in Stockholm (i.e. Swedens biggest city), whereas the Emån watershed is a sparsely populated area, however in the southern part of the country. Rönneån is the only river among these nine that is located on the west coast. Regarding the overall situation of PFASs concentrations, the west coast seems to have concentrations slightly above the general ones for PFOS, when compared to the rest of Sweden.

Although the rivers of Ångermanälven, Delångersån, Fyrisån, Emån and Helge Å showed high PFASs concentrations when compared to the other rivers in the study (maximum values just above 60 ng L^{-1}), their total amounts are low when compared to single compounds in more severely contaminated rivers such as Rhone (116 ng L^{-1} PFOA), Seine (97 ng L^{-1} PFOS) and Po (200 ng L^{-1} PFOA) (McLachlan et al., 2007; Loos et al., 2009).

The comparison of PFOS is of special interest. The PFOS concentrations of all sampled rivers are displayed in Figure 17. PFOS is, as mentioned before, the only compound screened in this study that is banned from use and production in the EU. When discarding the probably point-source affected sites with PFOS concentrations of more than 2 ng L^{-1}, it seems that the southern part of Sweden (i.e. rivers south of Gavleån) have higher concentrations of PFOS in their surface waters and rivers. This indicates that population density is one of the reasons as Swedens four largest cities (Stockholm, Gothenburg, Malmö and Uppsala) are all located in this part.

5.2.2. The PFASs fingerprint

The so-called fingerprint is a percentage compilation of the amounts of the different PFASs compounds in the rivers. PFASs fingerprints of all sites are compiled in Figure 15. In general, it can be stated that rivers in the northern, sparsely populated part of Sweden had a higher amount of short-chained compounds than the southern, more densely populated part of Sweden. All rivers south of Delångersån (Iggesund) showed detectable levels of both PFOS and PFOA, which are known as the most detected PFASs in the environment.

When regarding the variation of the fingerprint, it can be stated that PFSAs are of less weight in the northern part, with the high-load sites of Gubböle, Ångermanälven and Delångersån as exceptions. When comparing east- and west coast, it can be seen that almost all sites on the east coast had less than 20% PFOA, whereas all sampled rivers on the west coast showed PFOA-contributions of more than 20%. Probable explanations are the influence of atmospheric deposition due to shorter distance to densely populated areas of Europe. On the other hand, the detected PFCAs with the longest carbon chains (namely PFUnDA and PFDoDA) were of similar importance on the west coast (around 15%), but mainly found in samples where the loads of PFASs were above mean values. Rivers of the Stockholm area, Småland, Blekinge and Skåne were found to have

20%.

Figure 22: Fingerprint comparison of the four rivers with the highest screened PFASs-loads.

One first assumption is that the sites are influenced by a point source. Point sources such as WWTPs or industries have shown to be considerable contributors of PFASs to the aqueous environment (e.g. Loos et al., 2009; Takemine et al., 2014). Studying site maps, it can be seen that two of these four sites (Delångersån and Ume älv [Gubböle]) are clearly affected by a nearby WWTP (see Figures 18 and 23, respectively). This can be prominently seen in the case of Gubböle, where sampling was performed from the shore as no bridge was accessible in the nearby area. 2 km upstream and at the same side of the river, WWTP effluents are discharged into the river. As the PFASs concentrations are significantly lower in central Umeå (i.e. downstream of the Gubböle sampling site), the reason for the high concentrations at Gubböle are very likely to be affected by the point source, as highlighted in Figure 23.

Figure 23: Gubböle sampling site (black arrow) and the suspected contributor to the high values (blue circle). Water flow direction is towards the right. Map downloaded from the SLU Geodata Extraction Tool.

Similar to the Gubböle point source, this explanation might also be one of the reasons for the high PFASs amounts detected in Delångersån (see Figures 18 and 19). As stated earlier, the Delångersån sampling was performed from a bridge close to the Iggesund paperboard mill, thus contributions from the mills own WWTP could be a reason for the high concentrations. Despite the fact that the WWTP in that case downstream of the site, the samples can still have been influenced as the rivers water flow rate was low.

Different from Gubböle and Delångersån, the sites of Ångermanälven and Emån did not show such clear point sources. The Ångermanälven was sampled at the city of Sollefteå, but upstream of the area that could be affected by a WWTP. Further upstream is a military training area, and military areas has been shown to be the source of high PFASs levels in other parts of the world if e.g. fire fighting was practised and PFASs-containing AFFFs were used. If such activities are the reason for the high PFASs concentrations in Ångermanälven can although not be stated without doubt. Another possible factor affecting the results is the water power plant (WPP) upstream of the site (see Figures 24 and 25).

Figure 24 and 25: The Ångermanälven sampling site (shown with a black arrow) and the view upstream of the site. The map was downloaded from the SLU Geodata Extraction Tool. Water flow direction is towards the right in the map of Figure 24.

The sampling of Emån was performed near the village of Emsfors. The Emån river is located in Kalmar län in southern Sweden, and has had several issues with its water quality, mostly due to contamination by heavy metals (Sjöbäck et al., 1984). Upstreams of the sampling site is the former paper mill of Emsfors, which however was closed down and abandoned in 1989. Today, no ongoing industrial activities are found on site. A monitoring of the county administration showed however that Emsfors pappersbruk is still a place of great environmental concern (URL8). Still, the measured high values are not very likely of originating from the former paper mill as a point source.

Combining these uncertainties with the fingerprint found for Fyrisån, the statement of a "point source" or "WWTP" needs to be adjusted. WWTPs have inflows from different activities such as household greywater, industry discharges and sewage, which is considered to result in different PFASs fingerprints as the WWTP discharges into the rivers are also different. When comparing the fingerprint of the five most contaminated rivers, the Fyrisån fingerprint is different from the others, as seen in Figure 26.
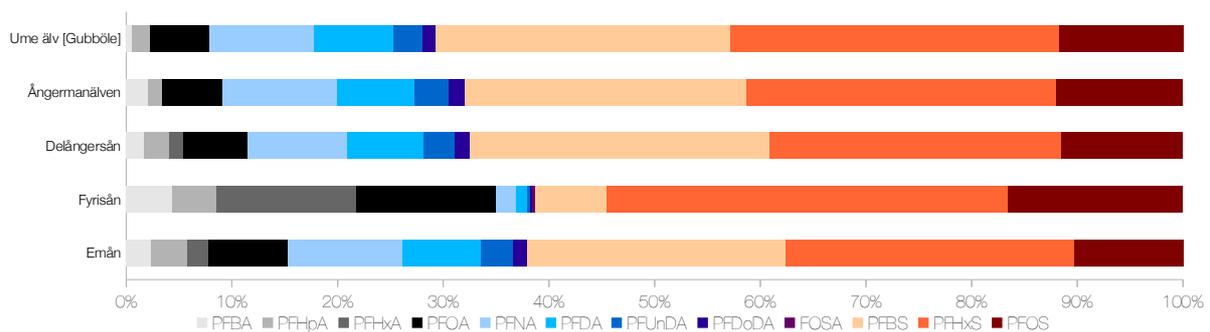
Figure 26: Fingerprint comparison of the five rivers with the highest screened PFASs-loads, now including the Fyrisån.

the different pattern in Fyrisån (see Figures 20, 21 and 26) might be caused by different input ratios of greywater, sewage and industrial waste water; however, this needs to be further investigated.

