Örebro University, School of Science and Technology

Master of Chemistry in Environmental Forensics

Independent Project for Degree of Master in Chemistry, 45 credits

Global Priority Perfluoroalkyl Substances in Surface Waters: Establishing Baseline Levels on Regional Basis.

Abeer Baabish
Supervisor: Anna Kärrman, Heidelore Fiedler
Examiner: Mattias Bäckström

Contents

List of Figures

List of Tables

List of Abbreviations

Abbreviation	Name
CIC	Combustion ion chromatography
CS	Native calibration standards
ECF	Electrochemical fluorination
EOF	Extractable organofluorine
FOSAAs	Perfluorooctanesulfonamidoacetic acids
FOSAs	Perfluoroctane sulfonamides
FTCAs	Fluorotelomer carboxylic acids
FTSAs	Fluorotelomer sulfonic acids
FTUCAs	Fluorotelomer unsaturated carboxylic acids
GMP	The Global Monitoring Plan (under the Stockholm Convention on Persistent Organic Pollutants)
GRULAC	Group of Latin America and Caribbean
IS	Internal standard
L-PFOS	Linear perfluorooctane sulfonic acid
br-PFOS	Branched perfluorooctane sulfonic acid
∑PFOS	Sum of linear and branched PFOS
OF	Organofluorine
PAC	Pacific Islands countries
PAPs	Polyfluoroalkyl phosphate esters
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkyl carboxylic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFPAs	Perfluoroalkyl phosphonic acids
PFSAs	Perfluoroalkyl sulfonic acids
POP	Persistent organic pollutant
RS	Recovery standard
SPE	Solid phase extraction
SRM	Standard reference material
TQS MS/MS	Xevo TQ-S tandem mass spectrometer
UNEP	United Nations Environment Programme
UPC^2	Acquity Ultra Performance Convergence Chromatography
UPLC	Acquity Ultra Performance Liquid Chromatography
WAX	Weak anion exchange
WWTP	Wastewater treatment plant

Abstract

Perfluorooctane sulfonic acid (PFOS) has been regulated under Stockholm Convention in 2009, perfluorooctanoic acid (PFOA) was listed in 2019. Perfluorohexane sulfonic acid (PFHxS) is under review and could be included in 2021. There are still permitted uses of these three chemicals, but it is expected that the production and application will decrease as a result of the international regulation and the environmental concentrations of PFOS, PFOA and PFHxS are expected to decline. However, without a reference point, it is difficult to judge if the levels are decreasing or not. Therefore, baseline levels of PFOS, PFOA and PFHxS in one of United Nations Environment Programme (UNEP) core matrices, surface water, were established with the support of samples collected from Africa (n=34), Asia (n=11), Group of Latin America and Caribbean (GRULAC) (n=35) and Pacific Islands (n=25) under a period of two years. The baseline levels were set as the median concentration (ng/L) in each region (interquartile range) based on a variance test (Kruskal-Wallis) and descriptive statistical testing.

Baseline levels for $\sum$PFOS, PFOA and PFHxS including all countries in Africa (n=6) was set at 0.38 (0.18 – 0.54) ng/L, 0.26 (0.13 – 0.80) ng/L and 0.042 (0.02 - 0.09) ng/L respectively, and excluding Kenya and Tunisia (n=4) at 0.22 (0.10 – 0.38) ng/L for $\sum$PFOS, 0.18 (0.10 – 0.25) ng/L for PFOA and 0.031 (0.02 – 0.04) ng/L for PFHxS.

In Pacific Islands the baseline levels for $\sum$PFOS, PFOA and PFHxS were established at 0.15 (0.04 – 1.24) ng/L, 0.046 (0.03 – 0.11) ng/L and 0.055 (0.01 – 0.63) ng/L including all countries (n=7), and 0.053 (0.03 – 0.15) ng/L, 0.033 (0.03 – 0.04) ng/L and 0.012 (0.01 – 0.05) ng/L excluding Vanuatu and Kiribati (n=5).

In Asia and Group of Latin America samples were in similar concentrations range within the region, so baseline levels for $\sum$PFOS, PFOA and PFHxS in Asia were set at 0.048 (0.04 - 0.12) ng/L, 0.11 (0.07 – 0.19) ng/L and 0.018 (0.01-0.03) ng/L, and in GRULAC at 1.31(0.39 – 1.88) ng/L, 0.50 (0.28 – 0.71) ng/L and 0.14 (0.06 – 0.44) ng/L for the three priority PFASs respectively.

The importance of the three PFASs in relation to other measured $\sum_{73}$ PFASs were assessed in selected samples (n=12) including six samples from Sweden. The results showed a contribution of 10% to 48% of the sum of the three priority PFASs to all 27 detected PFASs.
It is not clear whether a total of 73 PFASs is enough to explain the environmental contamination of PFASs and therefore the extractable organofluorine (EOF) was measured in selected samples (n=12). Due to the high EOF levels in procedural blanks, only two out of twelve samples were used to assess the contribution of detected PFASs to EOF. The contribution of 27 detected PFASs to EOF were 3% for Vanuatu and 5% for Sweden (Svartån). The contribution of the sum of the three PFASs to EOF accounted for 1.1% for Vanuatu and 1.4% for Svartån. Nevertheless, within the organofluorine fraction, a major percentage 95% to 97% of fluorine remains unknown in water samples, suggesting the occurrence of other organofluorine substances.

At the same time, some newly identified PFAS (novel PFASs) that are known to replace PFOS and PFOA in different applications were detected in surface water samples collected from Sweden (n=6) and from developing countries under UNEP/GMP2 project (n=6). Perfluoroethylcyclohexane sulfonate (PFECHS) was detected in four samples in concentrations ranging between 0.03 and 0.14 ng/L. Perfluoro-2-propoxypropanoic acid (HFPO-DA) was detected in three samples in the concentration range 0.03-0.06 ng/L.

1.0 Introduction

Fluorine is the most abundant halogen in the earth's crust. However, organofluorine substances produced biologically have been rarely found in the environment. The best known example of these natural occurring organofluorines is monofluoroacetate (MFA) which is produced by plants. For example, the West African plant Dichapetalum toxicarium produces fluorooleic acid, fluoropalmitic acid, and very likely fluorocaprate and fluoromyristate (Key, 1997). It is striking that all the known biologically produced fluorinated organics contain only one fluorine atom (Key, 1997), whereas the man-made organofluorines are partially or fully fluorinated. Besides, volcanic gases have been reported to produce small molecules with higher number of fluorine atoms such as tetrafluoroethylene (Gribble, 1994).

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic substances that are attracting increasing attention worldwide as some of them are frequently detected in the aquatic environment, wildlife, and humans (Houde, 2011; Post et al. 2012). Global production of PFASs occurred in USA, Germany, Italy, Belgium, China, Japan and Russia (Witteveen+Bos and TTE consultants). At industrial scale, two major processes are used to produce fluorinated chemicals; electrochemical fluorination (ECF) and telomerisation. ECF is a technology in which an organic raw material (octane sulfonyl fluoride, $C_8H_{17}SO_2F$) undergoes electrolysis in anhydrous hydrogen fluoride (HF), leading to the replacement of all the H atoms by F atoms (Alsmeyer et al. 1994). The free-radical process leads to carbon chain rearrangement and breakage, resulting in a mixture of linear and branched perfluorinated isomers of different chain lengths (Alsmeyer et al. 1994). The percentage of linear and branched PFOS produced by the ECF process is roughly 70% to 80% linear and 20% to 30% branched (3M Company, 1999). Telomerisation is a process in which iodic pentafluoroethane reacts with tetrafluoroethylene and ethylene to produce a polyfluoralkane, that is 100% linear if the starting materials are linear (Kärrman, (2007).

PFASs can be divided into two groups, specifically: non-polymers and polymers. Polymeric PFASs are fluorinated polymers consisting of a carbon backbone with fluorines attached to it (fluoropolymers) or a carbon and oxygen backbone with fluorines (perfluoropolyethers). Additionally, there are side chain fluorinated polymers which consists of variable composition of non-fluorinated carbon backbones with polyfluorinated side chains. Non-polymer PFASs are partially or fully fluorinated alkylated substances attached to a functional group. This includes polyfluoroalkyl acids, perfluoroalkane sulfonyl fluoride, perfluoroalkyl iodides and per-polyfluoroalkyl ethers based derivatives (Wang et. al, 2014). The most studied group is the non-polymers that mainly consists of surfactants. Surfactant PFASs have both hydrophobic and hydrophilic properties, thus they are used in multiple applications such as water and stain repellent for clothing, leather, and paper, as well as being surface tension lowering agents in firefighting foam and in metal plating industries (Prevedouros et al. 2006; Wang et al. 2014). PFASs can be emitted from point sources e.g. (fire-fighting training sites, wastewater treatment plants and metal plating industries) (Ahrens, 2015) or derive from diffuse sources such as atmospheric deposition and run-off (Taniyasu, 2013). They can undergo long-range transport to remote areas through atmosphere and water transport (Prevedouros et al. 2006).

The most studied perfluoroalkyl acids (PFAAs) are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). PFCAs and PFSAs have shown to be persistent in the environment. Recent studies have shown that some PFASs are toxic for both animals and humans (Håkansson et al. 2012). Further, the most frequently detected PFASs—perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) and more recently perfluorohexane sulfonic acid (PFHxS) are highly mobile once introduced to the aquatic environment (Fujii et al. 2007) and are not removed by conventional wastewater treatment (Arvaniti and Stasinakis 2015; Filipovic and

Berger 2015). Structures for the three priority PFASs are shown in Figure 1. Over the last decade, PFASs have been detected in surface- and groundwater worldwide (Yan et al. 2015). Global literature studies regarding these three PFASs levels in water are provided in Appendix, Table 3.

Perfluorooctane sulfonic acid (PFOS)

Perfluorohexane sulfonic acid (PFHxS)

Perfluorooctanoic acid (PFOA)
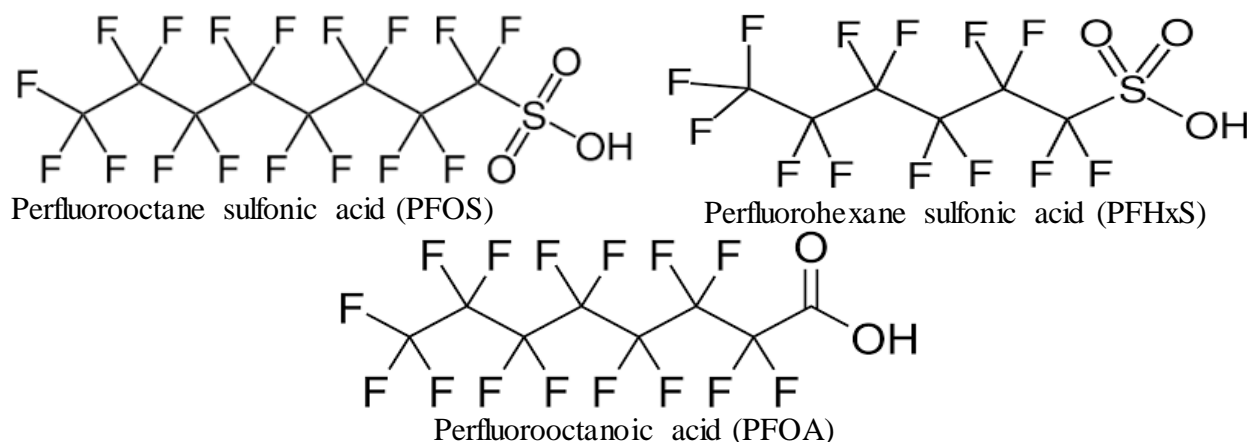
Figure 1: Structure for the three priority PFASs.

Following public concerns and environmental impacts of these global environmental contaminants, regulations have been introduced to decrease the production and use of these PFASs. The Stockholm Convention on Persistent Organic Pollutants (POPs), administered by the United Nations Environment Programme (UNEP), is a global treaty to protect human health and environment from adverse effects caused by POPs. Once released, POPs are stable in the environment for years or even decades. The Stockholm Convention was adopted in May 2001 at the Conference Plenipotentiaries in Stockholm, Sweden, and came into force three years later (Tang, 2013). PFOS and perfluorooctanesulfonyl fluoride (PFOSF) and its precursors have been listed into annex B of the Stockholm Convention in 2009; PFOA has been listed in 2019 in Annex A and PFHxS is scheduled for listing. With the listing of a new POP into the convention, its presence shall be measured around the globe in so called core matrices. Additionally, the long-chain C_{11} to C_{14} PFCAs, as well as PFOA and its ammonium salt (APFO), were listed in the Candidate List of substances of very high concern by the European Chemicals Agency (ECHA, 2015).

The generation of comparable analytical data plays an essential role to study the distribution and environmental transformations of POPs. The Global Monitoring Plan of POPs (GMP) has defined the chemicals and their transformation products as well as the matrices for analysis to generate such comparable data.

To protect human health, the Swedish Food Agency has established an action level for the sum of 11 PFAS including PFOS, PFOA and PFHxS of 90 ng/L in drinking water (Sahlin, 2017). Furthermore, within the EU Water Framework Directive (2000/60/EC), environmental quality standard values for PFOS and its derivatives was proposed at 0.65 ng/L (annual average) and 36 µg/L (maximum acceptable concentration) in inland surface waters (EU, 2012).

Driven by strict regulations and concerns about the PFAS undesired impacts on humans and the environment, the global producers shifted towards replacement of long-chain PFCAs, PFSAs and their potential precursors with their shorter-chain compounds (Ritter, 2010) or functionalized perfluoropolyethers. Figure 2 shows four novel PFASs that have been reported to replace PFOA and PFOS in different applications.

