

Ultra-short-chain perfluoroalkyl acids:
Environmental occurrence, sources and distribution

You can do anything you set your mind to, man

Eminem

Örebro Studies in Chemistry 29



MARIA K. BJÖRNSDOTTER

**Ultra-short-chain perfluoroalkyl acids:
Environmental occurrence, sources and distribution**

© Maria K. Björnsdotter, 2021

Title: Ultra-short-chain perfluoroalkyl acids: Environmental occurrence, sources
and distribution

Publisher: Örebro University 2021
www.oru.se/publikationer

Print: Örebro University, Repro 08/2021

ISSN 1651-4270
ISBN 978-91-7529-399-8

Abstract

Maria K. Björnsdotter (2021): Ultra-short-chain perfluoroalkyl acids: Environmental occurrence, sources and distribution. Örebro Studies in Chemistry 29.

Ultra-short-chain perfluoroalkyl acids (PFAAs) is a group of highly fluorinated and very stable chemicals. Their small molecular structure in combination with the acidic functional group result in highly polar compounds and concern has been raised as these substances may threaten our drinking water supplies.

The aim with this thesis was to study and assess the occurrence, sources, and distribution of ultra-short-chain PFAAs in the environment. The main objectives were to analyze ultra-short-chain PFAAs in surface water with different anthropogenic impact, in atmospheric deposition and surface snow at local and remote locations, and to examine the relevance of local and diffuse input pathways to Lake Vättern, Sweden.

The results revealed that ultra-short-chain PFAAs are released to the environment from various sources such as firefighting training sites, landfills, and hazardous waste management facilities. Trifluoroacetic acid (TFA) and perfluoropropanoic acid (PFPrA) were detected in all atmospheric deposition samples and surface snow samples, including those collected at remote sites in the Arctic. Atmospheric oxidation of volatile precursors was found to play a major role in the global distribution of these as well as being the main input pathway to Lake Vättern. A total annual flux of 120–170 kg and 1.3–2.0 kg was observed for TFA and PFPrA, respectively.

Trifluoromethane sulfonic acid (TFMS) was detected in most samples and was reported for the first time in atmospheric deposition and surface snow at local as well as remote locations. The discovery of TFMS at remote locations suggests that TFMS is globally distributed. Neither atmospheric degradation of volatile precursors, nor the long-range oceanic transport seem to be main sources of TFMS to the Arctic environment, and local sources seem to be of higher importance for TFMS input to Lake Vättern.

Keywords: PFASs, TFA, TFMS, point sources, precursors, solar radiation, atmospheric oxidation, atmospheric deposition, flux, Arctic

Maria K. Björnsdotter, School of Science and Technology
Örebro University, SE-701 82 Örebro, Sweden,
m.k.bjornsdotter@gmail.com

Sammanfattning

Perfluorerade alkylsyror (PFAAs) är en grupp högfluorerade och väldigt stabila kemikalier. Ultrakorta PFAAs är små och polära, vilket gör att de kan ansamlas i vattentäkter och kontaminera dricksvatten.

Syftet med denna avhandling var att studera ultrakorta PFAAs med avseende på deras förekomst i miljön, vilka deras kontamineringskällor är samt hur de sprids. Huvudmålen var att analysera ultrakorta PFAAs i ytvatten med olika typer av mänsklig påverkan, i nederbörd och nysnö, både på lokala och avlägsna platser, samt att undersöka betydelsen av lokala och diffusa kontamineringskällor till Vättern.