For the site of Helge Å, no direct point sources were found. The Helge Å upstream region is dominated by a lake Hammarsjön and the city of Kristianstad with around 35 000 inhabitants (URL7). Moreover, it is the Lake Hammarsjön that is the recipient for the WWTP discharges originating from the city. This is seen as one possible reason for the high amounts of PFASs detected in the Helge Å samples. Still, the results are astonishing; Helge Å has the highest concentration of PFBS of all rivers screened (19 ng L^{-1}) but no clear point source is found close to the sampling location. Sources that can significantly increase levels of PFASs in surface waters are rainfall and stormwater runoff (Müller et al. 2011), but this importance was discarded as the sampling was performed in a period of time that was not affected by rain. The Helge Å situation is shown in Figures 27, 28 and 29.

Figure 27–29: The Helge Å sampling. Figure 27 shows the suspected contributor to the high values of PFASs (yellow circle). Figure 28 shows the sampling site of Helge Å (blue circle). Both sites and the distance in between are illustrated in Figure 29, with the lake Hammarsjön in between.

Of special interest are also the results obtained for the Ume älv/Vindelälven rivers. Here, samples were taken at four different sites in order to screen background values and eventually to see the variation of the PFASs load when approaching more populated areas. A compilation of the Ume älv/Vindelälven concentrations is shown in Figure 30. The first two samples measured showed good correlation to the hypothesis that remote areas are sparsely affected by PFASs; the first, taken at the Krycklan catchment study outlet (marked site "D" in Figure 4) had among the lowest PFASs concentrations of all measured sites. Short-chained PFCAs were dominating the PFASs fingerprint and PFOA not detected at all. A few miles downstream, at Rödånäs (site "C" in Figure 4), the picture was similar: the values of PFASs were well below the average values obtained for Sweden, but as the river was approaching slightly more urbanised areas, longer-chained PFCAs and PFSAs were detected at increasing concentrations. PFOA was no longer absent in the sample. This indicated that human activities could possibly have a linear correlation to the PFASs load measured in river waters.

Continuing downstream, the sampling of Gubböle (site B in Figure 4) showed surprising results, as mentioned earlier. Still being part of a rather remote area, the values were the second highest of all analysed samples. Combined with the fact that the samples of Umeå showed no values of that magnitude, a small but close-to-site point source was considered to be the explanation. The site map with highlighted expected point source and sampling site is shown in Figure 24.
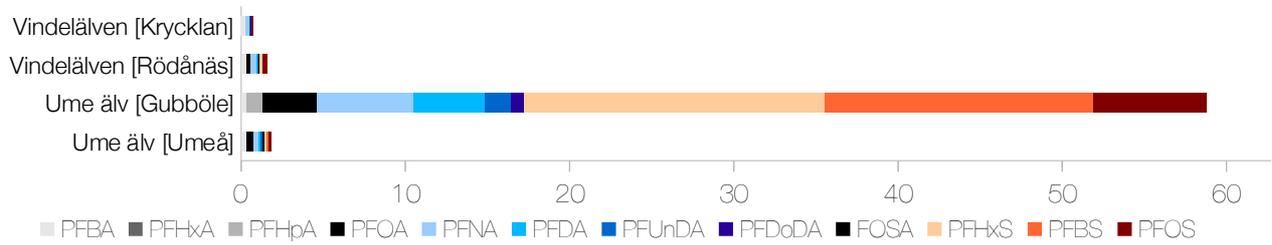
Figure 30: PFAS concentrations measured along the Vindelälven/Ume älv.

6. Conclusions and future perspectives

"I've got to be cautious about too much optimism"
Charles A. Lindbergh

EDCs are a large group of chemicals of different types that have adverse effects on the endocrine system. This study has been focusing on two sub-categories of EDCs (FRs and PFASs). FRs are compounds used in a large variety of everyday products in order to prevent or inhibit the spread of fires. FRs are generally hydrophobic, semivolatile and sparsely soluble in water (URL3; Bergman et al., 2012; Araki et al. 2013). Today's most commonly used FRs consist of one or more phenyl rings that are often halogenated (Andresen et al. 2004; Birnbaum and Cohen Hubal, 2006). FRs of interest in this project were emerging PFRs and BFRs that are known or suggested to be endocrine disrupting, persistent and bioaccumulative. The other group of chemicals investigated in this project were PFASs. These substances are used in food packaging, lubricants and fire fighting foams due to their surface tension lowering properties (Kissa, 2001; Giesy and Kannan, 2002, Ahrens, 2011; Vierke et al., 2012). PFASs consist of a fully (or partly) fluorinated carbon chain and a functional group such as a carboxylic (—OH) or sulfonic (—SO$_3$H) acids. For this project, only fully fluorinated PFCAs, PFSAs and FOSAs were screened and analysed.

This project was carried out in order to map the occurrence and distribution of EDC, primarily FRs and PFASs, in river water of all parts of Sweden. One goal was to identify sources at places where the measured concentrations were found to be high. Potential point sources identified for those sites where the detected concentrations were above the medium values were found to primarily consist of WWTP effluents. However, other sources are likely to be present as effluents from WWTP could not always be linked to high concentrations at site.

When considering EDCs (i.e. both FRs and PFASs), it can be stated that the population density does not correlate directly with the concentrations observed in the river samples. Pristine rivers passing densely populated areas and cities as well as polluted rivers in areas of low population were found, an observation that was valid for both FRs and PFASs. The best results proving this statement were achieved in Vindelälven/Ume älv, where two of three upstream (i.e. remote area) samples showed low levels but one showed very high concentrations of PFASs but also elevated concentrations of FRs. The reason for this is most likely to be explained by the fact that the concentrations downstream of point sources were generally found to be elevated when compared to upstream values (Figures 16, 17, 23 and 30). WWTPs were found to be the most common point source, although the presence of other point sources is also expected.

Considering the patterns of the investigated EDCs found in Swedish rivers, significant differences could be seen between the northern and southern parts of Sweden. For the FRs, 2,4,6-TBP was frequently detected in rivers from the southern part, whereas HBCDD was more commonly detected in river samples from the northern part. For all FR samples, TCIPP was however found to be the major contaminant. The PFASs fingerprint, on the other hand, showed significant geographical differences between different parts of the country. Rivers from the west coast had generally almost 30% PFOS, which was different from the rest of the screened rivers. Rivers in the northern parts of Sweden had generally lower PFASs concentrations, but rivers exceeding the EQS for PFOS were found in all parts of the country. Interestingly, four of the sites with the highest concentrations showed very similar distributions of PFASs 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). However, when comparing the PFASs fingerprints from all sites with >20 ng L⁻¹ PFASs, all patterns were not in good correlation – the samples from Fyrisån and Helge Å were similar to the four earlier mentioned rivers in concentration, but very different in pattern.

The concentrations of FRs and PFASs were sometimes very dissimilar and need therefore to be regarded separately when studying their loads all over Sweden. For the FRs, the loads and concentrations in the Swedish rivers along the east coast were discovered to be comparable to other studies done. Except for the four rivers of Delångersån, Ljusnan, Fyrisån and Helge Å, the FR loads in the rivers were below 0.5 µg L⁻¹. The FR concentrations seemed not to correlate particularly well with neither catchment size nor population density. Studies on FRs in natural river waters are rare and often affected of high MDL and MQL values (e.g. Quintana et al., 2008; Schlabach et al., 2011), a problem that was also observed for this project.