ADONA

HFPO-DA

F53-B

PFECHS
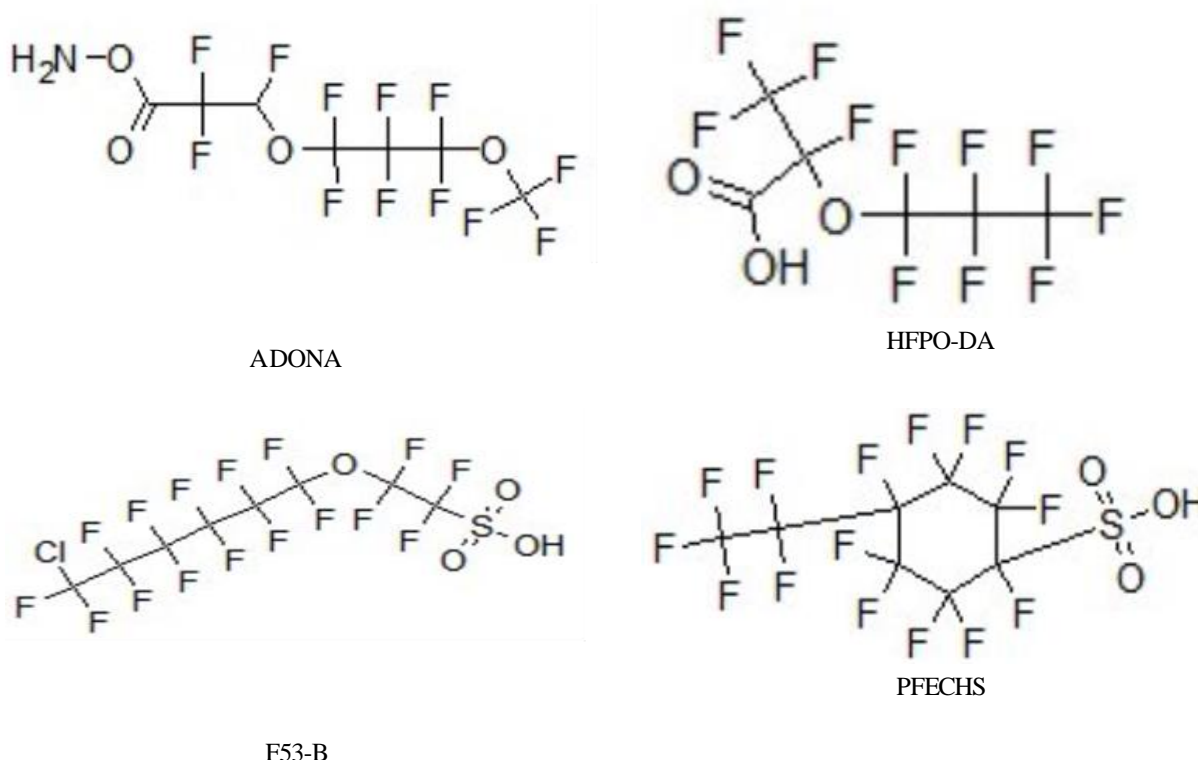
Figure 2: Structure for some of the studied alternative compounds called "Novel PFASs" in the current study.

One substituted for PFOA is 3H-perfluoro-3-[(3-methoxy-propoxy) propanoic acid] (ADONA), other replacement substances are the ammonium salt of 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3- heptafluoropropoxy) propanoic acid (HFPO-DA), used in the GenX process and ammonium salt of perfluoro[(2-ethyloxy-ethoxy) acetic acid] (EEA-NH$_4$). These novel PFASs have been produced to replace legacy PFOA as processing aids in the production of fluoropolymer high performance materials (Wang et al., 2013); but small amount of these aids can stay in the final product (Pan et.al, 2018). A technical mixture of potassium salt of 6:2 chlorinated polyfluorinated ether sulfonate, known as F53-B is used as replacement for PFOS in mist suppressants in the Chinese chromium - plating industry (Heydebreck et al., 2015). A cyclic PFSA (perfluoroethylcyclohexane sulfonate (PFECHS) has been reported to replace PFOS as an erosion inhibitor in aircraft hydraulic fluids. This cyclic PFAS has similar physicochemical properties as its linear counterpart PFOS (Wang et al., 2013).

ADONA was reported in water samples collected close to a point source (fluorochemical factory) in concentrations ranging from 320 ng/L to 6200 ng/L in River Alz (Germany) (Wang et.al, 2013). Perfluoro-2-propoxypropanoic acid (HFPO-DA) has also been detected in river waters downstream of fluorochemical plants at concentration of 631 ng/L in the United States (Strynar et al., 2012), 108 ng/L in Germany, 107.6 ng/L in Rhine River (EU) system (Heydebreck et al., 2015), and at concentration range of 1.7 ng/L - 812 ng/L in the Netherland (Gebbink et al., 2017). Recently, F-53B was detected at a maximum level of 78.5 ng/L in samples collected near metal-plating facilities in China (Wang et al., 2016a). Also, it was detected in the influent (43mg/L-78 mg/L) and effluent (65 mg/L -112 mg/L) of WWTPs receiving electroplating wastewater (Wang et al., 2013). Pan et al. (2018) measured HFPO-DA and F-53B in 160 surface water samples collected globally from China (n = 106), the United States (n = 12), the United Kingdom (n = 6), Sweden (n = 10), Germany (n = 14), The Netherlands (n = 6), and Korea (n = 6), and reported a median concentration of 0.95ng/L and 0.31 ng/L, respectively. PFECHS was detected at concentrations ranging from 0.16 to 5.65 ng/L in

the surface water of the Great Lakes (De Silva et al., 2011). It was also observed in surface water near the Beijing International Airport at concentration up to 195.1 ng/L (Wang et al., 2016b), and reported at concentrations up to 0.94 ng/L in the surface water and 0.01 ng/L to 0.35 ng/L in the WWTP effluent collected from Nordic countries (Kärrman et al., 2019). This demonstrates that HFPO-DA, F-53B and PFECHS are distributed globally.

According to the recent survey conducted by OECD, 4370 PFASs have been registered with CAS numbers (OECD 2018). Due to the insufficient analytical methods and standards to detect all PFASs, their precursors and the novel PFASs, combustion ion chromotograph is used for the determination of extractable organofluorine (EOF). The mass balance analysis is expected to provide useful information regarding the contribution of detected PFASs, as well as to give idea on the percentage of unidentified fluorinated chemicals in environmental samples (Miyake et al., 2007). The EOF is measured by a method in which organofluorines are extracted from the samples and inorganic fluoride is removed. EOF can be measured using combustion ion chromatography (CIC). Using the mass balance analysis approach, the proportion of measured PFASs in target analysis to total EOF can be determined. Evidence has shown that legacy PFASs account for only a small fraction of the total organic fluorine present in the environment and wildlife. For example, unidentified PFASs account for 70 to 90% of organofluorine in seawater (Miyake et al., 2007). Most recently, 51 PFASs were measured in a wastewater treatment plant receiving wastewater from a fluorochemical manufacturing facility. It was found that unidentified PFASs account for 9 to 89% and 48 to 73% of the total adsorbable organofluorine in WWTP influent and effluent samples, respectively (Dauchy et al., 2017).

2.0   Aim of the study

The aim of the study is to analyze PFOS, PFOA and PFHxS in water samples collected from developing countries in Africa, Asia, Group of Latin America and Caribbean, and Pacific Islands within the UNEP/GMP2 project and to set a baseline level for these three PFASs. This level will be used to compare the levels of these three PFASs in the next global monitoring plan after ten years, to achieve one of the Stockholm convention goals regarding the 50% reduction in POP concentrations in the environment in ten years. Additionally, to explain if PFOS, PFOA and PFHxS in samples selected from Swedish cities and developing countries are representatives of the overall PFAS contamination in the environment. Furthermore, the presence of new PFOS/PFOA alternatives in water samples from Swedish cities and developing countries will be investigated.

Specific tasks in this study include: 1) Analysis of water samples collected under the UNEP project, and to evaluate the variation of the concentrations between regions, within each region, and between different time points. Based on the results a baseline concentration for the different regions and for each priority PFAS will be established, 2) Analysis of an extended list of PFASs and extractable organofluorine (EOF) in selected water samples from Sweden and developing countries, to assess the contribution of PFOS, PFOA and PFHxS to $\sum_{73}$ PFAS and to EOF, 3) Evaluation of the global distribution of new PFOS/PFOA alternatives released into environment by measuring the concentration of these compounds in selected samples collected from Sweden and developing countries.

3.0   Materials and Methods

3.1   <u>Chemicals</u>:
Native standards of PFCAs (C_2-C_{14}, C_{16}, C_{18}), PFSAs (C_2- C_{12}) and four PFSA (C_4, C_6, C_{10} linear; C_8 linear and branched), perfluorooctanesulfonamidoacetic acids (FOSAAs) (FOSAA, MeFOSAA, EtFOSAA), FTSAs (4:2, 6:2, 8:2), FTUCAs (6:2, 8:2, 10:2), PFPAs (C_6, C_8, C10), PFPiAs (6:6, 6:8, 8:8), PAPs (SAmPAP, diSAmPAP, 6:2 PAP, 8:2 PAP, 6:2 diPAP, 8:2 diPAP, 6:2/8:2 diPAP,

10:2 monoPAP, 10:2 diPAP), and native of 9ClPF3ONS, 11ClPF3OUdS, PFECHS, ADONA and HFPO-DA were used.

Mass-labelled of PFCAs (C_4-C_{12}, C_{14}, C_{16}), PFSAs (C_4, C_6, C_8), EtFOSAA, fluorotelomer sulfonic acid (FTSAs) (6:2, 8:2), FTUCAs (6:2, 8:2, 10:2), PAPs (6:2 monoPAP, 8:2 monoPAP, 6:2 diPAP, 8:2 diPAP), and mass-labelled of HFPO-DA were used. All native and mass-labelled internal standards were purchased from Wellington Laboratories (Guelph, ON, Canada), except 10:2 mono PAP and 10:2 diPAP, which were purchased from Chiron (Trondheim, Norway), TFA and PFPrA from Sigma Aldrich (Darmstadt, Germany) and PFEtS, which was purchased from Kanto Chemical Co. Inc (Tokyo, Japan).

Glacial acetic acid, ammonium acetate ($\geq$ 99.0%), and N-methylpiperidine ($\geq$ 99.0%) were purchased from Sigma Aldrich (Darmstadt, Germany); sodium hydroxide ($\geq$ 97%), ammonium hydroxide (25%), acetonitrile (HPLC-grade, $\geq$ 99.99%), isopropanol ($\geq$ 99%) and methanol (HPLC grade, $\geq$ 99.99% and LCMS grade, $\geq$ 99.9%) were obtained from Fisher Scientific (Leicestershire, UK). Water used during the analysis was MilliQ (18.6 MΩ). Oasis® WAX 6cc cartridges 150mg 30µm were obtained from Waters (Milford, USA).

3.2 Samples:

All samples analyzed during the current project were collected according to the protocol for the sampling of water as a core matrix in the UNEP/GEF GMP2 projects (UNEP, 2017). In total 40 water samples were analyzed, 34 water samples under the UNEP/GMP2 project and six Swedish samples.

Water samples provided by UNEP/GMP2 project were taken from a large river, estuary or bay in each country. One location for each country was used with the exception of Brazil where the location was changed in the middle of the project. Water samples were collected in 2018 from four regions. Asia (n=4), Africa (n=8), Pacific Island (n=9), and Group of Latin America and Caribbean (GRU-LAC) (n=13) (Figure 3-a). Samples were taken at the end of each quarter of the year, classified into four intervals using the Roman numbers I, II, III, and IV, respectively. Detailed information about all sample locations and analyzed intervals under the current project are provided in Appendix, Table 4.

Swedish water samples were collected from three rivers of different sizes in Södertälje (n=2), Göteborg (n=2), and Örebro (n=2) (Figure 3-b).

Samples were collected at two sites in the Södertälje Canal that connects lake Mälaren with the Baltic Sea at the city of Södertälje and where large parts of the vessel traffic from Lake Mälaren goes into the Baltic Sea. Both samples were taken at the Baltic Sea side of the city. Igelstaviken is closest to the city and there are numerous industries and Södertälje harbor at that site. The mouth of Himmerfjärden bay was the second site. Much of the wastewater from the southern parts of Greater Stockholm is discharged into Himmerfjärden after first having been treated in the Himmerfjärdsverket. Both samples were taken on 17 of October 2017.

Samples from Göteborg were collected from Göta älv at Alelyckan upstream of the city of Gothenburg. Göta älv runs from Sweden's largest lake, Vänern, for 93 km before it exits to Kategatt at the city of Gothenburg. Samples were collected on 18 of February 2017 (sample 1) and 7 of August 2017 (sample 2).

In addition, two water samples from river Svartån in Örebro were collected on 20 November 2018 (sample 1), and 11 February 2019 (sample 2). Svartån is a river in Örebro County (Sweden), that connects several small lakes with Lake Hjälmaren and it is approximately 100 km. The samples were taken downstream of Örebro city in the mouth to Lake Hjälmaren.

Figure 3: a) Map of all samples analyzed during the current project. b): Detailed map of the Swedish samples. Maps were generated using Google Maps.

3.3 Sample extraction and clean up:

Target Compounds:

Solid phase extraction was used for the extraction of PFASs from water samples collected. Prior the SPE extraction, all samples were sonicated for 10 min then weighed in their containers that were used during analysis. All samples, procedural blanks and quality control samples were then spiked with internal standards. The Oasis ® WAX 150 mg cartridges were conditioned by passage of 4 mL of 0.1% ammonium hydroxide (NH_4OH) in methanol, 4 mL of methanol and 4 mL of MilliQ-H_2O, in sequence, prior to loading of 500 mL samples.

After loading the samples the cartridges were washed with 4 mL of MilliQ-water, then 4 mL of an ammonium acetate buffer solution (pH = 4) and dried under vacuum for 30 min. Empty containers

in which the samples were stored, were rinsed with 4 mL methanol that was used for eluting the first, neutral fraction into 15 mL polypropylene (PP) tubes. The second, anionic fraction was eluted with 0.1% ammonium hydroxide (NH$_4$OH) in methanol and collected in separate 15 mL PP-tubes. The samples were evaporated under nitrogen gas to 500 μL for fraction one and 200 μL for fraction two. 300 μL aqueous mobile phase were added to fraction two. Both fractions were spiked with recovery standard, vortexed and centrifuged for 10 minutes. The extracts were transferred to LC vials and were injected on LC-MS/MS. Fraction one was analysed as 100 % methanol, whereas fraction two was 40 % methanol and 60% 2mM ammonium acetate in MilliQ.

Determination of extractable organofluorine:

A similar extraction procedure as mentioned above was followed for the analysis of EOF, except that IS was not spiked before extraction for EOF. In addition, a more extensive wash was used after loading the sample on SPE, cartridges were washed with 20 mL 0.01% ammonium hydroxide in water, three times 10 mL MilliQ, followed by 4 mL ammonium acetate buffer and 4 mL 20% methanol in water solution. The final extract was split into three fractions. The two first fractions were added IS for quantification of target compounds. One fraction had the final composition of 80 % methanol and 20 % 2mM ammonium acetate in MilliQ, the second contained 40 % methanol and 60% 2mM ammonium acetate in MilliQ. The third and last fraction was not added IS or water and was analysed using CIC.

3.4 Instrumental analysis and quantification

The analysis of all target PFASs mentioned in the Appendix, Table 11 were done on three different instruments. The ultrashort chain (C$_2$-C$_3$) PFASs were analyzed on an Acquity Ultra Performance Convergence Chromatography (UPC^2) system coupled to a tandem mass spectrometer (Waters Corporation, Milford, USA); HFPO-DA and ADONA were analysed on an Acquity Ultra-Performance Liquid Chromatograph (UPLC) coupled to triple quadrupole 5500 mass spectrometer (AB Sciex) at Eurofins Environment Testing Sweden and the remaining PFASs were analysed on an Acquity UPLC system coupled to a Xevo TQ-S tandem mass spectrometer (Waters Corporation, Milford, USA).

For separation the ultrashort chain PFASs a Torous^{TM} DIOL column (3 mm x 150 mm, 1.7 μm; Waters Corporation Milford, USA) was used. The mobile phases were supercritical CO$_2$ (A) and 0.1% ammonium hydroxide in methanol (B). Instrument settings for the UPC^2-MS/MS system were electrospray ionization operating in a negative mode with the source temperature at 150 °C, desolvation temperature at 400 °C, desolvation gas flow 800 L/h, a cone gas flow 150 L/h and a capillary voltage at 0.85 kV.

For analysis of HFPO-DA and ADONA compounds, an Acquity HSS T3 100 mm x 1.8 μm column with an inner diameter of 2.1 mm (Waters Corporation Milford, USA) was used. Mobile phases used for HFPO-DA and ADONA analysis were MilliQ-water with the addition of 5 mM ammonium acetate and 5% methanol (Mobile phase A) and methanol (Mobile phase B). Flow rate was 0.4 mL/min and column temperature was 50°C. MS/MS instrument settings were negative mode electrospray ionization with a source temperature at 300 °C.

For analysis of the remaining targeted compounds, an Acquity BEH 100 mm x 1.7 μm column with an inner diameter of 2.1 mm (Waters Corporation Milford, USA) was used. Mobile phases used for PFAS analysis were MilliQ-water and methanol with addition of 2 mM ammonium acetate. The same composition was used for analysis of PAPs, FOSAs/FOSEs, but with the addition of 5 mM 1-methylpiperidine. MS/MS instrumental settings were electrospray ionisation operated in negative

mode with a source temperature at 150 °C, desolvation temperature at 400 °C, desolvation gas flow 800 L/h, a cone gas flow 150 L/h and a capillary at 0.84 kV. Column temperature was 50°C.

The EOF were analyzed by a Combustion Ion Chromatograph (CIC) (Metrohm, Switzerland). The CIC contains a combustion module, a 920 absorbent module and a 930 compact IC flex. An ion exchange column (Metrosep A Supp5, 4 mm x 150 mm) was used for separation of anions. The eluent solution was 64 mM sodium carbonate and 20 mM sodium bicarbonate in water using an isocratic elution. The sample volume of 150 μL was placed on a quartz boat and combusted at 900–1050 °C, all fluorine was converted to hydrogen fluorine and was adsorbed into the water. The dissolved fluoride was then analyzed by the ion chromatograph.

Quantification:
For LC-MS/MS and UPC², one batch standard was prepared for each extraction batch of samples to quantify the results and was injected after every ten samples. All batch standards were quantified using a twelve-point calibration curve and $\pm$ 20% deviation from the theoretical concentration was accepted. The calibration curve made up of a sequence of concentrations of 5, 10, 20, 40, 80, 150, 300, 500, 1000, 2000, 3000 and 4000 pg/mL.

Quantification of target PFASs was done using response factor for sample (the area of native PFAS divided by the area of the corresponding mass labelled internal standards) and compared with the response factor for the standard. IS was spiked before extraction to give a recovery-corrected concentration. Branched isomers of PFOS were quantified using PFOS isomer standard and reported as the sum of the isomer groups of 3/4/5-PFOS and 6/2-PFOS. ∑PFOS is the sum of linear and branched PFOS.

Mass balance analysis was carried out by comparing the concentrations of measured target PFASs using LC-MS/MSs and UPC² with the levels of EOF using CIC. The target PFAS concentrations used were from the quantification to which the IS were added after extraction. This was done since the concentrations used to compare with EOF should be the concentration in the extracts and not recovery corrected as target concentrations using IS quantification are. All concentrations were expressed in fluoride concentration (ng F/L) and reported in Appendix, Table 8 and Table 9. The target PFASs concentrations (ng/L) were converted to fluoride using the following equation:

$$c_F = \frac{n_F \ MW_F}{MW_{PFAS}} \times c_{PFAS}$$

c_F: fluoride concentration (ng F/mL)
n_F: number of fluorine in the PFAS molecule
MW_F: molecular weight of fluorine
MW_{PFAS}: molecular weight of PFAS molecule
c_{PFAS}: measured PFAS concentration in UPLC-MS

Extractable organofluorine was quantified using a five-point calibration curve. The calibration curve made up of a sequence of concentrations of 50, 100, 250, 500 and 1000 ng F/mL. Comparing the known PFASs concentration (ng F/mL) to EOF used to determine the contribution of known PFASs to EOF. Besides, the percentage level of unidentified PFASs was determined by subtracting the know PFASs concentrations from the extractable organofluorine.

In the current project, the following groups of PFAS were defined to assess the contribution of each of them to the total PFASs and EOF.
- Priority PFASs: PFOS, PFOA and PFHxS.
- PFCAs: all detected perfluoroalkyl carboxylic acids excluding PFOA and ultra short PFCA.
- PFSAs: all detected perfluoroalkyl sulfonic acids excluding PFOS, PFHxS and ultra short PFSA.
- Ultra-short PFASs: C_2 (TFA, PFEtS) and C_3 (PFPrA, PFPrS).

- Novel PFASs: PFECHS, F-53B, ADONA and HFPO-DA.
- Rest of PFASs: PFCA precursors (N-MeFOSAA, N-EtFOSAA) and PFSA precursors (FTSA).
- Extractable organofluorine (EOF): includes all organofluorine as determined by combustion ion chromatography (CIC).

3.5   Quality control and quality assurance

For each extraction batch, SPE manifolds and all equipment used for solvents preparation were cleaned twice with methanol. The Hamilton syringes used for spiking were designated for either IS, native and RS, to avoid cross-contamination.

Two procedural blanks (MilliQ water) and one spiked MilliQ-water sample (QC) were extracted in parallel with seven samples and quantified using mass-labelled standards. Procedural blanks were used to check any contamination during the analysis procedure whereas QC samples were used to assess the extraction efficiency, accuracy, and repeatability of the method (Appendix, Table 5).

For LC-MS/MS instrumental quality control during sample analysis, an injection of instrument blank (methanol) after each ten samples were done to ensure the absence of any contamination from the instrument. While for CIC, two combustion blanks were injected between each sample to avoid carry-over between samples.

Target PFAS:

The limit of detection (LOD) was determined as average concentrations in procedural blanks plus three times the standard deviation. In case an analyte was not present in the blanks, the lowest point of the calibration curve was used. The limit of quantification (LOQ) was determined as average concentrations in procedural blanks plus ten times the standard deviation. LOD and LOQ are presented in Appendix, Table 5.

Recoveries of internal standards are presented in Table 2. Recoveries of internal standards for PFOS, PFOA and PFHxS ranged between 80-109%, 76-103%, and 78-104% respectively.

Precision and accuracy were also assessed by spiking 2 ng native PFASs to MilliQ water. Precision and accuracy for native compounds in QC-samples (n=7) are provided in Appendix, Table 5. The majority of PFASs showed an average recovery of 75-115% except the ultrashort PFASs (TFA and PFPrA) which had an average of 33-51% (RSD < 20%) and PFOcDA with an average of 53% (RSD < 20%).

EOF analysis

The limit of detection was determined as average concentrations in procedural blanks plus three times the standard deviation. The limit of quantification (LOQ) was determined as average concentrations in procedural blanks plus ten times the standard deviation.

Detectable organofluorine was found in the extraction blanks and the limit of detection was 50 ng F/L. Sample concentrations were corrected for the blank level and were reported when their levels were at least two times higher than the LOD.

Precision and accuracy have been investigated previously (Kärrman et al., 2019) by combustion of 100 ng (n=3) and 500 ng (n=3) of SRM 2143 – p-fluorobenzoic and the results were between 90-98%. To evaluate the precision of CIC during sample analysis, a 100 ng F/mL of PFOS standard was injected for every 10 samples, and fluoride was quantified according to the calibration curve and resulted in 83.7 ng F/L (RSD=15%).

4.0 Results and Discussion

4.1 Baseline concentrations of PFOS, PFOA, and PFHxS

The three priority PFASs were detected in all developing countries samples analyzed in the range of 0.01-5 ng/L for ∑PFOS, 0.02-3.2 ng/L for PFOA and 0.01-2.8 ng/L for PFHxS. The highest concentrations of ∑PFOS and PFHxS were found in Vanuatu (Pacific) with a concentration of 5 ng/L for ∑PFOS and 2.8 ng/L for PFHxS. However, highest concentration of PFOA was from Kenya with a concentration of 3.2 ng/L. All data are presented in Appendix, Table 6.

Branched PFOS (sum of 3/4/5-PFOS and 6/2-PFOS) showed a contribution ranging from 10-65% of the total ∑PFOS in all developing countries samples. A contribution of 20-30% of branched PFOS to total ∑PFOS was found in 40% of samples, where 60% of the data showed a contribution above 30%. In the production of PFOS by ECF 20-30 % of branched PFOS are formed (3M Company, 1999). Isomer profiles may differ depending on the environmental compartments, branched isomers are more water soluble which explains the higher contribution in water samples compared to the PFOS product.

The three PFASs were detected at different concentrations in all samples analyzed in Africa, Asia, GRULAC and Pacific Islands. From Figure 3 we can observe that specific countries in each region showed higher concentrations of the three PFASs. For instance, Kenya samples (Africa), Argentina samples (GRULAC) and Vanuatu samples (Pacific) showed the highest concentrations of the three PFASs in each region. Asia samples had the lowest average concentrations of ∑PFOS, PFOA and PFHxS in comparison to other regions. It was also noticed that there is a wide range of concentrations of each of the three PFASs within the country and between different time points, i.e. Brazil (PFOS), Kenya (PFOA and PFHxS), and Kiribati (PFOS and PFHxS). Brazil samples were different from the other countries because two different locations were used. It was noted that there was a variation between the two different locations, for example 0.05 - 0.3 ng/L for ∑PFOS for location 1 and 1.9 - 3.3 ng/L for ∑PFOS for location 2 (see appendix, Table 6).

To assess if there is a significant difference of the three PFASs between the four regions within a year, a variance test (Kruskal-Wallis) was performed for the 2017 and 2018 data separately. The test did not show any significant difference ($p < 0.05$) in ∑PFOS, PFOA and PFHxS levels between the four regions. The same test was carried out again by combining data for both years to investigate the longer trend differences for these three PFAS levels and the results demonstrate that ∑PFOS and PFHxS average levels were not significantly difference ($p < 0.05$) between the four regions. On the other hand, PFOA showed a significant difference ($p < 0.05$) in average concentrations between the four regions (Appendix, Table 7). A Dunn Test was carried out using the Bonferroni correction to investigate which regions differed significantly. Three pairs of regions showed significant difference for average PFOA levels ($p < 0.05$), Asia – GRULAC, Africa - Pacific Islands, and GRULAC - Pacific Islands.
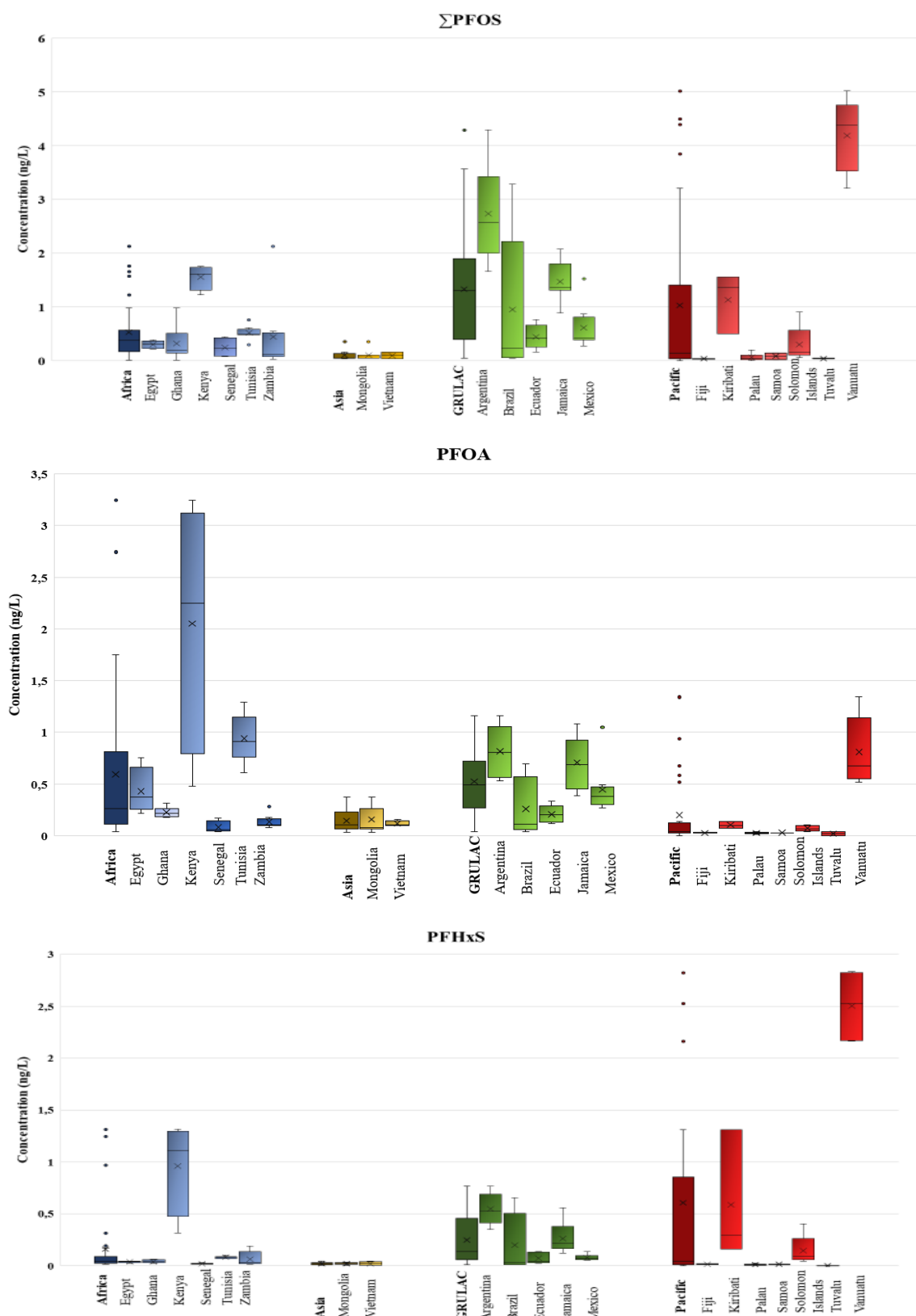
Figure 3: Boxplots for PFOS, PFOA and PFHxS concentrations in the studied countries in Africa, Asia, Group of Latin America and Caribbean (GRULAC) and Pacific Islands (2017-2018). The whisker represented the minimum and maximum concentrations. The lower border of the box represented the first quartile (25%), the line inside the box is the median and the upper border is the third quartile (75%). The mean is represented as (X) and the individual points are outliers which were defined as all points that are higher than interquartile range multiplied by 1.5.