The comparison between the two substance classes showed that the concentrations of FRs were considerably higher in Swedish rivers than the concentrations of PFASs. This was not very surprising as the total production and use of FRs is significantly higher than production and usage of PFASs. Despite that fact that PFASs were found at lower riverine concentrations, they were still found in all rivers screened. Geographically speaking, the northern rivers showed generally lower amounts of PFSAs and long-chained PFCAs, and generally lower concentrations than the southern rivers. However, the river samples of Ume älv near Gubböle, Ångermanälven and Delångersån marked exceptions with rather high loads. Interestingly, the three rivers with a sum of PFASs of more than 40 ng L⁻¹ showed similar fingerprints, indicating that the reason was to be found in similar inputs, albeit with different dilutions and source distances. As the sites of Gubböle and Iggesund were in the area of WWTPs, the assumption can be made that effluents of WWTPs detected in river waters of sparsely populated areas have similar PFASs distributions. Rivers on the west coast all had generally more than 30% PFOS, whereas the rest of the country generally had PFOS of less than 20%. PFOS is regulated in the European EQS and should not exceed 0.65 ng L⁻¹. However, 12 of all 44 rivers located in all parts of the country exceeded these values. These rivers were Ume älv at Gubböle, Ångermanälven, Delångersån, Fyrisån, Norrström, Nyköpingsån, Emån, Lyckebyån, Rönneån, Nissan, Viskan and Göta älv at Alelyckan. However, it can be stated that Swedish rivers in general have low loads of FRs and PFASs. No real distinction could be made between so-called "big" and "small" streams in terms of pollution by FRs and PFASs.

Regarding the objectivities of this study, it can be seen that real estimations and conclusions on connections between the one-time grab samples and the general situation in the environment were hard to prove. WWTPs were seen as contributors to higher loads of both FRs and PFASs, but the inflows to the WWTP might be different (i.e. industrial or urban). Samples taken at locations upstream were generally seen to be less contaminated. In total, the calculated fluxes of PFASs into the sea showed that the Swedish rivers contributed with lower amounts than the European average calculated by Filipovic et al. (2013), but the need for reducing the high concentrations is however present.

Future research is needed in several categories. More accurate extraction and techniques for analysis are needed at least for the FR, as these compounds were influenced of high values in the blanks and partly noisy chromatograms. Considering the screening part, more studies on an multinational or international scale are needed in order to calculate fluxes, environmental behaviours and

possible sinks such as lakes or seas. Also, detailed investigations on individual rivers are required in order to check point sources such as WWTPs and industries, as well as the behaviour of EDCs in the riverine and aquatic systems, e.g. if and how substances are degraded or the risks for sedimentation in lakes and slow-flow areas. Carrying out studies using passive samplers or simply several grab samples over time and at different water flows could clarify if the achieved results show a representative result and if they are more than just a snapshot of the situation of EDCs in Swedish rivers.

7. List of abbreviations

Abbrevia-tion	Explanation
BFR	Brominated flame retardant
CAS	Chemical Abbreviation Standard
CFR	Chlorinated flame retardant
DDT	Dichlorordiphenyltrichloroethane
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
e-EDC	Estrogenic endocrine disruptor
EDC	Endcrine disrupting compound
EOC	Emerging organic contaminant
EQS	Environmental quality standard
EU	European union
FR	Flame retardant
GC	Gas chromatography
GW	Glass wool
HPLC	High-performance liquid chromatography
IS	Internal standard
InjS	Injection standard
Koc	Organic carbon-Water partitioning coefficient
Kow	Octanol-Water partitioning coefficient
LC	Liquid chromatography
LRT	Long-range transport
M-	Mass-labeled prefix
MDL	Method detection limit
MQL	Method quantification limit
MS	Mass spectrometry
MS2	Tandem mass spectrometry

Abbrevia-tion	Explanation
MW	Molecular weight
Pa	Pascal
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkylated substance
PFCA	Perfluoroalkylated carboxylic acid
PFR	Phosphorous flame retardant
PFSA	Perfluoroalkylated sulfonic acid
POP	Persistent organic pollutant
PP	Polypropylene
PPCP	Pharmaceuticals and personal care product
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RT	Retention time
S/N	Signal to noise ratio
SPE	Solid-phase extraction
SPM	Suspended particulate matter
STP	Sewage treatment plant
SVHC	Substance of very high concern
t-EDC	Testosterionic endocrine disruptor
TOC	Total organic carbon
Vp	Vapour pressure
WAX	Weak anion exchange
WPP	Water power plant
WTP	Water treatment process
WWTP	Waste water treatment plant

Number	Numeral
0	non
1	mono
2	di
3	tri
4	tetra
5	penta
6	hexa
7	hepta
8	octa
9	nona
10	deca

Number	Numeral
11	undeca
12	dodeca
13	trideca
14	tetradeca
15	heptadeca
16	hexadeca
18	octadeca

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[4] *"This does not mean anything. Anyway, one is always a bit wrong."*

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All pictures and drawings done by the author unless other stated.