Some of the studied countries showed that there was a high variation in the level of the three PFAS between different time points in each country. For example, Kenya sample was observed to have higher average concentrations of the three PFASs than all other studied Asian countries. The four studied intervals for this sample were plotted separately to assess if there was a variation of these three PFASs between different time points (Figure 4-a). It was noticed that ∑PFOS had a narrow concentration range of 1.2 -1.8 ng/L in the four intervals, but the concentration is higher than all studied samples in this region, except one Zambian sample that showed as an outlier in Figure 3. On the other hand, PFOA and PFHxS had a wide concentration range (i.e. PFOA 0.5 – 3.2 ng/L and PFHxS 0.3 – 1.3 ng/L). As shown in Figure 4-a, PFHxS showed concentrations range from 0.96 - 1.3 ng/L on the last three intervals but lower concentration 0.3 ng/L in the first interval, while PFOA concentration was different in the four intervals. Another example is Kiribati samples which were studied in three intervals, the third and the fourth intervals samples were collected in 2017, while the first interval sample was collected in 2018. This sample showed a variation in concentration of PFHxS in the three studied intervals (Figure 4-b). The concentrations of ∑PFOS in the first and third intervals were in similar range 1.4 -1.6 ng/L, but it was declined to 0.5 ng/L in the fourth interval. These two samples can explain the within country variation on the concentration of these priority PFASs. The variance test (Kruskal-Wallis) showed however that there was no significant difference $(p<0.05)$ in the different interval concentrations.
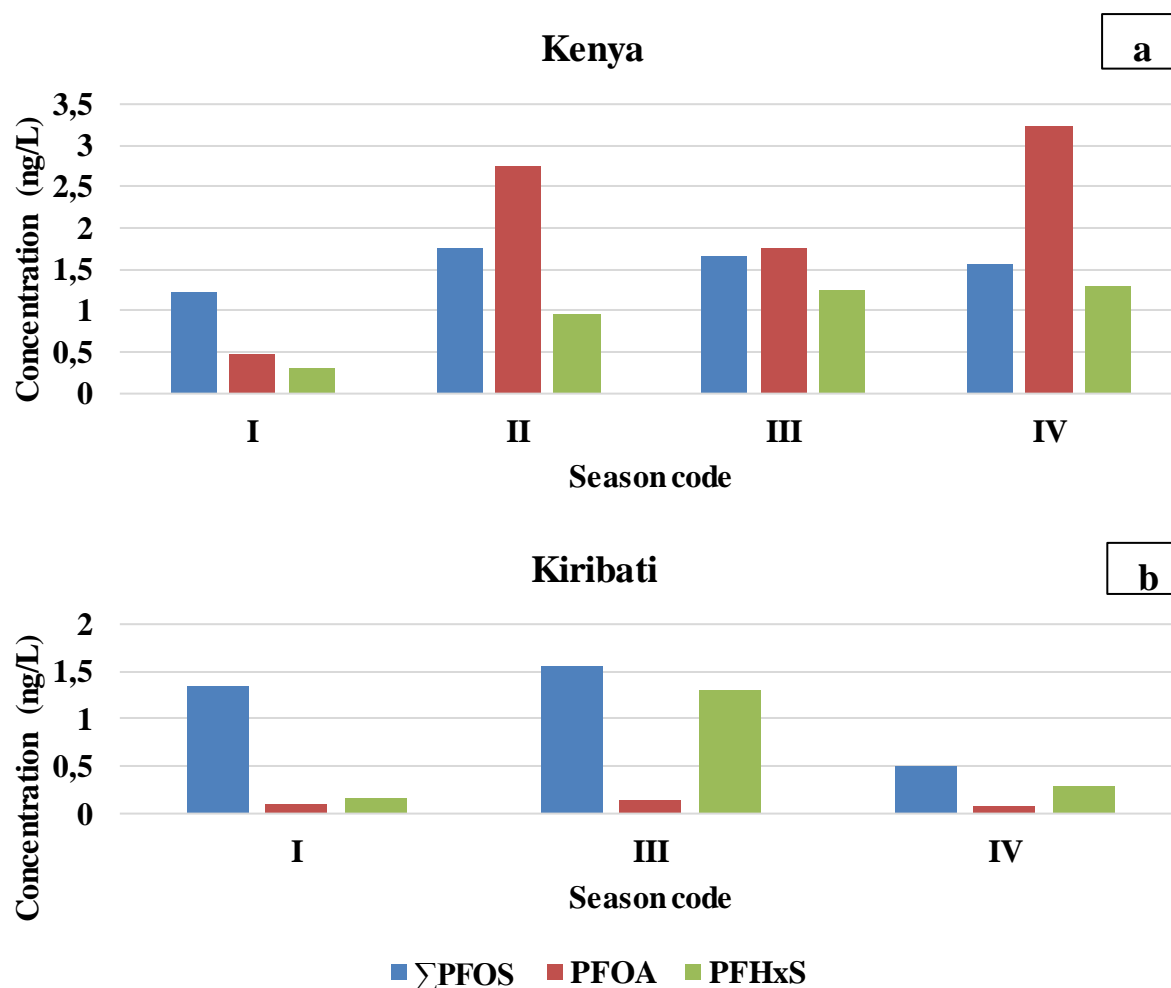
Figure 4: a) PFOS, PFOA and PFHxS concentrations (ng/L) in Kenya samples in the four intervals of the year. b) PFOS, PFOA and PFHxS concentrations (ng/L) in Kiribati samples in the three studied intervals. The Roman numbers (I, II, III and IV) represented the end of each quarter of the year.

The priority PFAS levels could be different between regions and within a region due to the source of contamination (e.g. use of firefighting foam, wastewater treatment plants, etc..), and historical activities associated to PFAS in that area. The difference between time points in the same location could be due to dilution factors (rain or dry seasons) or activities applied at specific time of the year (e.g. firefighting training) may play a role in PFAS levels in surface water.

Levels of the three priority PFAS in Kenya and Vanuatu samples, PFOA levels in Tunisia samples and Kiribati samples in ∑PFOS and PFHxS levels demonstrated the highest levels in all investigated African and Pacific Islands region countries (Figure 3). Based on the above discussed variations in concentration between regions, the baseline concentration was established for each priority PFAS for the different regions separately by taking the median concentration for each region (interquartile range, IQR, in parenthesis). The median concentration was taken to compare different region periods. Although not significantly different, the baselines for Africa and Pacific Islands were established both with and without the countries that demonstrate deviating levels. The baseline levels are presented in Table 1.

Table 1: Baseline levels for ∑PFOS, PFOA and PFHxS in the four regions reported as median concentration (interquartile range, in parenthesis).

Region	number of samples	Baseline levels (ng/L)		
		∑PFOS	PFOA	PFHxS
Africa excluding Kenya and Tunisia	22	0.22 (0.10 – 0.38)	0.18 (0.10 – 0.25)	0.031 (0.02 – 0.04)
Africa including Kenya and Tunisia	34	0.38 (0.18 – 0.54)	0.26 (0.13 – 0.80)	0.042 (0.02 - 0.09)
Asia	11	0.048 (0.04 - 0.12)	0.11 (0.07 – 0.19)	0.018 (0.01-0.03)
GRULAC	35	1.31 (0.39 – 1.88)	0.50 (0.28 – 0.71)	0.14 (0.06 – 0.44)
Pacific Islands excluding Vanuatu and Kiribati	17	0.053 (0.03 – 0.15)	0.033 (0.03 – 0.04)	0.012 (0.01 – 0.05)
Pacific Islands including Vanuatu and Kiribati	25	0.15 (0.04 – 1.24)	0.046 (0.03 – 0.11)	0.055 (0.01 – 0.63)

4.1.1 PFOS, PFOA and PFHxS levels in relation to other studies

The levels of the three PFASs in the current study are different from the levels reported for water samples from many other countries. For example, PFOS concentration in South Africa was reported to be six times higher than the highest concentration detected in African samples in the current study (Fredriksson, 2018). PFOS, PFOA and PFHxS concentrations in Asian samples studied under this project ranged from 0.04 – 0.35 ng/L, 0.03 - 0.37 ng/L and 0.01 - 0.031 ng/L, respectively. However, they were reported in previous studies at higher concentration ranges 0.29 – 94 ng/L for PFOS, 0.86 – 245 ng/L for PFOA and 0.0025 - 3.1 ng/L for PFHxS (Senthilkumar et al., 2007), (So et al., 2007). The highest concentrations in the previously discussed studies were probably taken from a contaminated site of these PFASs. Furthermore, Pacific Islands samples in the current study showed concentrations ranged from 0.01 – 0.3 ng/L for PFOS, 0.02 – 0.1 ng/L for PFOA and 0.01 – 0.09 ng/L for PFHxS excluding Vanuatu and Kiribati samples. Literature studies for this region reported a concentration ranged from 0.02 – 0.08 ng/L for PFOS, 0.06 -0.14 ng/L for PFOA and 0.002 – 0.003 ng/L for PFHxS (Yamashita et al., 2005).

Moreover, one study from Vietnam reported concentration of PFOS from the Red river in range of 0.18-5.3 ng/L, PFOA 0.09-18 ng/L and PFHxS 0.10-3.1 ng/L, the highest concentrations were from highly populated and industrialized areas (Duong, 2015). In the current study, Vietnam samples

concentrations ranged from 0.04-0.13 ng/L for PFOS, 0.10-0.16 ng/L for PFOA and 0.01-0.03 ng/L for PFHxS, which is lower than what was reported in literature.

In addition, previous studies from Brazil reported PFOS, PFOA and PFHxS in concentrations ranging from 0.05-1.32 ng/L, 0.04-3.25 ng/L and 0.05-0.21 ng/L respectively (Quinete, 2009). These samples were taken from Paraíba do Sul river before water treatment plant and the river is heavily contaminated by agricultural and discharges from untreated industrial wastes. In the current study, the concentrations of these PFASs ranging from 0.05-3.3 ng/L for PFOS, 0.04-0.7 ng/L for PFOA and 0.01-0.7 ng/L for PFHxS for two different locations. It was noted that there was a variation between different locations within the country due to sample location and source of contamination. Detailed results from literature studies are reported in Appendix, Table 3.

4.2 Importance of PFOS, PFOA, and PFHxS to $\sum_{73}$ PFASs

PFASs were extracted from water samples using SPE and 27 out of 73 measured PFASs were detected in the extracted samples. Extractable organic fluorine was measured using CIC. To assess the contribution of all detected PFASs to EOF, a mass balance analysis was done for twelve water samples. In the following sections, the total of 27 detected PFASs in selected samples are discussed as well as the contribution of the three priority PFASs to total detected PFASs.

Thirteen PFASs (PFDS, PFUnDA, PFDoDA and the 11 PFASs excluding 6_2 FTSA) were detected in samples from developing countries and an investigation of a partial correlation between them were done. Partial correlation measures the strength and direction of a linear relationship between two variables. As observed in Figure 5, two groups were highly correlated to each other. The sulfonate group (L-PFOS, br-PFOS, PFHxS) and the carboxylic acid group (PFPeA, PFHxA, PFOA); these groups are the major PFASs in surface water due to the high water solubilities and contamination degree. PFOS, PFOA and PFHxS were frequently detected due to their usage worldwide in various applications as discussed in section 1 (Prevedouros et al. 2006; Wang et al. 2014). In addition, PFOA, PFPeA and PFHxA were reported to be three out of nine dominated PFCAs in surface water samples collected under the Nordic screening study (Kärrman, 2019). These three PFCAs were also detected in all studied Swedish samples under the current study.
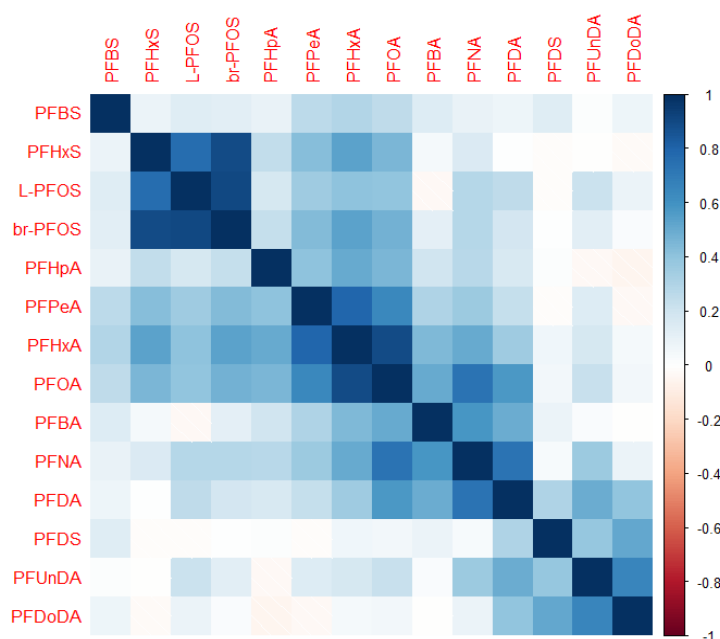

Figure 5: Correlation within and between the thirteen PFASs across samples provided under UNEP project.

The following PFASs classes were detected in Swedish and developing countries samples; PFCAs, PFSAs, PFCA precursors (N-MeFOSAA, N-EtFOSAA), PFSA precursors (FTSA) and ultra-short PFASs including C_2 (TFA, PFEtS) and C_3 (PFPrA, PFPrS) (Appendix, Table 10). The levels of $\sum_{27}$ PFASs detected in surface water from the UNEP project and Sweden ranged between 3 ng/L and 17 ng/L, with a median of 9.4 ng/L. Lowest concentrations were found in samples from Mongolia 3 ng/L; the highest concentrations were found in Argentina samples 17 ng/L. The highest concentration of the sum of the three PFASs was in Vanuatu sample 6.33 ng/L, and the lowest concentration was in Mongolia sample with 0.17 ng/L; the remaining samples fall in range from 0.5 – 5.7 ng/L (Figure 6-a).

The contribution of the sum of the three priority PFASs to $\sum_{27}$ detected PFASs were between 6% to 48% (Figure 6-b). The lowest contribution was from Mongolia sample, while the highest contribution was from Vanuatu samples. The Swedish samples showed a contribution of these priority PFASs that ranged from 19 to 35% with a mean of 26%, while the developing countries samples had a contribution range from 6 to 48% with a mean of 25%.

Swedish and developing countries samples showed similar profile across all classes except for Mongolia and Solomon Islands samples. PFCAs was the dominant class in these samples except for these two samples where the ultra-short chain (C_2-C_3) class was the dominant. PFCAs showed a contribution of 38 to 52% in Swedish samples and 14 to 59% in developing countries samples. Ultra-short chain PFASs showed a varied contribution range in both Swedish and developing countries samples. For example, the highest concentration of trifluoroacetic acid (TFA) in waters was found in Tunisia with 2 ng/L, other samples fall in the range from 0.2 to 1.5 ng/L. The detection of TFA in surface water could be due to the atmospheric deposition as Key et al. (1997) reported that certain volatile fluorinated compounds could be oxidized in the troposphere yielding nonvolatile compounds (i.e. TFA). In addition, TFA is used as a building block in fluorine chemistry, pharmaceutical and pesticides applications (Dreveton, 2016). The highest concentration of perfluoropropanoic acid (PFPrA) was found in Svartån (sample 2) with 2 ng/L, other samples fall in range from below LOD to 1.7 ng/L. Ultra-short acids (TFA, PFPrA) was detected as impurities in historical aqueous film forming foams (AFFFs) (Barzen-Hanson and Field, 2015).

PFSAs showed similar profile in all sample with a low contribution up to 8% of the total. Novel PFASs showed a contribution up to 3% in Swedish samples and 0.4% in developing countries samples, only one of the new novel PFAS was detected in one sample only from the developing countries at a low concentration.

Rest of PFASs are the sum of PFCA and PFSA precursors that were detected in three of the developing countries samples with a contribution of 4 - 24%, and three Swedish samples with a lower contribution up to 1%.

The results showed that the dominant class in surface water globally was PFCA followed by the three priority PFASs and the ultra short PFASs. To assess the environmental contamination of PFASs it is therefore not sufficient to only analyze the three priority PFASs. The substances included in the group of PFCAs can easily be analyzed together with the priority ones, it can however be more problematic to analyze the ultra short PFAS due to chromatographic issues. It should be noted that the environmental and human hazard for most PFASs are not known, besides the fact that they are extremely persistent.
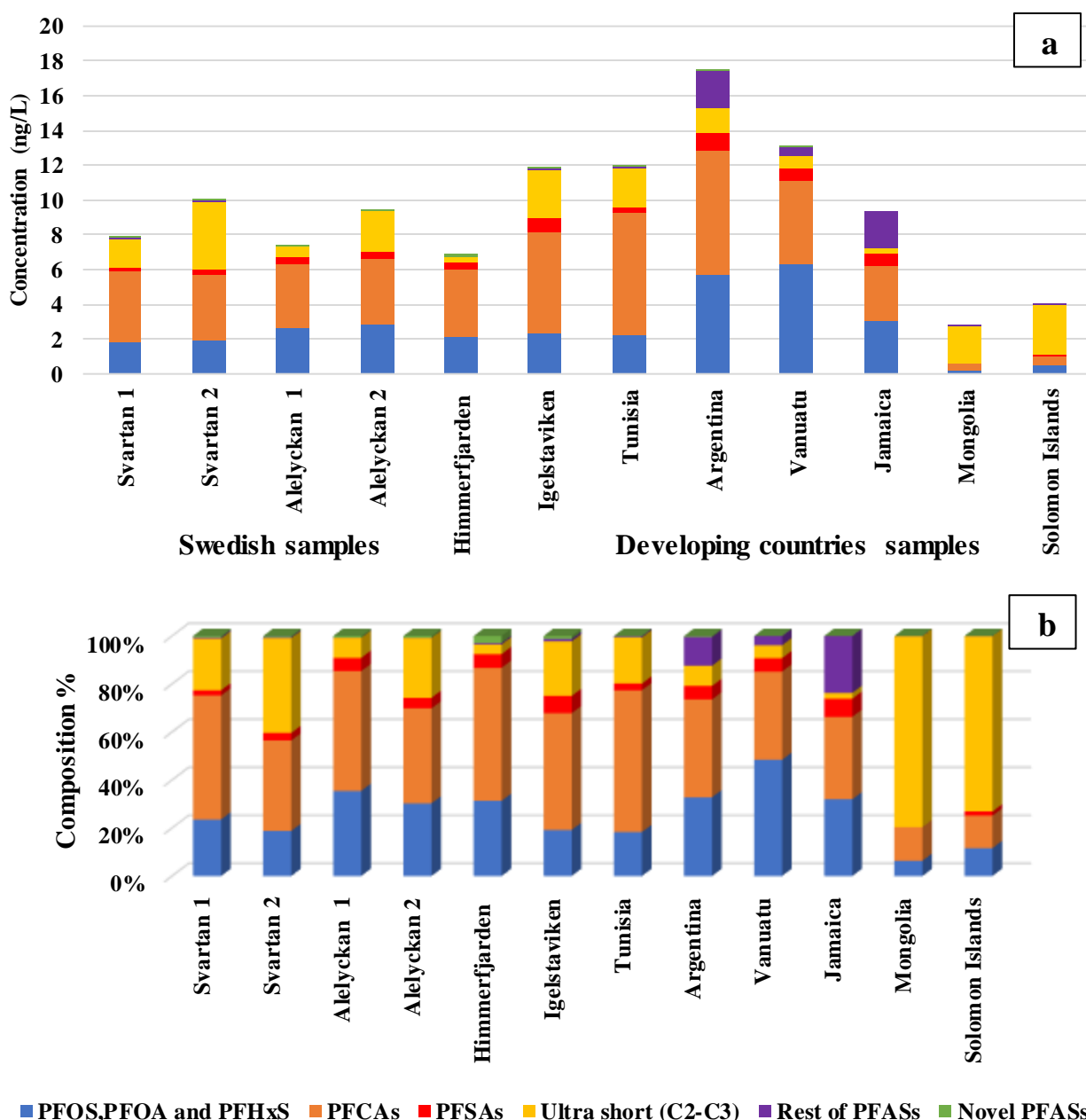
Figure 6: a) Concentration (ng/L) of different detected PFAS classes in Swedish and developing countries surface water samples, b) relative composition of these classes in surface water samples.

4.3   Importance of PFOS, PFOA, and PFHxS to the overall organofluorine

Extractable organofluorine (EOF) was measured in twelve samples using CIC. The limit of detection was determined as average concentrations in procedural blanks plus three times the standard deviation. Detectable organofluorine was found in extraction blanks; the limit of detection was 50 ng F/L. Sample concentrations were reported when their levels were at least two times higher than LOD. Due to the high blank level, only two out of twelve samples could be reported and used to assess the contribution of the detected 27 PFASs to EOF. The EOF in the Tunisia sample was two times higher than LOD, but this sample was excluded from the study as the fluoride and chloride peaks were overlapped.

As shown in Figure 7, the two samples that had extractable organofluorine levels two times higher than LOD were the samples from Svartån (sample 1) and Vanuatu. The detected PFASs could explain 3% of the measured EOF for the Vanuatu sample and 5% of the Svartån sample. The mass balance approach is anticipated to provide useful information on the extent of unidentified fluorinated chemicals in environmental samples. In the current study the unidentified fluorinated chemicals accounted for 95% and 97%; whereas Miyake et al. (2007) reported the contribution of the unidentified PFASs in sea water in range of 70 to 90%. The proportion of unidentified PFAS was also reported in the range between 83 and 98% in surface water and 56 – 98% in effluent water (Kärrman, 2019). These unidentified fluorinated chemicals could be from pharmaceuticals, agrochemicals or other organofluorine substance (Key et al, 1997).

Two major groups of PFASs dominated in these two samples; PFCAs and the three priority PFASs (PFOS, PFOA and PFHxS). The three priority PFASs showed similar contribution to EOF in both samples and was in range of 1.1% to 1.4 %. The contribution of detected PFCAs to EOF were 1.1% in Vanuatu and 2.6% in Svartån. These two groups are the most studied and detected compounds in surface water. PFSAs showed low contribution to EOF in both samples and was in range 0.1% to 0.2%. The ultra- short PFASs (C_2-C_3) showed higher contribution to EOF in Svartån sample (0.4%) than Vanuatu (0.04%). Rest of PFASs had one order of magnitude higher contribution to EOF in Vanuatu sample than Svartån sample. In addition, Vanuatu sample demonstrated similar contribution for PFSAs and the rest of PFASs (FTSA and FOSAA) to EOF.
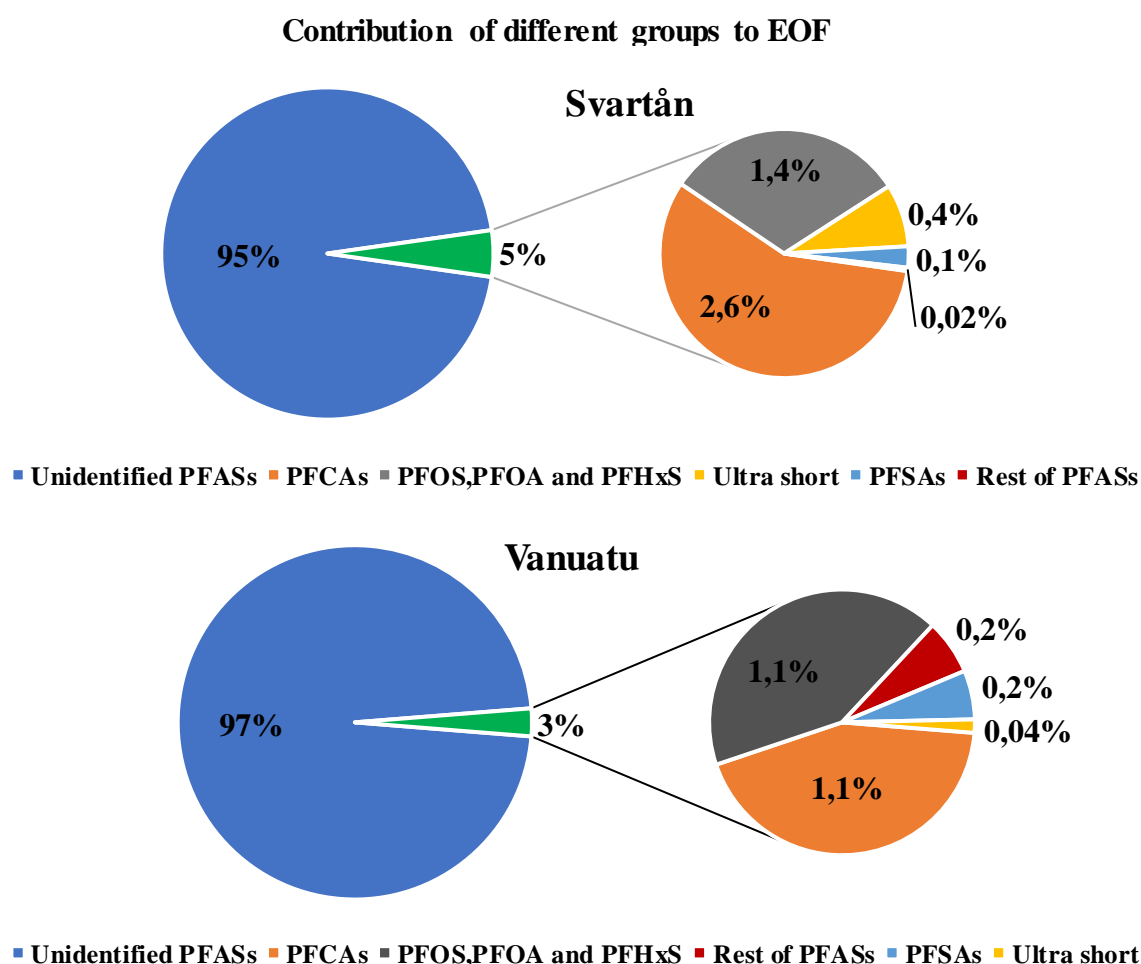
Figure 7: The PFASs profile for Svartån and Vanuatu samples. The detected PFASs were divided into five groups; (PFOS, PFOA and PFHxS), PFCAs, PFSAs, Ultra short (C_2-C_3), and Rest of PFASs. The percentage of unidentified PFASs was determined by subtracting the know PFAS concentrations from the extractable organofluorine. These groups are shown with different colors, the contribution is reported in percentage.

4.4   New PFOS and PFOA alternatives

Novel PFASs were detected in four out of six analyzed Swedish samples and one out of six analyzed developing countries samples in concentrations ranging between 0.02-0.14 ng/L. PFECHS was detected in concentration of 0.02- 0.03 ng/L for Alelyckan samples, 0.10 ng/L for Igelstaviken sample, 0.14 ng/L Himmerfjärden and 0.07 ng/L for Argentina sample. All detected novel PFASs results are presented in Appendix, Table 10.

 PFECHS was detected previously in a Nordic screening project and was reported in a concentration ranging from below LOD up to 0.94 ng/L (Kärrman et al.,2019). The highest concentration of PFECHS, 0.94 ng/L, in surface water from that study was from Finland. It was also detected in a Swedish sample (Lake Vättern) at 0.24 ng/L, presumably due to military airport activities. The detected concentration of PFECHS in the current study was in same range as the Swedish sample in the mentioned Nordic screening report. PFECHS is used as anticorrosive additive in aircraft hydraulic fluids and could also be a raw product for cosmetics (as adsorbent, anticaking, skin conditioning, binding, emulsion stabilising) (Kärrman et. al, 2019).

HFPO-DA was detected at or very close to the LOD in three Swedish samples in concentrations ranging between 0.03 and 0.06 ng/L. Strynar et al. (2012) detected HFPO-DA in Cape Fear River water downstream of effluent discharges from the DuPont factory in North Carolina (USA). Pan et al. and Gebbink et al. detected HFPO-DA in river waters with concentration range of 1.7- 812 ng/L in Netherland (Gebbink et al., 2017), and at a median concentration of 0.95 ng/L in 160 samples around the world (Pan et al., 2018). ADONA were not detected in any of the studied samples. ADONA was observed in the River Alz (Germany) downstream of wastewater effluent discharges from 3M/Dyneon's factory and was detected in all samples range from 0.32 to 6.2 µg/L (Wang et. al, 2013) which may be related to local production and application of these compounds.

5.0   Conclusion and future perspectives

Per and polyfluorinated alkyl substances are used on the global market in a wide range of applications, such as fire-fighting foams, metal plating and fluoropolymer manufacture. Worldwide attention has been drawn to PFOS, PFOA and PFHxS due to their global environmental presence, persistence, and toxicity to humans and wildlife.