Appendix
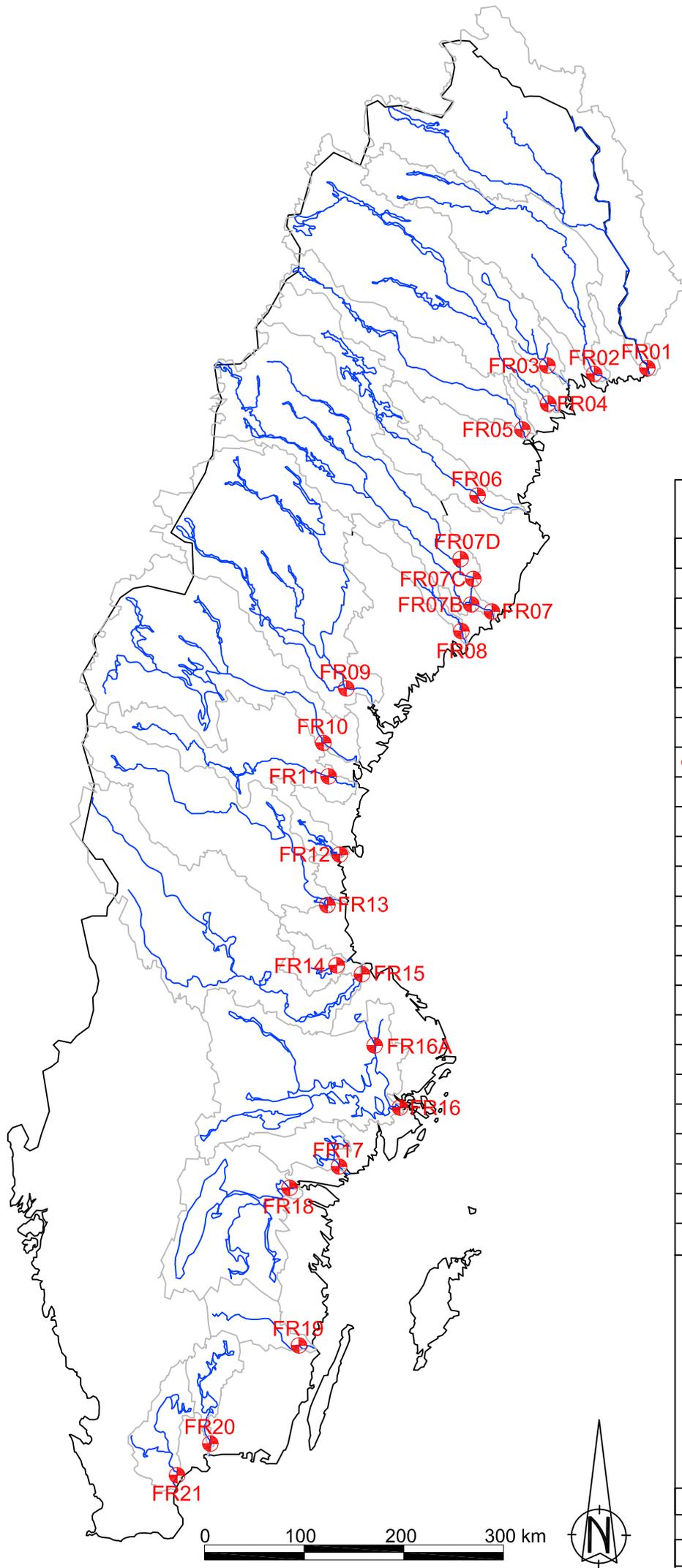
LIST OF ATTACHED MAPS

Figure 01: Sampling sites FRs

Figure 02: Sampling sites PFASs

LEGEND

	Boarders	
	Rivers	
	Discharge areas	
⊕FR01	Sampling site locations FRs	

LIST OF SITES

FR01	Torne älv	FR11	Ljungan
FR02	Kalix älv	FR12	Delångersån
FR03	Råne älv	FR13	Ljusnan
FR04	Lule älv	FR14	Gavleån
FR05	Pite älv	FR15	Dalälven
FR06	Skellefte älv	FR16A	Fyrisån
FR07D	Vindelälven [Krycklan]	FR16	Norrström
FR07C	Vindelälven [Rödånäs]	FR17	Nyköpingsån
FR07B	Ume älv [Gubböle]	FR18	Motala ström
FR07	Ume älv [Umeå]	FR19	Emån
FR08	Öre älv	FR20	Mörrumsån
FR09	Ångermanälven	FR21	Helge Å
FR10	Indalsälven		

NOTES:

Sites FR07D, FR07C (Vindelälven) and FR07B (Ume älv) (part of the Krycklan catchment study) and site FR16A (Fyrisån) are not used for the calculations of the fluxes into the Baltic Sea.

This map is part of the master thesis "Screening of EDCs in Swedish rivers" at the Swedish university of agricultural sciences and Uppsala university, March 2014.

Original size:	Scale:	Date:		
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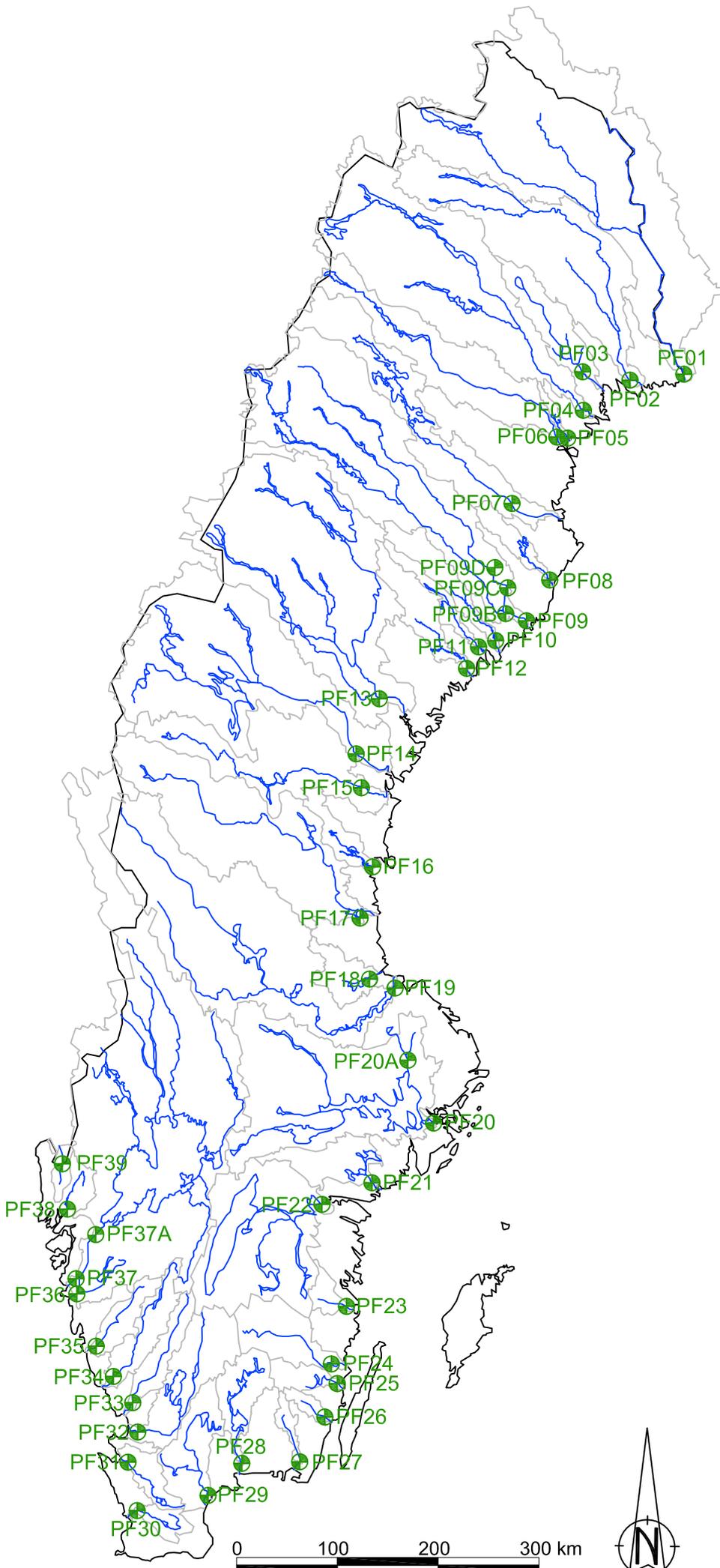
LIST OF ATTACHED MAPS

| Figure 01: Sampling sites FRs |
| Figure 02: Sampling sites PFASs |

LEGEND

	Boarders
	Rivers
	Discharge areas
⊕ PF01	Sampling site locations PFASs

LIST OF SITES

PF01	Torne älv	PF20	Norrström
PF02	Kalix älv	PF21	Nyköpingsån
PF03	Råne älv	PF22	Motala ström
PF04	Lule älv	PF23	Botorpsströmmen
PF05	Alterälven	PF24	Emån
PF06	Pite älv	PF25	Alsterån
PF07	Skellefte älv	PF26	Ljungbyån
PF08	Rickleån	PF27	Lyckebyån
PF09D	Vindelälven [Krycklan]	PF28	Mörrumsån
PF09C	Vindelälven [Rödånäs]	PF29	Helge Å
PF09B	Ume älv [Gubböle]	PF30	Kävlingeån
PF09	Ume älv	PF31	Rönneån
PF10	Öre älv	PF32	Lagan
PF11	Lögde älv	PF33	Nissan
PF12	Gide älv	PF34	Ätran
PF13	Ångermanälven	PF35	Viskan
PF14	Indalsälven	PF36	Nordre älv
PF15	Ljungan	PF37A	Göta älv [Trollhättan]
PF16	Delångersån	PF37	Göta älv [Alelyckan]
PF17	Ljusnan	PF38	Örekilsälven
PF18	Gavleån	PF39	Enningdalsälven
PF19	Dalälven		
PF20A	Fyrisån		

NOTES:

Sites PF09D, PF09C (Vindelälven) and PF09B (Ume älv, all three part of the Krycklan catchment study) and site PF16A (Fyrisån) are not used for the calculations of the fluxes into the Baltic Sea.