In this project, samples from developing countries under UNEP project were studied for ∑PFOS, PFOA and PFHxS, other selected developing countries and Swedish samples were studied for an extended list of PFASs and extractable organofluorine and below the outcomes of this study:

- The baseline levels of ∑PFOS, PFOA and PFHxS were established in each region separately. These levels could be used to assess the decline in concentrations of these three PFASs in the next monitoring plan after 10 years.
- PFOS, PFOA and PFHxS are major PFAS contaminants detected in surface water sample. They demonstrated the second highest contribution to EOF in Svartån sample 1.4% and the highest contribution in Vanuatu sample besides the PFCAs 1.1%. In addition, the total 27 detected PFASs in selected Swedish and developing countries samples were dominated by PFCA with a contribution ranged from 14% to 59%, followed by the three priority PFASs with a contribution of 6% to 48%. Since these priority PFASs are globally regulated, but they still highly contributed in water samples, strict regulation should be considered to ensure human health protection.
- Extractable organofluorine was done in developed countries and it is a useful way to evaluate the percentage of unidentified fluorinated compound. The 27 detected PFASs in samples explained 3% of the measured EOF of Vanuatu sample and 5% of Svartån sample. A major

portion $> 93\%$ was unidentified fluorinated compound in the two investigated samples. These compounds maybe low fluorination chemicals that still not known if they are persistence in the environment or if they can bioaccumulate in human tissues and pose an adverse effect to human health and environment. As well as they would be highly fluorinated compounds that are persistent and transported globally. More attention should be drawn toward the assessment of the large proportion of unidentified fluorinated compounds in water samples.

- From the samples and detection limits in the present study it can be concluded that there is no global distribution of the novel PFASs but there seems to be some sort of usage in Sweden and Argentina. The novel PFASs should be included in future studies as there is a risk that they will be distributed worldwide, even though there is insufficient information regarding their environmental fate and health effects.

6.0 Acknowledgement

7.0   References

3M. (2000). Letter to US EPA, re: phase-out plan for POSF-based products (226-0600). US EPA Administrative.

Ahrens, L. F. (2009). Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany. Marine Pollution Bulletin, 58(9), 1326-1333.

Ahrens, L. N. (2015). Stockholm Arlanda Airport as a source of per-and polyfluoroalkyl substances to water, sediment and fish. Chemosphere, 129, 33-38.

Alsmeyer, Y. W. (1994). Electrochemical fluorination and its applications. In Organofluorine Chemistry (pp. 121-143). Springer, Boston, MA.

Arvaniti, O. S., & Stasinakis, A. S. (2015). Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. Science of the Total Environment, 524, 81-92.

Barzen-Hanson, K. A. (2015). Discovery and implications of C2 and C3 perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. Environmental Science & Technology Letters, 2(4), 95-99.

Company., 3. (1999). Fluorochemical Use, Distribution of Release Overview; U.S. EPA Public Docket AR226-0550.

Dauchy, X., Boiteux, V., Bach, C., Colin, A., Hemard, J., Rosin, C., & Munoz, J. F. (2017). Mass flows and fate of per-and polyfluoroalkyl substances (PFASs) in the wastewater treatment plant of a fluorochemical manufacturing facility. Science of the Total Environment, 576, 549-558.

De Silva, A. O., Spencer, C., Scott, B. F., Backus, S., & Muir, D. C. (2011). Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the Great Lakes of North America. Environmental Science & Technology, 45(19), 8060-8066.

Directive, E.C., 2000. (u.d.). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy OJ L 327, 22.12.2000,. p. 1–73.

Dreveton, A. (2016). Overview of the fluorochemicals industrial sectors. Procedia Engineering, 138, 240-247.

Duong, H. T. (2015). Occurrence of perfluoroalkyl acids in environmental waters in Vietnam. Chemosphere, 122, 115-124.

ECHA European Chemicals Agency. (2015). Candidate List of substances of very high concern for Authorisation. http://echa.europa.eu/candidate-list-table (accessed January 16, 2015).

Filipovic, M., & Berger, U. (2015). Are perfluoroalkyl acids in waste water treatment plant effluents the result of primary emissions from the technosphere or of environmental recirculation? Chemosphere 129: 74–80.

Fredriksson, F. (2018). Distribution of Total Fluorine, Extractable Organofluorine and Per-and Poly-fluoroalkyl Substances in Environmental Matrices from South Africa and Nordic Countries.

Fujii, S., Polprasert, C., Tanaka, S., Lien, H., Pham, N., & Qiu, Y. (2007). New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated compounds–a review paper. Journal of Water Supply: Research and Technology-AQUA,, 56(5), 313-326.

Gebbink, W. A. (2017). Presence of emerging per-and polyfluoroalkyl substances (PFASs) in river and drinking water near a fluorochemical production plant in the Netherlands. Environmental Science & Technology, 51(19), 11057-11065.

Gribble, G. W. (1994). Natural organohalogens: many more than you think! Journal of Chemical Education,. 71(11), 907.

Heydebreck, F., Tang, J., Xie, Z., & Ebinghaus, R. (2015). Alternative and legacy perfluoroalkyl substances: differences between European and Chinese river/estuary systems. Environmental Science & Technology, 49(14), 8386-8395.

Houde, M., De Silva, A. O., Muir, D. C., & Letcher, R. J. (2011). Monitoring of perfluorinated compounds in aquatic biota: an updated review: PFCs in aquatic biota. Environmental Science & Technology, 45(19), 7962-7973.

Håkansson, D. B. (2012). Environmental and Health Risk Assessment of Perfluoroalkylated and Polyfluoroalkylated Substances(PFASs) in Sweden. Sweden: Swedish Environmental Protection Agency .

Key, B. D. (1997). Fluorinated organics in the biosphere. Environmental Science & Technology, 31(9), 2445-2454.

Kim, S. K. (2007). Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. Environmental Science & Technology, 41(24), 8328-8334.

Kärrman, A. L. (2007). Identification and pattern of perfluorooctane sulfonate (PFOS) isomers in human serum and plasma. Environment International, 33(6), 782-788.

Kärrman, A., Wang, T., Kallenborn, R., Langseter, A. M., Grønhovd, S. M., Ræder, E. M., ... & Aro, R. (2019). PFASs in the Nordic environment: Screening of Poly-and Perfluoroalkyl Substances (PFASs) and Extractable Organic Fluorine (EOF) in the Nordic Environment.

Miyake, Y. Y. (2007). Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: a mass balance approach to determine individual perfluorinated chemicals in water. Journal of Chromatography A,, 1143(1-2), 98-104.

Miyake, Y., Yamashita, N., Rostkowski, P., So, M.K., Taniyasu, S., Lam, P.K.S.,Kannan, K. (2007). Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: a mass balance approach todetermine individual perfluorinated chemicals in water. Journal of Chromatography A, 1143(1-2), 98-104.

Möller, A. A. (2010). Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environmental Pollution, 158(10), 3243-3250.

Nakayama, S. S. (2007). Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. Environmental Science & Technology, 41(15), 5271-5276.

Pan, Y. Z. (2018). Worldwide distribution of novel perfluoroether carboxylic and sulfonic acids in surface water. Environmental Science & Technology, 52(14), 7621-7629.

Post, G. B., Cohn, P. D., & Cooper, K. R. (2012). Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: a critical review of recent literature. Environmental Research, 116, 93-117.

Poulsen, P. B., Jensen, A. A., Wallström, E., & Aps, E. N. P. R. O. (2005). More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project, 1013, 2005.

Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, fate and transport of perfluorocarboxylates. Environmental Science & Technology, 40(1), 32-44.

Quinete, N. W. (2009). Specific profiles of perfluorinated compounds in surface and drinking waters and accumulation in mussels, fish, and dolphins from southeastern Brazil. Chemosphere, 77(6), 863-86.

Ritter. (2010). Fluorochemicals go short. Chem Eng News;88(5):12–7.

Sahlin, S. (2017). PFAS in the Baltic Sea Region. Inventory of awareness, actions and strategies related to highly fluorinated substances, PFAS, including PFOS. Policy Area Hazards, EUSBSR, Swedish Environmental Protection Agency.

Senthilkumar, K. O. (2007). Perfluorinated compounds in river water, river sediment, market fish, and wildlife samples from Japan. Bulletin of Environmental Contamination and Toxicology, 79(4), 427-431.

Shi, Y. V. (2015). Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environmental Pollution, 206, 104-112.

So, M. K. (2007). Perfluorinated compounds in the Pearl river and Yangtze river of China. Chemosphere, 68(11), 2085-2095.

Strynar, M. D. (2015). Identification of novel perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass spectrometry (TOFMS). Environmental Science & Technology, 49(19), 11622-11630.

Tang, H. P. (2013). Recent development in analysis of persistent organic pollutants under the Stockholm Convention. TrAC Trends in Analytical Chemistry, 45, 48-66.

Taniyasu, S. Y. (2013). Does wet precipitation represent local and regional atmospheric transportation by perfluorinated alkyl substances? Environment International, 55, 25-32.

UNEP. (2017). Protocol for the Sampling of Water as a Core Matrix in the UNEP/GEF GMP2 Projects for the Analysis of PFOS.

UNEP. (2012). Technical paper on the identification and assessment of alternatives to the useof perfluorooctane sulfonic acid in open applications. UNEP/POPS/POPRC.8/INF/17.

Wang, T., Vestergren, R., Herzke, D., Yu, J., & Cousins, I. T. (2016a). Levels, isomer profiles, and estimated riverine mass discharges of perfluoroalkyl acids and fluorinated alternatives at the mouths of Chinese rivers. Environmental Science & Technology, 50(21), 11584-11592.

Wang, Y., Vestergren, R., Shi, Y., Cao, D., Xu, L., Cai, Y., ... & Wu, F. (2016b). Identification, tissue distribution, and bioaccumulation potential of cyclic perfluorinated sulfonic acids isomers in an airport impacted ecosystem. Environmental Science & Technology, 50(20), 10923-10932.

Wang, Z. C. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environment International, 60, 242-248.

Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., & Hungerbühler, K. (2014). Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environment International, 70, 62-75.

Witteveen+Bos and TTE consultants, . (No year). Emerging contaminants. Hämtat från https://www.emergingcontaminants.eu/index.php/background-info/Factsheets-PFOS-intro/Factsheets-PFOS-production 28/02/2019

Yamashita, N. K. (2005). A global survey of perfluorinated acids in oceans. Marine Pollution Bulletin, 51(8-12), 658-668.

Yamashita, N. T. (2008). Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere, 70(7), 1247-1255.

Yan, H., Cousins, I. T., Zhang, C., & Zhou, Q. (2015). Perfluoroalkyl acids in municipal landfill leachates from China: Occurrence, fate during leachate treatment and potential impact on groundwater. Science of the Total Environment, 524, 23-31.

8.0 Appendix:

Table 2: Results of mean internal standard recovery (%) in surface water. Relative standard deviation (RSD%) are presented in parentheses.

Analyte	Mean Recovery (RSD%) (n=40)
^{13}C-PFBA	58 (31)
^{13}C -PFPeA	89 (9)
^{13}C -PFHxA	86 (10)
^{13}C -PFHpA	90 (8)
^{13}C -PFOA	86(11)
^{13}C -PFNA	87 (9)
^{13}C -PFDA	82 (8)
^{13}C -PFUnDA	82 (13)
^{13}C -PFDoDA	75 (21)
^{13}C -PFTDA	60 (31)
^{13}C -PFHxDA	91 (41)
^{13}C -PFBS	93 (28)
^{18}O-PFHxS	94 (14)
^{13}C -PFOS	82 (14)
^{13}C -6:2 FTSA	90 (22)
^{13}C 8:2 FTSA	94 (21)
^{13}C 6_2FTUCA	70(29)
^{13}C 10_2FTUCA	64 (50)
^{13}C 8_2_FTUCA	68 (22)
^{13}C HFPO-DA	43(3)

Table 3: Compiled global literature studies on PFOS, PFOA and PFHxS concentration (ng/L) in water sample.

Country/sampling site	PFOA	PFOS	PFHxS	Reference
USA				
Haw River	287	127	8.43	Nakayama et.al 2007
Haw River	200	33.4	7.87	
Haw River	191	36.4	9.49	
Haw River	201	31.5	7.49	
Tributary to Cape Fear	58.6	30	3.36	
Haw River	152	31.2	7.7	
Cape Fear river	70.3	66.7	5.59	
Cape Fear river	71.5	50.4	4.82	
Cape Fear river	72.7	40.7	4.1	
Cape Fear river	46.8	56.3	6.84	
Germany				
River Elbe	7.44	1.16	0.85	Ahrens et al.2009
River Elbe	8.2	2.1	0.9	
River Elbe	7.8	1.9	1	
River Elbe	8.1	2.2	1.2	
River Elbe	7.2	2	0.8	
River Elbe	9.6	2.9	1.3	
River Elbe	7.4	1.5	0.9	
River Elbe	8.1	0.6	1.1	
River Elbe	6.8	0.5	0.9	
River Elbe	5.6	1.6	0.7	
River Elbe	5.9	2.1	0.7	
River Elbe	3.8	2	0.7	
River Elbe	3.6	1.6	0.8	
River Elbe	3.1	1.2	0.3	
River Elbe	2.8	1	0.3	
Rhine	11.6	3.7	3.04	
Rhine	12.3	4.13	1.93	
River Ruhr	14.3	4.21	0.18	
River Moehne	42.1	3.11	1.03	
Other tributaries	3.47	3.62	1.41	
Nederrijn. Waal. Ijssel	3.05	4.88	1.8	Möller et al. 2010
Hollands Diep	3.91	3.95	4.39	
Volkerak-Zoom	7.96	3.51	2.63	
Meuse	9.09	3.74	1.16	
New Meuse	33.9	3.94	6.76	
Old Meuse	7.03	3.92	4.31	
New Waterway	18.01	1.34	4.92	
Ijsselmeer	4.02	4.12	2.3	
North Sea Canal	8.06	12.4	7.05	
Haringvliet	3.74	4.33	3.93	
Scheldt	34.01	15.4	8.51	
Western Scheldt	6.86	3.32	1.53	
Eastern Scheldt	1.92	1.07	0.51	
Ghent-Terneuzen Canal	20.09	24.8	9.52	
North Sea	0.345	1.2	0.11	
Bight	5.25	2.32		
Japan				
Kamo river	36	4.1	3.3	Senthilkumar et al. 2007
Uji river station-1	100	8.7	3.3	
Uji river station-2	110	10	3.3	
Tenjin river	39	4.7	3.3	
Katsura river	7.9	2.6	3.3	
China				
JJ	0.855	1	0.065	

LJ	0.925	2.3	0.065	
LS	1.25	4	0.065	
YC	13	12	0.065	
XT	5.3	25	0.065	
DG	4.35	94	0.335	
CQ1	33.5	0.37	0.005	
CQ2	25.5	0.15	0.005	
YG1	4.2	0.5	0.0025	
YG2	4.2	0.29	0.0025	So et al. 2007
YG3	5.1	0.705	0.0025	
NJ1	2.05	0.375	0.0025	
NJ2	2.2	0.335	0.0025	
NJ3	2.5	0.36	0.0025	
SH1	24.5	0.655	0.05	
SH2	34	1.75	0.05	
SH3	245	13	0.38	
Brazil				
ETA 1	1.2	1.32	0.21	
P1	0.15	0.17	0.05	
P2	0.04	0.05	0.05	
P3	0.04	0.05	0.05	
P4	1.22	0.64	0.05	Quinete et al.2009
P5	1.13	0.69	0.05	
BV	2.04	0.92	0.18	
VC	3.25	0.4	0.17	
JJ	1.37	0.4	0.13	
Urca beach	0.77	0.57	0.14	
MG	1.4	0.53	0.13	
Canada				
LO-02-1	5.9	6.6	nd	
LO-04-1	6.7	6.8	nd	
LO-04-2	3.3	3.6	nd	
LO-04-3	2.5	6.8	0.7	
LO-04-4	2.3	7.1	nd	
LO-04-5	2	5.4	1.8	
LO-05-1	6.4	37.6	0.5	
LO-05-2	2	3.6	nd	
LO-05-3	1.8	4.8	nd	
LE-04-1	1.6	5.3	nd	Furdui et al. 2008
LE-04-2	2.2	4.2	1.8	
LE-04-3	1.9	4	0.4	
LH-04-1	0.9	2	0.7	
LH-05-1	0.4	1.2	nd	
LH-05-2	1.1	1.2	nd	
LH-05-3	0.4	1.8	0.4	
LS-05-1	0.2	0.3	nd	
LS-05-2	0.5	0.1	nd	
LS-05-3	1.2	0.3	nd	
Pacific Ocean				
Central to Eastern Pacific Ocean	0.062	0.02	0.0016	Yamashita et al, 2005
Western Pacific Ocean	0.142	0.078	0.0028	
North Atlantic Ocean	0.338	0.036	0.0061	
Mid Atlantic Ocean	0.439	0.073	0.012	
Asia				
Vietnam	18	5.3	3.1	Duong et al., 2015
South Africa		14		Fredriksson, 2018

Table 4:Samples provided under UNEP project, detailed location information and the analyzed samples intervals under the current project. The Roman numbers (I, II, III and IV) represented the end of each quarter of the year.