This map is part of the master thesis "Screening of EDCs in Swedish rivers" at the Swedish university of agricultural sciences and Uppsala university.March 2014.

Original size:	Scale:	Date:		
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Appendix B: Tables

Table B1: Results from the SPM analysis for FRs.

Nr	ID	Site	Bottle	Bottle weight:			Filter weights before SPM:		Filter weights after SPM:		Weight SPM	SPM (corr)
				Full	Empty	Volume [l]	Filter+foil	Filter	Filter+foil	Filter		
1	P0101	Torne älv	P6	1187,3	100,0	1,0873	0,38702	0,09744	0,39015	0,10064	0,00320	0,00357
2	P0201	Kalix älv	P16	1184,6	103,5	1,0811	0,38209	0,09978	0,38488	0,10250	0,00272	0,00309
3	P0301	Råne älv	P15	1184,8	101	1,0838	0,41580	0,09649	0,41801	0,09869	0,00220	0,00257
4	P0401	Lule älv	P10	1190,5	100,3	1,0902	0,44343	0,09891	0,44463	0,10000	0,00109	0,00146
5	P0601	Pite älv	P17	1185,5	101,2	1,0843	0,35948	0,09774	0,36038	0,09872	0,00098	0,00135
6	P0701	Skellefte älv	P18	1188,5	101,6	1,0869	0,41229	0,09903	0,41318	0,10000	0,00097	0,00134
7	P0711	Skellefte älv	P9	1184,6	100,3	1,0843	0,46785	0,09772	0,46802	0,09798	0,00026	0,00063
8	P0941	Krycklan C16	P1	1191,2	100	1,0912	0,37618	0,09842	0,37733	0,09954	0,00112	0,00149
9	P0951	Rödånäs D1	P2	1190,9	100,5	1,0904	0,38390	0,09774	0,38552	0,09940	0,00166	0,00203
10	P0961	Gubböle D2	P9	1188,6	100	1,0886	0,37720	0,09801	0,37932	0,10006	0,00205	0,00242
11	P0901	Ume älv	P21	1186,2	100,6	1,0856	0,35272	0,09709	0,35438	0,09881	0,00172	0,00209
12	P1001	Öre älv	P5	1191,3	100	1,0913	0,43222	0,09856	0,43419	0,10060	0,00204	0,00241
13	P1301	Ångermanälven	P3	1191,8	100,6	1,0912	0,43078	0,09058	0,43242	0,09235	0,00177	0,00214
14	P1401	Indalsälven	P8	1191,9	99,0	1,0929	0,40487	0,08956	0,40533	0,08999	0,00043	0,00080
15	P1601	Delångersån	P23	1187,2	100,1	1,0871	0,48408	0,09066	0,48444	0,09173	0,00107	0,00144
16	P2901	Helge Å	P7	1193,3	99,3	1,094	0,34071	0,08981	0,34311	0,09218	0,00237	0,00274
17	P2801	Mörrumsån	P12	1191,5	100,2	1,0913	0,38482	0,09075	0,38687	0,09286	0,00211	0,00248
18	P2401	Emån	P14	1187,4	100,3	1,0871	0,31998	0,08973	0,32063	0,09048	0,00075	0,00112
19	P2411	Emån	P22	1183,9	103,4	1,0805	0,33864	0,08793	n.a.			
20	P2201	Motala Ström	P4	1192,8	100,9	1,0919	0,37836	0,09014	0,37922	0,09104	0,00090	0,00127
21	P2101	Nyköpingsån	P13	1184,3	101,4	1,0829	0,41346	0,08855	0,41711	0,09228	0,00373	0,00410
22	P2001	Norrström	P24	1190,4	100,9	1,0895	0,39275	0,08774	0,39423	0,08923	0,00149	0,00186
23	P1501	Ljungan	P335	1189,1	101,3	1,0878	0,41732	0,08965	0,41799	0,09030	0,00065	0,00102
24	P1701	Ljusnan	P332	1192,2	99,7	1,0925	0,42201	0,08859	0,42299	0,08951	0,00092	0,00129
25	P1711	Ljusnan	P333	1192,0	100,2	1,0918	0,38208	0,08944	0,38338	0,09077	0,00133	0,00170
26	P1801	Gavleån	P320	1187,3	100,3	1,087	0,40133	0,09048	0,40471	0,09414	0,00366	0,00403
27	P1901	Dalälven	P311	1191,9	98,8	1,0931	0,38850	0,08980	0,39320	0,09449	0,00469	0,00506
28	P0001	Fyrisån	P440	1188,0	102,4	1,0856	0,33615	0,08815	0,34215	0,09420	0,00605	0,00642
29	P0011	Fyrisån	P441	1189,6		1,1896	0,35207	0,08959	not filtr			
30	P0200	Kalix älv	BD0004	1187,9		1,1879	0,36549	0,09020	not filtr			
31	P0300	Råne älv	BD0006	1188,3		1,1883	0,34542	0,08901	not filtr			
32	P0400	Lule älv	BD1008	1179,3	100	1,0793	0,37405	0,08960	0,37501	0,09044	0,00084	0,00121
33	P0500	Alterälven	BD0009	1188,4	100,7	1,0877	0,35831	0,08743	0,56249	0,09162	0,00419	0,00456

Nr	ID	Site	Bottle	Bottle weight:		Volume [l]	Filter weights before SPM:		Filter weights after SPM:		Weight SPM	SPM (corr)
				Full	Empty		Filter+foil	Filter	Filter+foil	Filter		
34	P0600	Pite älv	BD1010	1189,4		1,1894	0,38861	0,08993	not filtr			
36	P0800	Rickleån	AC1015	1150,6	100,2	1,0504	0,35725	0,08932	0,35880	0,09093	0,00161	0,00198
37	P0900	Ume älv	AC1017	1189,0		1,189	0,35952	0,08861				
38	P1000	Öre älv	AC1019	1147,2	101	1,0462	0,41343	0,08996	0,41435	0,09092	0,00096	0,00133
39	P1100	Lögde älv	AC0020	1155,4	100	1,0554	0,37187	0,08955	0,37338	0,09104	0,00149	0,00186
40	P1200	Gide älv	Y0021	1184,3	100,7	1,0836	0,39107	0,09051	0,39307	0,09239	0,00188	0,00225
41	P1300	Ångermanälven	Y0022	1166,4	100,1	1,0663	0,37743	0,09205	0,37850	0,09358	0,00153	0,00190
42	P1400	Indalsälven	Y0023	1177,3		1,1773	0,37118	0,08873				
43	P1500	Ljungan	Y0026	1190	100,7	1,0893	0,34733	0,09013	0,34785	0,09067	0,00054	0,00091
44	P1600	Delångersån	X0027	1190,7	102,1	1,0886	0,37529	0,08897	0,37585	0,08955	0,00058	0,00095
45	P1700	Ljusnan	X0028	1183,7	100,6	1,0831	0,43103	0,09019	0,43169	0,09091	0,00072	0,00109
46	P1800	Gavleån	X0030	1184,5		1,1845	0,41972	0,09091				
47	P1900	Dalälven	C0031	1156,6		1,1566	0,36160	0,08877				
48	P2000	Norrström	AB0038	1190,5	99,6	1,0909	0,37491	0,08814	0,37669	0,09000	0,00186	0,00223
49	P2100	Nyköpingsån	D0040	1190	100,6	1,0894	0,41370	0,08946	0,42924	0,09498	0,00552	0,00589
50	P2200	Motala Ström	E0041	1186,5	100,6	1,0859	0,40310	0,08941	0,40355	0,08999	0,00058	0,00095
51	P2300	Botorpsström	H0043	1188,6	100,6	1,088	0,35544	0,08863	0,35577	0,08899	0,00036	0,00073
52	P2400	Emån	H0044	1169,9		1,1699	0,35892	0,09092				
53	P2500	Alsterån	H0070	1184,7	100,7	1,084	0,38524	0,08787	0,38772	0,09058	0,00271	0,00308
54	P2600	Ljungbyån	H0045	1166,2	101,2	1,065	0,38585	0,08835	0,38767	0,09058	0,00223	0,00260
55	P2700	Lyckebyån	K0046	1182,5	100,2	1,0823	0,39020	0,08929	0,39148	0,09063	0,00134	0,00171
57	P2900	Helge Å	M0048	1192	101,2	1,0908	0,47139	0,08988	0,47397	0,09239	0,00251	0,00288
58	P3000	Kävlingeån	M0073	1164,9	101,8	1,0631	0,36164	0,08889	0,36333	0,09056	0,00167	0,00204
59	P3100	Rönneån	M0053	1187,5	100,8	1,0867	0,34887	0,08988	0,35695	0,09803	0,00815	0,00852
60	P3200	Lagan	N0054	1187,2	100,5	1,0867	0,38034	0,09014	0,38336	0,09296	0,00282	0,00319
61	P3300	Nissan	N0056	1192,1	100,4	1,0917	0,41028	0,08914	0,41226	0,09115	0,00201	0,00238
62	P3400	Ätran	N0057	1188,3	100,1	1,0882	0,40619	0,08944	0,40837	0,09163	0,00219	0,00256
63	P3500	Viskan	N0059	1185,7	99,9	1,0858	0,44496	0,09041	0,44845	0,09410	0,00369	0,00406
64	P3600	Alelyckan	O0069	1191,1	100,4	1,0907	0,43456	0,09049	0,43823	0,09414	0,00365	0,00402
65	P3700	Nordre älv	O3075	1192,6	100,3	1,0923	0,41477	0,08866	0,41827	0,09222	0,00356	0,00393
66	P3800	Göta älv	O0060	1188,5	100,3	1,0882	0,42972	0,08840	0,43260	0,09139	0,00299	0,00336
67	P3900	Örekilsälven	O0063	1191,4	100,1	1,0913	0,40521	0,09035	0,40954	0,09311	0,00276	0,00313
68	P4000	Enningedalsälven	O0064	1184,1	101,0	1,0831	0,39012	0,09038	0,39097	0,09120	0,00082	0,00119
70	BP11	Blank1		1100	100	1	0,41826	0,08957	0,41772	0,08895	**−0,00062**	−0,00025
71	BP21	Blank2		1100	100	1	0,40494	0,08948	0,40492	0,08943	**−0,00005**	0,00032
72	BP31	Blank3		1100	100	1	0,40330	0,08819	0,40280	0,08775	**−0,00044**	−0,00007

Nr	ID	Site	Bottle	Full	Empty	Volume [l]	Filter+foil	Filter	Filter+foil	Filter	Weight SPM	SPM (corr)
			Bottle weight:				**Filter weights before SPM:**		**Filter weights after SPM:**			
		Blank correction	−0,00037									
73	X1						0,38840	0,08947				
74	X2						0,46962	0,09003	0,47125		−0,09003	−0,08966
75	X3						0,39556	0,08896	0,39024		−0,08896	−0,08859
76	X4						0,39109	0,08983	0,39274		−0,08983	−0,08946
77	X5						0,41391	0,09736	0,41449		−0,09736	−0,09699
78	X6						0,37039	0,08793			−0,08793	−0,08756
79	X7						0,37446	0,09063			−0,09063	−0,09026
80	X8						0,38740	0,08836			−0,08836	−0,08799
81	X9										0,00000	
82	X10										0,00000	
83	X11										0,00000	
84	X12								0,36937		0,00000	
85	X13										0,00000	
86	X14										0,00000	
87	X15										0,00000	
88	X16										0,00000	

Table B2: Summary of all sampled rivers

| Log Nr | Site | Site ID | Date | Time | POP-can nr | TOC-bottle | TOC (mg/L) | Precipitation | T(air) (°C) | Weather | | pH | Measurements | | Coordinates | |
										Weather	Wind	pH	T(water) (°C)	U (mV)	X	Y
1	Torne älv	11-0-01	2013-10-01	10:15	6	8	4,128	0,0	3,0	Sunny		6,962	5,7	−0,8	7 330 503	1 880 556
2	Kalix älv	12-0-01	2013-10-01	11:15	1	10	5,825	0,0	6,0	Cloudy		7,194	7,6	−7,6	7 325 285	1 833 885
3	Råne älv	13-0-01	2013-10-01	14:00	5	4	8,089	0,0	5,0	Partly cloudy		7,139	10,2	−5,5	7 338 361	1 779 226
4	Lule älv	14-0-01	2013-10-01	16:30	3	21	3,089	0,0	6,0	Cloudy	SV 3 m/s	7,333	9,4	−16,2	7 290 561	1 786 921
5	Pite älv	15-0-02	2013-10-02	09:30	4	3	4,425	0,0	8,0	Partly cloudy	V 3 m/s	6,546	6,8	12,3	7 264 163	1 755 232
6	Skellefte älv	16-0-02	2013-10-02	12:11	8	22	3,775	0,0	10,0	Sunny	V 4 m/s	7,063	10,3	−5,2	7 190 964	1 736 256
6	Skellefte älv DUPL	16-1-02	2013-10-02	12:11	9	23	3,773	0,0	10,0	Sunny		7,063	10,3	−5,2	7 190 964	1 736 256
6,3	Krycklan C16	17-0-02-C16	2013-10-02	15:23	14	11	13,440	0,0	11,0	Partly cloudy		7,109	7,2	−3,4		
6,3	Krycklan TOC-Dupl	17-3-02-C16	2013-10-02	15:23	14	11	13,740	0,0	11,0	Partly cloudy		7,109	7,2	−3,4		
6,5	Krycklan Rödånäs D1	17-0-02-D1	2013-10-02	16:15	11	12	4,159	0,0	11,0	Sunny	V 3 m/s	7,374	9,1	−18,0	7 115 827	1 701 376
6,8	Krycklan Gubböle D2	17-0-02-D2	2013-10-02	18:50	15	9	4,457	0,0	8,0	Partly cloudy	V 2 m/s	7,216	8,2	-11.8	7 092 989	1 701 914
7	Ume älv/Krycklan D3	17-0-03-D3	2013-10-03	08:02	7	19	4,712	0,0	2,0	Sunny	NV 2 m/s	6,861	7,9	7,0	7 087 353	1 718 699
8	Öre älv	18-0-03	2013-10-03	09:30	10	25	16,250	0,0	3,0	Sunny	N 1 m/s	6,432	8,5	26,2	7 061 011	1 691 347
8	Öre älv TOC Dupl	18-3-03	2013-10-03	09:30	10	25	16,190	0,0	3,0	Sunny	N 1 m/s	6,432	8,5	26,2	7 061 011	1 691 347
9	Ångermanälven	19-0-03	2013-10-03	13:55	2	13	6,487	0,0	13,0	Sunny	SV 3 m/s	6,672	9,6	4,2	7 007 585	1 573 842
10	Indalsälven	110-0-03	2013-10-03	16:55	12	2	5,947	0,0	12,0	Sunny	S 3 m/s	7,252	10,3	−13,2	6 934 786	1 580 851
12	Delångersån	112-0-04	2013-10-04	11:45	13	1	6,741	0,0	11,0	Sunny	SV 4 m/s	6,778	10,2	3,2	6 836 677	1 567 893
12	Delångersån TDS	112-3-09	2013-10-09	16:15	—	335	7,106	0,0	14,0	Partly cloudy	SV 0 m/s	—	—	—	6 836 677	1 567 893
21	Helge Å	221-0-06	2013-10-06	07:20	18	7	11,210	0,0	11,0	Cloudy	V 3 m/s	7,560	11,2	−32,2	6 202 819	1 400 869
0	Helge Å BLANK	221-2-06	2013-10-06	07:20	16	—	0	0,0	11,0	Cloudy	V 3 m/s	7,560	11,2	−32,2	6 202 819	1 400 869
20	Mörrumsån	220-0-06	2013-10-06	09:50	19	6	12,020	0,0	13,0	Sunny		7,108	10,6	−7,2	6 230 020	1 434 417
19	Emån	219-0-06	2013-10-06	12:30	23	14	11,020	0,0	13,0	Sunny		7,270	11,0	−15,3	6 335 205	1 539 225
19	Emån DUPL	219-1-06	2013-10-06	12:30	24	24	10,800	0,0	13,0	Sunny		7,270	11,0	−15,3	6 335 205	1 539 225
18	Motala Ström	218-0-06	2013-10-06	15:35	20	18	7,963	0,0	14,0	Sunny	SO 3 m/s byv 5	7,436	11,8	−27,2	6 496 919	1 518 441
0	Motala Ström BLANK	218-2-06	2013-10-06	15:35	17	—	0	0,0	14,0	Sunny	SO 3 m/s byv 5	7,436	11,8	−27,2	6 496 919	1 518 441
17	Nyköpingsån	217-0-06	2013-10-06	17:00	21	5	13,590	0,0	14,0	Partly cloudy	SV 3 m/s byv 5	7,538	9,9	−32,2	6 523 002	1 564 896
16	Norrström	216-0-06	2013-10-06	18:50	22	15	9,531	0,0	12,0	Night	SV 5 m/s byv 7	7,444	13,1	−28,0	6 580 773	1 628 741
11	Ljungan	311-0-09	2013-10-09	13:45	25	317	7,229	0,1	12,0	Partly cloudy	NV 3 m/s byv 8	6,923	10,7	−4,2	6 917 403	1 559 911
0	Ljungan BLANK	311-2-09	2013-10-09	13:45	30	—	0	0,1	12,0	Partly cloudy	NV 3 m/s byv 8	6,923	10,7	−4,2	6 917 403	1 559 911
13	Ljusnan	313-0-09	2013-10-09	17:45	26	337	7,421	0,3	13,0	Rainy	S 1 m/s byv 2	6,886	11,6	1,5	6 789 337	1 568 698