Region	Country name	Site name	Latitude (deg)	Longitude (deg)	Latitude (decimal)	Longitude (decimal)	2018 sample intervals
Africa	Egypt	River Nile					
	Ghana	Volta River					II
	Kenya	Sabaki	03° 09' 41.0 S	40° 07' 50.0 E	-3,161389	40,130556	
	Senegal	River Senegal	15°59'10''N	16°30' 55" W			
	Tunisia	Oued Medjerda	37° 01' 16.6" N	10° 08' 24.2" E	37,02125	10,14083333	II, III and IV
	Zambia	Kafue/Zambezi Confluence	15° 56' 60.2 S	28° 54' 85.6 E	-15,9500556	28,92377778	I, II, III and IV
Asia	Mongolia	Tuul River	47°53'21 N	106°54'37 E			II and III
	Vietnam	River Mekong, Do Quan Bridge	20°23'9.02"N	106° 9'30.82"E	20,385840	106,158559	II and IV
GRULAC	Argentina	Rio de la Plata	34°42'18"S	58°12'51.6"W	-34,705	58,21433	I, II, III and IV
	Brazil	São Vicente channel	23°56´08.4´´S	46°23´28.2"W	-23,9356666	-46,3911667	II and III
		Amazon River	03° 09' 00.3" S	58° 29' 13.6" W	-3,15008333	-58,487111	
	Ecuador	Babahoyo river	02°11' 9.499945'' S	79° 52' 4.00" W	-2,186	-79,8678	I
	Jamaica	Hunts Bay River, Causeway Bridge	17° 59' 0.3804" N	76° 49' 42.8664" W	17,983439	-76,828574	II, III and IV
	Mexico	Ohuira Bay	25°39'24.96" N	109° 2'8.61"O	25,6569333	-109,035725	II, III and IV
Pacific Islands	Fiji	Waimanu River			-18.026698	178.368659	
	Kiribati				173.14612	1.3826333	
	Palau		07°23'09"N	134°33'09"E			
	Samoa	Vaisigano River – Lelata Point			-13.845287	-171.757821	I, II and III
	Solomon Islands		09°26'2.64S	159°58'1.61E	-9.435732	159.967115	II and III
	Tuvalu	Fongafale Islet	08°32.420'S	179°10.318'E			II
	Vanuatu		S	E	17.70538	168.28786	I, II and III

Table 5: Data for LOD, LOQ, accuracy, precision and internal standards for all studied PFASs. Limit of detection and limit of quantification in (ng/L) for all studied PFASs. Accuracy and precision for all PFASs. Accuracy represent average concentrations (n=4, n=7) of native standards in QC samples. Precision represent the relative standard deviation (RSD%) of native standards concentration in QC sample. Internal standards are IS used for quantification of the target compounds.

Compounds	LOD (ng/L)	LOQ (ng/L)	Accuracy %	RSD% (n=7)	Internal standard
TFA	0.62	1.70	33	5 *	^{13}C-PFBA
PFPrA	0.87	2.35	51	20 *	^{13}C-PFBA
PFBA	0.14	0.38	102	5	^{13}C-PFBA
PFPeA	0.12	0.37	104	3	^{13}C-PFPeA
PFHxA	0.06	0.17	101	2	^{13}C-PFHxA
PFHpA	0.07	0.19	100	4	^{13}C-PFHpA
PFOA	0.01	0.20	102	6	^{13}C-PFOA
br-PFOA	0.01	0.02			13C-PFOA
PFNA	0.05	0.13	103	7	^{13}C-PFNA
PFDA	0.05	0.15	107	11	^{13}C-PFDA
PFUnDA	0.04	0.11	105	16	^{13}C-PFUnDA
PFDoDA	0.01	0.02	113	21	^{13}C-PFDoDA
PFTrDA	0.01	0.02	93	19	^{13}C-PFDoDA
PFTDA	0.03	0.08	100	19	^{13}C-PFTDA
PFHxDA	0.06	0.17	111	22*	^{13}C-PFHxDA
PFOcDA	0.07	0.22	53	18*	^{13}C-PFHxDA
PFBS	0.04	0.09	102	5	^{13}C-PFBS
PFPeS	0.03	0.08	103	4*	^{13}C-PFPeS
PFHxS	0.01	0.10	101	5	^{18}O-PFHxS
br- PFHxS	0.01	0.02			^{18}O-PFHxS
PFHpS	0.03	0.09	103	11*	^{13}C-PFOS
PFOS99	0.01	0.34	102	9	^{13}C-PFOS
3/4/5-PFOS80/98.9	0.01	0.01			^{13}C-PFOS
6/2-PFOS169/80	0.01	0.03			^{13}C-PFOS
PFNS	0.01	0.04	101	9*	^{13}C-PFOS
PFDS	0.02	0.06	85	19	^{13}C-PFOS
PFDoDS	n.d	n.d	73	16	^{13}C-PFOS
PFOSA	n.d	n.d			^{13}C-PFOSA
N-MeFOSA	n.d	n.d			^{13}C-MeFOSA
N-EtFOSA	n.d	n.d			^{13}C-MeFOSA
N-MeFOSE	n.d	n.d			^{13}C-MeFOSA
N-EtFOSE	n.d	n.d			^{13}C-MeFOSA
FOSAA	n.d	n.d	106	16*	^{2}H -Et-FOSAA
N-MeFOSAA	n.d	n.d	103	3*	^{2}H -Et-FOSAA
N-EtFOSAA	n.d	n.d	108	9*	^{2}H -Et-FOSAA
4_2_FTSA	0.01	0.02	95	14*	^{13}C-6_2 FTSA
6_2_FTSA	0.04	0.10	103	6	^{13}C-6_2 FTSA
8_2_FTSA	0.01	0.03	112	15*	^{13}C-8_2 FTSA
3_3FTCA195	0.01	0.01	88	14*	^{13}C-6_2 FTUCA
5_3FTCA237	0.01	0.01	90	9*	^{13}C-6_2 FTUCA
5_3FTCA217	n.d	n.d	101	6*	^{13}C-6_2 FTUCA
6_2FTUCA293	0.01	0.01	100	8*	^{13}C-6_2 FTUCA
7_3FTCA317	n.d	n.d			^{13}C-8_2 FTUCA
8_2_FTUCA393	n.d	n.d	106	11*	^{13}C-8_2 FTUCA
10_2_FTUCA493	n.d	n.d	109	20*	^{13}C-10_2 FTUCA
PFEtS	0.07	0.19	103	6*	^{13}C-PFBS

PFPrS	0.01	0.02	109	15*	^{13}C-PFBS
ADONA	0.02	0.05	96	8*	^{18}O-PFHxS
HFPO-DA (GenX)	0.01	0.01	104	1*	^{13}C-HFPO-DA
11ClPF3OUdS99	n.d	n.d	83	12*	^{13}C-PFOS
9ClPF3ONS99	n.d	n.d	99	15*	^{13}C-PFOS
PFECHS381	0.01	n.d	109	9*	^{13}C-PFOA

n.d for not deteced PFASs.

* number of samples equal four.

Table 6: Concentration of PFOS (Linear and branched), PFOA and PFHxS in (ng/L) for samples collected under the UNEP project in year 2017 and 2018.

year			2017 Concentration (ng/L)				2018 Concentration (ng/L)			
Region	Country	Season	L-PFOS	br-PFOS	PFOA	PFHxS	L-PFOS	br-PFOS	PFOA	PFHxS
Africa	Egypt	I	0,12	0.10	0.22	0.02				
		II	0.12	0.16	0.37	0.04				
		III	0.20	0.13	0.38	0.04				
		IV	0.27	0.12	0.75	0.03				
	Ghana	I	0.17	0.05	0.25	0.05	0.01	0.01	0.18	0.02
		II	0.28	0.08	0.19	0.03	0.12	0.06	0.18	0.03
		III	0.77	0.21	0.25	0.06				
		IV	0.13	0.06	0.32	0.04				
	Kenya	I	0.84	0.39	0.48	0.31				
		II	1.04	0.71	2.74	0.96				
		III	0.63	1.03	1.75	1.25				
		IV	0.97	0.60	3.24	1.31				
	Senegal	I	0.07	0.01	0.06	0.01				
		II	0.32	0.04	0.07	0.02				
		III	0.33	0.12	0.17	0.03				
		IV	0.07	0.03	0.04	0.02				
	Tunisia	I	0.31	0.17	0.83	0.07	0.25	0.23	1.18	0.09
		II	0.28	0.22	0.74	0.07	0.20	0.09	0.61	0.10
		III	0.37	0.15	1.00	0.07	0.67	0.10	1.29	0.09
		IV	0.30	0.18	1.06	0.09	0.40	0.21	0.81	0.07
	Zambia	I	0.44	0.11	0.28	0.19	0.07	0.04	0.11	0.04
		II	1.70	0.43	0.18	0.17	0.06	0.04	0.10	0.04
		III	0.36	0.09	0.11	0.02	0.04	0.02	0.10	0.02
		IV	0.07	0.03	0.11	0.01	0.03	0.01	0.08	0.02
Asia	Mongo-lia	I	0.04	0.01	0.07	0.01	0.07	0.03	0.23	0.02
		II	0.30	0.05	0.37	0.02	0.05	0.01	0.07	0.03
		III	0.04	0.01	0.03	0.01	0.02	0.03	0.08	0.03
		IV	0.03	0.01	0.26	0.01				
	Vietnam	II					0.12	0.05	0.11	0.01
		III	0.11	0.03	0.10	0.01				
		IV	0.03	0.01	0.16	0.03	0.04	0.01	0.11	0.04
GRULAC	Argen-tina	I	1.98	0.35	0.96	0.52	2.18	0.81	0.89	0.52
		II	1.48	0.41	0.54	0.38	1.11	0.55	0.53	0.35
		III	1.74	0.91	0.72	0.61	3.35	0.94	1.16	0.71
		IV	2.64	0.93	1.08	0.77	1.69	0.79	0.64	0.52
	Brazil	I	0.26	0.02	0.07	0.01				
		II	0.13	0.03	0.10	0.04	1.22	0.64	0.53	0.45
		III	0.04	0.01	0.04	0.02	2.13	1.16	0.70	0.66
		IV	0.04	0.01	0.12	0.01				
	Ecuador	I	0.12	0.04	0.12	0.04	0.36	0.19	0.14	0.04
		II	0.62	0.14	0.34	0.12				
		III	0.26	0.17	0.24	0.14				
		IV	0.31	0.04	0.21	0.02				
	Jamaica	I	1.14	0.17	0.64	0.21	1.11	0.47	1.08	0.55
		II	1.03	0.34	0.82	0.42	1.37	0.50	0.96	0.16
		III	1.31	0.76	0.69	0.24	0.92	0.43	0.39	0.12
		IV	1.02	0.29	0.69	0.22	0.52	0.37	0.39	0.17

	Mexico	I	0.34	0.06	0.27	0.07	0.18	0.09	0.39	0.05
		II	1.27	0.25	0.30	0.10	0.26	0.13	0.39	0.06
		III	0.27	0.11	0.49	0.07	0.56	0.30	0.37	0.13
		IV	0.29	0.16	1.05	0.06	0.48	0.16	0.32	0.08
Pacific Islands	Fiji	III	0.02	0.01	0.03	0.02				
		IV	0.02	0.02	0.03	0.01				
	Kiribati	I					1.13	0.22	0.10	0.16
		III	1.00	0.55	0.14	1.31				
		IV	0.39	0.10	0.07	0.29				
	Palau	I	0.19	0.02	0.04	0.01	0.01	0.01	0.03	0.02
		II	0.06	0.01	0.02	0.01	0.04	0.01	0.03	0.01
		III	0.01	0.01	0.01	0.01				
		IV	0.01	0.01	0.02	0.01				
	Samoa	II					0.01	0.01	0.03	0.01
		IV	0.08	0.06	0.03	0.01				
	Solomon Islands	I					0.12	0.04	0.05	0.09
		II					0.62	0.29	0.10	0.40
		III	0.05	0.01	0.04	0.04	0.19	0.04	0.09	0.12
		IV	0.10	0.05	0.07	0.07				
	Tuvalu	II					0.02	0.01	0.04	0.01
		IV	0.04	0.01	0.01	0.01				
	Vanuatu	I	2.89	1.50	1.34	2.82	3.37	1.65	0.58	2.17
		II					2.39	1.45	0.67	2.52
		III	1.85	1.36	0.94	2.83	2.78	1.71	0.52	2.16

Table 7: The p-value and degree of freedom results from a variance test (Kruskal-Wallis) for the three priority PFAS for all studied developing countries samples.

Difference between regions	Degree of freedom	p-value
∑PFOS	68	0.217
PFOA	61	0.04831
PFHxS	39	0.3095
Different countries within region		
Asia		
∑PFOS	6	0.5324
PFOA	8	0.265
PFHxS	3	0.4459
GRULAC		
∑PFOS	31	0.3316
PFOA	25	0.3276
PFHxS	25	0.1205
Pacific Islands		
∑PFOS	19	0.2391
PFOA	13	0.2762
PFHxS	14	0.1484

Table 8: Fluoride concentration (ng F/L) of all detected targeted PFASs from LC-MS/MS and UPCC used for the assessment of contribution of target PFASs to EOF.