Log Nr	Site	Site ID	Date	Time	POP-can nr	TOC-bottle	TOC (mg/L)	Precipitation	T(air) (°C)	Weather		Measurements			Coordinates	
										Weather	Wind	pH	T(water) (°C)	U (mV)	X	Y
13 Ljusnan DUPL		313-1-09	2013-10-09	17:45	27	338	**7,410**	0,3	13,0	Rainy	S 1 m/s byv 2	6,886	11,6	1,5	6 789 337	1 568 698
14 Gavleån		314-0-09	2013-10-09	19:50	28	333	**11,760**	0,0	12,0	Night	SV 3 m/s	6,845	9,8	−2,6	6 729 091	1 572 721
15 Dalälven		315-0-09	2013-10-09	21:10	29	334	**6,326**	0,0	10,0	Night	S 2 m/s	6,775	10,3	8,3	6 717 372	1 589 704
22 Fyrisån		400-0-25	2013-10-25	11:00	31	340	**10,500**	0,0	10,0	Partly cloudy	V 4m/s	6,970	11,1	−0,3		
22,5 Fyrisån DUPL		400-1-25	2013-10-25	11:00	32	441	**10,400**	0,0	10,0	Partly cloudy	V 4m/s	6,970	11,1	−0,3		

Table B3: All screened compounds for FRs. Values below detection limit are displayed as "<MDL". All values in [ng l^{-1}]

Site:	246 TBP	BEHTBP	BTBPE	DBDPE	EHTBB	HBB	HBCD	PBP	PBT	TBBPA	TCIPP	TPHP	alfa	beta	Sum DBE DBCH
Torne älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	11,418	<MDL	<MDL	<MDL	<MDL	14,557	<MDL	<MDL	<MDL
Kalix älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,118	<MDL	<MDL	115,659	8,482	<MDL	<MDL	2,854
Råne älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	52,377	<MDL	<MDL	0,706	0,438
Lule älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	8,292	<MDL	<MDL	<MDL
Pite älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Skellefte älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	15,597	<MDL	<MDL	<MDL	49,860	11,247	<MDL	<MDL	<MDL
Vindelälven [Krycklan]	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Vindelälven [Rödånäs]	<MDL	1,554	<MDL	<MDL	<MDL	<MDL	6,834	<MDL	<MDL	<MDL	130,274	<MDL	<MDL	<MDL	<MDL
Ume älv [Gubböle]	<MDL	<MDL	<MDL	<MDL	1,948	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,538
Ume älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	58,034	<MDL	<MDL	<MDL	<MDL
Öre älv	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Ångermanälven	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5,113	<MDL	<MDL	<MDL	47,736	8,823	<MDL	<MDL	<MDL
Indalsälven	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	150,282	<MDL	<MDL	3,228	1,432
Ljungan	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,020	<MDL	<MDL	<MDL	8,315	<MDL	<MDL	<MDL
Delångersån	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5,441	31,657	299,516	<MDL	1987,376	<MDL	<MDL	<MDL	<MDL
Ljusnan	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	319,966	<MDL	<MDL	0,950	0,922
Gavleån	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	0,017	<MDL	<MDL	129,450	<MDL	<MDL	<MDL	<MDL
Dalälven	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,020	<MDL	<MDL	44,362	<MDL	<MDL	<MDL	<MDL
Fyrisån	6,444	9,135	<MDL	<MDL	<MDL	<MDL	<MDL	0,054	<MDL	<MDL	698,737	34,230	<MDL	<MDL	<MDL
Norrström	9,101	<MDL	<MDL	<MDL	<MDL	<MDL	6,387	0,177	<MDL	<MDL	152,411	13,901	<MDL	0,707	1,041
Nyköpingsån	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	10,350	0,059	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Motala ström	6,585	<MDL	<MDL	<MDL	<MDL	<MDL	8,279	0,014	<MDL	<MDL	120,001	11,786	<MDL	<MDL	<MDL
Emån	7,841	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,055	<MDL	<MDL	133,478	<MDL	<MDL	<MDL	<MDL
Mörrumsån	8,134	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	0,127	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Helge Å	9,809	<MDL	<MDL	<MDL	<MDL	<MDL	n.a.	0,164	<MDL	<MDL	310,678	<MDL	<MDL	<MDL	<MDL
Motala ström FB	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,059	<MDL	<MDL	<MDL	9,854	<MDL	2,746	<MDL
Helge Å FB	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,011	<MDL	<MDL	<MDL	<MDL	<MDL	0,221	0,285

Table B4: All screened compounds for PFASs. Values below method detection limit are displayed as "<MDL". MDL values: PFBA=0.232 ng l⁻¹, PFHxA=0.638 ng l⁻¹, PFHpA=0.533 ng l⁻¹, PFOA=0.174 ng l⁻¹, PFNA=0.063 ng l⁻¹, PFDA=0.030 ng l⁻¹, PFUnDA=0.036 ng l⁻¹, PFDoDA=0.030 ng l⁻¹, FOSA=0.030 ng l⁻¹, PFBS=0,030 , PFHxS=0.030 ng l⁻¹, PFOS=0.030 ng l⁻¹. All values in the table given as [ng l⁻¹].

River name	PFOS	PFHxS	PFBS	FOSA	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFBA	SUMMA
Torne älv	0,082	0,069	0,390	0,148	0,053	0,077	0,134	0,152	0,255	<MDL	<MDL	0,509	1,871
Kalix älv	0,053	<MDL	<MDL	<MDL	0,100	0,098	<MDL	0,229	0,225	<MDL	<MDL	0,409	1,115
Råne älv	0,342	0,152	<MDL	<MDL	0,194	0,156	0,277	1,321	0,208	<MDL	<MDL	0,635	3,285
Lule älv	0,058	0,051	<MDL	0,123	0,033	0,073	0,145	0,227	0,393	<MDL	<MDL	0,328	1,431
Alterälven	0,116	<MDL	<MDL	<MDL	<MDL	0,044	0,112	0,184	<MDL	0,608	<MDL	0,527	1,592
Pite älv	0,276	0,308	4,085	0,056	0,069	0,081	0,220	0,404	0,445	0,541	<MDL	0,429	6,913
Skellefte älv	0,296	0,187	5,146	0,372	0,119	0,174	0,268	0,365	0,386	<MDL	<MDL	0,493	7,806
Rickleån	0,042	<MDL	0,030	0,075	<MDL	0,041	<MDL	0,091	<MDL	<MDL	<MDL	0,519	0,798
Vindelälven [Krycklan]	0,074	<MDL	<MDL	<MDL	0,067	0,074	<MDL	0,258	<MDL	<MDL	<MDL	0,259	0,732
Vindelälven [Rödånäs]	0,254	0,138	0,048	0,093	<MDL	0,058	0,064	0,319	0,265	<MDL	<MDL	0,344	1,583
Ume älv [Gubböle]	6,882	18,297	16,397	<MDL	0,772	1,604	4,382	5,843	3,330	0,998	<MDL	0,309	58,815
Ume älv [Umeå]	0,176	0,117	0,166	0,064	0,043	0,084	0,138	0,363	0,388	<MDL	<MDL	0,336	1,874
Öre älv	0,060	<MDL	<MDL	0,181	<MDL	<MDL	<MDL	0,162	<MDL	<MDL	<MDL	0,503	0,905
Lögde älv	<MDL	<MDL	<MDL	0,052	<MDL	<MDL	<MDL	0,121	<MDL	<MDL	<MDL	0,419	0,593
Gide älv	0,163	<MDL	<MDL	<MDL	<MDL	0,100	0,125	0,402	<MDL	<MDL	<MDL	0,522	1,313
Ångermanälven	3,118	7,626	6,921	<MDL	0,402	0,836	1,910	2,810	1,489	0,359	<MDL	0,528	25,999
Indalsälven	0,091	0,081	<MDL	<MDL	0,077	0,068	<MDL	0,140	<MDL	<MDL	<MDL	0,405	0,862
Ljungan	0,121	<MDL	<MDL	0,032	<MDL	0,044	0,024	0,214	<MDL	<MDL	<MDL	0,634	1,069
Delångersån	6,802	16,402	16,869	<MDL	0,819	1,761	4,281	5,593	3,605	1,357	0,823	1,046	59,358
Ljusnan	0,046	0,103	0,441	0,061	0,035	0,087	0,092	0,334	0,337	0,190	<MDL	0,592	2,316
Gavleån	0,293	0,383	4,881	0,052	<MDL	0,078	0,174	0,411	0,916	0,818	1,084	1,118	10,209
Dalälven	0,606	0,132	0,420	0,053	0,046	0,162	0,151	0,372	0,400	0,563	1,051	0,637	4,594
Fyrisån	5,318	12,188	2,197	0,094	0,034	0,092	0,341	0,629	4,248	1,375	4,234	1,378	32,128
Norrström	2,386	1,200	0,831	0,465	0,061	0,075	0,216	0,506	1,558	1,326	1,876	1,571	12,071
Nyköpingsån	0,711	0,636	0,608	0,076	<MDL	0,093	0,176	0,441	1,080	1,355	1,507	2,017	8,699
Motala ström	0,628	0,291	<MDL	0,070	<MDL	0,047	<MDL	0,318	0,613	<MDL	<MDL	1,140	3,108
Botorpsström	0,106	<MDL	<MDL	<MDL	<MDL	0,057	<MDL	0,194	0,217	<MDL	<MDL	1,069	1,643
Emån	5,144	13,665	12,204	<MDL	0,700	1,497	3,707	5,431	3,755	1,711	1,000	1,193	50,008
Alsterån	0,247	<MDL	<MDL	<MDL	<MDL	0,097	0,038	0,378	0,418	<MDL	<MDL	0,884	2,062
Ljungbyån	0,285	0,461	0,042	<MDL	<MDL	0,051	0,065	0,191	0,908	0,740	1,288	0,814	4,845
Lyckebyån	1,059	0,473	<MDL	<MDL	0,031	0,118	0,170	0,453	0,641	0,887	0,641	1,010	5,484

River name	PFOS	PFHxS	PFBS	FOSA	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFBA	SUMMA
Mörrumsån	0,604	0,423	0,505	0,201	0,080	0,139	0,220	0,598	0,980	0,852	0,756	0,966	6,324
Helge Å	0,538	1,902	18,524	0,100	0,095	0,176	0,298	0,606	1,219	1,021	1,504	1,033	27,016
Kävlingeån	0,502	0,728	0,151	0,163	<MDL	0,037	0,088	0,119	1,145	0,963	2,641	0,943	7,481
Rönneån	3,920	3,005	0,873	0,072	<MDL	<MDL	<MDL	0,260	1,310	0,928	1,553	1,259	13,180
Lagan	0,560	0,345	0,083	<MDL	0,016	0,018	0,058	0,356	0,999	<MDL	<MDL	0,917	3,352
Nissan	0,808	0,405	0,440	0,072	0,030	0,050	0,111	0,525	1,223	0,848	1,085	1,483	7,079
Ätran	0,355	0,199	<MDL	<MDL	<MDL	<MDL	0,045	0,329	0,692	<MDL	<MDL	0,815	2,434
Viskan	0,785	0,390	<MDL	0,079	<MDL	0,081	0,195	0,540	1,591	0,953	1,300	0,772	6,685
Göta älv [Trollhättan]	0,347	0,278	0,035	<MDL	<MDL	0,062	0,047	0,258	0,747	<MDL	<MDL	0,755	2,529
Göta älv [Alelyckan]	0,785	0,339	0,041	0,037	<MDL	0,039	0,108	0,410	1,085	0,545	<MDL	0,731	4,121
Nordre älv	0,575	0,259	0,098	0,144	<MDL	<MDL	0,060	0,379	0,980	<MDL	<MDL	0,480	2,974
Örekilsälven	0,405	0,111	<MDL	0,041	<MDL	<MDL	0,049	0,270	0,869	<MDL	<MDL	1,160	2,904
Enningdalsälven	0,247	0,244	<MDL	<MDL	<MDL	0,046	0,042	0,356	0,901	<MDL	<MDL	1,113	2,949