	Svartan 1	Himmerfjar-den	Alelyckan 1	Alelyckan 2	Svartan 2	Igelsta-viken	Mongolia	Tunisia	Solomon Islands	Argen-tina	Vanuatu	Jamiaca
Compounds	Concentration (ngF/L)											
TFA	0.28	0.07	0.13	0.18	0.44	0.23	0.52	0.12	0.11	0.34	0.06	0.33
PFPrA	0.00	0.00	0.00	0.83	0.76	0.46	0.00	0.00	0.00	0.49	0.00	0.26
PFBA	0.58	0.32	0.41	0.33	0.68	0.46	0.10	1.83	0.10	1.26	0.28	0.53
PFPeA	0.30	0.33	0.35	0.72	0.29	0.56	0.00	0.22	0.05	0.88	1.10	0.38
PFHxA	0.26	0.38	0.41	0.58	0.36	0.63	0.00	0.53	0.07	1.06	0.93	0.25
PFHpA	0.25	0.34	0.51	0.53	0.34	0.66	0.00	6.48	0.04	0.66	0.79	0.17
L-PFOA	0.37	0.41	0.76	0.87	0.36	0.45	0.05	0.71	0.06	0.73	0.34	0.20
br-PFOA	0.07	0.04	0.08	0.06	0.05	0.05	0.01	0.04	0.01	0.07	0.02	0.06
PFNA	0.59	0.18	0.27	0.31	0.15	0.26	0.00	0.00	0.00	0.27	0.06	0.00
PFDA	0.05	0.06	0.06	0.12	0.05	0.05	0.03	0.23	0.03	0.13	0.03	0.04
PFUnDA	0.20	0.02	0.02	0.02	0.02	0.02	0.01	0.03	0.01	0.05	0.02	0.00
PFDoDA	0.00	0.00	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.02	0.00	0.00
PFTrDA	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFTDA	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00
PFHxDA	0.04	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.04
PFOcDA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFBS	0.11	0.15	0.19	0.29	0.16	0.33	0.00	0.44	0.03	0.50	0.13	0.24
PFPeS	0.00	0.06	0.06	0.00	0.00	0.04	0.00	0.00	0.00	0.11	0.19	0.06
L-PFHxS	0.30	0.17	0.22	0.27	0.23	0.24	0.02	0.06	0.06	0.49	1.60	0.16
br- PFHxS	0.08	0.05	0.06	0.06	0.07	0.06	0.01	0.02	0.02	0.13	0.30	0.04
PFHpS	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.11	0.00
L-PFOS99	0.40	0.33	0.46	0.66	0.41	0.34	0.05	0.28	0.11	2.16	1.44	0.42
br-PFOS	0.05	0.07	0.08	0.07	0.04	0.06	0.00	0.01	0.01	0.20	0.24	0.04
PFNS	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
PFDS	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
PFDoDS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFOSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N-MeFOSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N-EtFOSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N-MeFOSE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N-EtFOSE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FOSAA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00

N-MeFOSAA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00
N-EtFOSAA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00
4_2_FTSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01
6_2_FTSA	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.02	0.00	0.90	0.47	0.11
8_2_FTSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.11	0.01	0.00
PFEtS	0.03	0.02	0.02	0.03	0.03	0.03	0.06	0.04	0.03	0.03	0.03	0.02
PFPrS	0.02	0.02	0.01	0.03	0.00	0.04	0.02	0.01	0.00	0.04	0.03	0.04
ADONA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HFPO-DA (GenX)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11ClPF3OUdS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9ClPF3ONS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PFECHS381	0.00	0.08	0.01	0.02	0.00	0.05	0.00	0.00	0.00	0.05	0.00	0.00

Table 9: Extractable organofluorine concentration (ng F/L) for all studied samples before and after correction for the blank concentrations.

Sample	Concentration (ng F/L) before blank correction	Concentration (ng F/L) after blank correction
Svartån 1	141.4	114.3
Himmerfjärden MH-17-027:6	65.2	38.1
Alelyckan 1	74.6	47.5
Alelyckan 2	41.2	23.1
Svartån 2	45.2	27.1
Igelstaviken 170720	24.0	5.9
Mangolia (2018-II)	69.9	36.1
Tunisia (2018-III)	117.9	84.1
Solomn Islands (2018-III)	46.4	12.6
Argentina (2018-III)	100.6	66.8
Vanuatu (2018-III)	347.3	279.7
Jamaica (2018-II)	37.7	19.6

*Blank concentrations were higher than samples concentrations.

Table 10: All studied PFASs concentrations (ng/L) along Swedish samples (n=6) and developing countries samples (n=6).

	Svartan 1	Himmer-fjarden	Alelyckan 1	Alelyckan 2	Svartan 2	Igelsta-viken	Mongolia	Tunisia	Solomon Islands	Argen-tina	Vanuatu	Jamaica
Compounds	Concentration (ng/L)											
TFA	1.20	0.20	0.37	0.54	1.86	1.21	1.15	1.87	1.49	0.97	0.54	<0.01
PFPrA	0.40	<0.01	0.17	1.70	2.03	1.37	0.86	<0.01	1.31	0.36	0.03	0.03
PFBA	1.69	1.35	1.00	0.93	1.57	1.57	0.18	3.49	0.19	2.85	0.67	0.85
PFPeA	0.43	0.60	0.56	0.66	0.56	1.20	<0.01	0.44	0.07	1.39	1.47	0.60
PFHxA	0.39	0.71	0.87	0.76	0.60	1.16	0.06	0.73	0.08	1.37	1.34	0.90
PFHpA	0.34	0.63	0.68	0.72	0.60	1.26	<0.01	1.14	0.05	0.84	1.06	0.60
PFOA	0.67	0.94	1.26	1.27	0.59	0.85	0.07	1.29	0.09	1.16	0.67	0.96
br-PFOA	0.09	0.08	0.11	0.08	0.07	0.07	0.01	0.08	0.01	0.11	0.02	0.14
PFNA	0.79	0.38	0.38	0.43	0.23	0.45	0.03	0.78	0.02	0.36	0.10	0.12
PFDA	0.11	0.14	0.12	0.15	0.08	0.09	0.04	0.38	0.04	0.16	0.08	0.08
PFUnDA	0.25	0.03	0.03	0.04	0.04	0.03	0.02	0.04	0.02	0.07	<0.01	0.02
PFDoDA	<0.01	<0.01	<0.01	<0.01	0.03	0.02	<0.01	<0.01	<0.01	0.03	<0.01	<0.01
PFTrDA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFTDA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFHxDA	0.04	<0.01	0.04	0.05	0.05	0.05	0.06	0.06	0.06	0.04	0.05	0.05
PFOcDA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFBS	0.17	0.29	0.31	0.41	0.32	0.70	<0.01	0.34	0.07	0.76	0.23	0.55
PFPeS	<0.01	0.11	0.07	<0.01	<0.01	0.16	<0.01	<0.01	<0.01	0.14	0.33	0.16
PFHxS	0.35	0.28	0.30	0.38	0.36	0.48	0.03	0.09	0.12	0.71	2.52	0.38
br- PFHxS	0.12	0.10	0.09	0.08	0.10	0.13	<0.01	0.05	0.04	0.19	0.47	0.12
PFHpS	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.09	0.18	<0.01
PFOS99	0.56	0.70	0.78	0.96	0.72	0.69	0.05	0.67	0.19	3.35	2.39	1.37
br-PFOS	0.23	0.37	0.38	0.33	0.13	0.25	0.01	0.10	0.04	0.94	1.45	0.50
PFNS	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFDS	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFDoDS	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
FOSAA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
N-MeFOSAA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	<0.01	<0.01
N-EtFOSAA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	<0.01	1.51
4_2_FTSA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.04	<0.01
6_2_FTSA	<0.01	<0.01	<0.01	<0.01	0.03	0.11	<0.01	0.05	<0.01	1.73	0.47	0.72

8_2_FTSA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.14	<0.01	<0.01
6_2FTUCA	0.04	0.04	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFEtS	0.05	0.03	0.06	0.06	0.06	0.06	0.11	0.20	0.09	0.05	0.05	0.19
PFPrS	0.04	0.04	<0.01	0.05	<0.01	0.07	0.02	0.23	<0.01	0.08	0.08	<0.01
ADONA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
HFPO-DA (GenX)	0.05	0.06	0.03	0.04	0.05	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
11ClPF3OUdS	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
9ClPF3ONS	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
PFECHS	<0.01	0.14	0.02	0.03	<0.01	0.10	<0.01	<0.01	<0.01	0.07	<0.01	<0.01

<0,01 is below limit of detection for all PFASs which were not detected.

Table 11: All studied target polyfluorinated alkylated substances with chemical abbreviation.

Per- and polyfluoroalkyl substances (PFASs)			
Abbreviation	**Name**	**Abbreviation**	**Name**
FTSAs	**Fluorotelomer sulfonic acids**	**PAPs**	**Polyfluoroalkyl phosphate esters**
4:2 FTSA	4:2 fluorotelomer sulfonic acid	SAmPAP	Perfluorooctane sulfonamide phosphate ester
6:2 FTSA	6:2 fluorotelomer sulfonic acid	diSAmPAP	Perfluorooctane sulfonamide phosphate diester
8:2 FTSA	8:2 fluorotelomer sulfonic acid	6:2 monoPAP	6:2 polyfluoroalkyl phosphate monoester
FTCAs	**Fluorotelomer carboxylic acids**	8:2 monoPAP	8:2 polyfluoroalkyl phosphate monoester
3:3 FTCA	3:3 fluorotelomer carboxylic acid	10:2 monoPAP	10:2 polyfluoroalkyl phosphate monoester
5:3 FTCA	5:3 fluorotelomer carboxylic acid	4:2 diPAP	4:2 polyfluoroalkyl phosphate diester
7:3 FTCA	7:3 fluorotelomer carboxylic acid	4:2/6:2 diPAPs	4:2/6:2 polyfluoroalkyl phosphate diester
FTUCAs	**Fluorotelomer unsaturated carboxylic acids**	2:2/8:2 diPAPs	2:2/8:2 polyfluoroalkyl phosphate diester
6:2 FTUCA	6:2 fluorotelomer unsaturated acid	6:2 diPAP	6:2 polyfluoroalkyl phosphate diester
8:2 FTUCA	8:2 fluorotelomer unsaturated acid	4:2/8:2 diPAP	4:2/8:2 polyfluoroalkyl phosphate diester
10:2 FTUCA	10:2 fluorotelomer unsaturated acid	2:2/10:2 diPAP	2:2/10:2 polyfluoroalkyl phosphate diester
PFCAs	**Perfluoroalkyl carboxylates**	8:2 diPAP	8:2 polyfluoroalkyl phosphate diester
TFA	Trifluoroacetic acid	6:2/10:2 diPAP	6:2/10:2 polyfluoroalkyl phosphate diester
PFPrA	Perfluoropropanoic acid	4:2/12:2 diPAP	4:2/12:2 polyfluoroalkyl phosphate diester
PFBA	Perfluorobutanoic acid	6:2/8:2 diPAP	6:2/8:2 polyfluoroalkyl phosphate diester
PFPeA	Perfluoropentanoic acid	4:2/10:2 diPAP	4:2/10:2 polyfluoroalkyl phosphate diester
PFHxA	Perfluorohexanoic acid	8:2/10:2 diPAP	8:2/10:2 polyfluoroalkyl phosphate diester
PFHpA	Perfluoroheptanoic acid	6:2/12:2 diPAP	6:2/12:2 polyfluoroalkyl phosphate diester
L-PFOA	Linear perfluorooctanoic acid	10:2 diPAP	10:2 polyfluoroalkyl phosphate diester
PFNA	Perfluorononanoic acid	8:2/12:2 diPAP	8:2/12:2 polyfluoroalkyl phosphate diester
PFDA	Perfluorodecanoic acid	6:2/14:2 diPAP	6:2/14:2 polyfluoroalkyl phosphate diester
PFUnDA	Perfluoroundecanoic acid	10:2/12:2 diPAP	10:2/12:2 polyfluoroalkyl phosphate diester
PFDoDA	Perfluorododecanoic acid	8:2/14:2 diPAP	8:2/14:2 polyfluoroalkyl phosphate diester
PFTrDA	Perfluorotridecanoic	12:2 diPAP	12:2 polyfluoroalkyl phosphate diester
PFTDA	Perfluorotetradecanoic acid	10:2/14:2 diPAP	10:2/14:2 polyfluoroalkyl phosphate diester
PFHxDA	Perfluorohexadecanoic acid	8:2/16:2 diPAP	8:2/6:2 polyfluoroalkyl phosphate diester
PFOcDA	Perfluorooctadecanoic acid	**PFSAs**	**Perfluoroalkyl sulfonates**
PFPAs	**Perfluoroalkyl phosphonic acids**	PFEtS	Perfluoroethane sulfonic acid
PFHxPA	Perfluorohexanephosphonic acid	PFPrS	Perfluoropropane sulfonic acid
PFOPA	Perfluorooctanephosphonic acid	PFBS	Perfluorobutane sulfonic acid
PFDPA	Perfluorodecanephosphonic acid	PFPeS	Perfluoropentane sulfonic acid
PFPiAs	Perfluoroalkyl phosphinic acids	L-PFHxS	Linear perfluorohexane sulfonic acid
6:6 PFPiA	6:6 phosphinic acid	br-PFHxS	Branched perfluorohexane sulfonic acid
6:8 PFPiA	6:8 phosphinic acid	PFHpS	Perfluoroheptanesulfonic acid
8:8 PFPiA	8:8 phosphinic acid	L-PFOS	Linear perfluorooctane sulfonic acid
FOSAs	**Perfluoroalkane sulfonamides**	br-PFOS	Branched perfluorooctane sulfonic acid
FOSA	Perfluorooctanesulfonamide	∑PFOS	Sum of linear and branched PFOS
FOSAAs	**Perfluorooctanesulfonamidoacetic acids**	PFNS	Perfluorononane sulfonic acid
FOSAA	Perfluorooctane sulfonamidoacetic acid	PFDS	Perfluorodecane sulfonic acid
MeFOSAA	N-methylperfluorooctanesulfonamido-acetic acid	PFDoDS	Perfluorododecane sulfonic acid
EtFOSAA	N-ethylperfluorooctanesulfonamidoacetic acid	**Novel PFASs**	
		ADONA	3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid]

		HFPO-DA	Perfluoro-2-propoxypropanoic acid (GenX)
		11ClPF3OUdS	Chlorinated polyfluorinated ether sulfonate (F-53B)
		9ClPF3ONS	Chlorinated polyfluorinated ether sulfonate (F-53B)
		PFECHS	Perfluoro-4-ethylcyclohexane sulfonate