Resultaten visade att det finns många olika kontamineringskällor från vilka ultrakorta PFAAs släpps ut i miljön, till exempel brandövningsplatser, deponier och anläggningar för hantering av farligt avfall. Trifluorättisyra (TFA) och perfluorpropansyra (PFPrA) hittades också i samtliga prover på nederbörd och nysnö, även i de prover som tagits på avlägsna platser på ön Spetsbergen i Arktis. Resultaten i studien visade att oxidation av luftburna föregångarämnen i atmosfären, en process som är beroende av solljus, spelar en stor roll för förekomsten av TFA och PFPrA i miljön, och förklarar varför dessa kemikalier hittas på avlägsna platser där inga kända lokala kontamineringskällor finns. Det visade sig även att denna process har en stor betydelse för kontamineringen i Vättern. Under ett år hamnar 120–170 kg TFA och 1,3–2,0 kg PFPrA i Vättern via nederbörd och tillrinnande vattendrag, och en stor del av detta tros komma från oxidation av luftburna föregångarämnen i atmosfären.

Trifluormetansulfonsyra (TFMS) återfanns i nästan alla prover och upptäcktes i nederbörd och nysnö för första gången, både på lokala och avlägsna platser. Denna upptäckt tyder på en global spridning även för TFMS, men varken oxidation av luftburna föregångarämnen eller långväga transport med havsvattenströmmar verkar ha en betydande roll för förekomsten av TFMS i Arktis och lokala källor har en större betydelse än diffusa källor för kontamineringen i Vättern.

List of papers

This thesis is based on the following papers, which hereafter will be referred to by their Roman numerals.

Paper I:

Björnsdotter M. K., Yeung L. W. Y., Kärrman A., Ericson Jogsten I., 2020. Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health. *Analytical and Bioanalytical Chemistry*, 412, 4785–4796.

Paper II:

Björnsdotter M. K., Yeung L. W. Y., Kärrman A., Ericson Jogsten I., 2019. Ultra-Short-Chain Perfluoroalkyl Acids Including Trifluoromethane Sulfonic Acid in Water Connected to Known and Suspected Point Sources in Sweden. *Environmental Science and Technology*, 53 (19), 11093–11101.

Paper III:

Björnsdotter M. K., Hartz W. F., Kallenborn R, Ericson Jogsten I., Humby J. D., Kärrman A., Yeung L. W. Y. Levels and seasonal trends of C₁-C₄ perfluoroalkyl acids and the discovery of trifluoromethane sulfonic acid in surface snow in the Arctic. Submitted to *Environmental Science and Technology*, July 16, 2021.

Paper IV:

Björnsdotter M. K., Yeung L. W. Y., Kärrman A., Ericson Jogsten I. Mass balance of perfluoroalkyl acids including trifluoroacetic acid in a freshwater lake. Submitted to *Environmental Science and Technology*, July 5, 2021.

Papers II–IV have been reprinted with permission from American Chemical Society.

Papers not included in this thesis:

Marios Stylianou, Maria K. Björnsdotter, Per-Erik Olsson, Ingrid Ericson Jogsten, Jana Jass. Distinct transcriptional response of *Caenorhabditis elegans* to different exposure routes of perfluorooctane sulfonic acid. *Environmental Research*, 168, 406–413, 2019.

List of abbreviations

Abbreviation	Name
AFFF	Aqueous film forming foam
API	Atmospheric pressure ionization
CFC	Chlorofluorocarbon
DF	Detection frequency
ESI	Electrospray ionization
FFTS	Fire-fighting training site
FTOH	Fluorotelomer alcohol
GC	Gas chromatography
GDAS	Global Data Assimilation System
HBE	High-bound estimate
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HFC-134a	1,1,1,2-tetrafluoroethane
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane
HFO	Hydrofluoroolefin
HFO-1234yf	2,2,2,3-tetrafluoropropene
HILIC	Hydrophilic interaction liquid chromatography
HWMF	Hazardous waste management facility
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
KHO	Kjell Henriksen Observatory
LBE	Low-bound estimate
LF	Landfill
MMLC	Mixed-mode liquid chromatography
MS/MS	Tandem mass spectrometry
n.d.	Not detected
NA	Not available
N-EtFBSA	<i>N</i> -ethyl perfluorobutane sulfonamide
N-MeFBSA	<i>N</i> -methyl perfluorobutane sulfonamidoethanol
PBT	Persistent, bioaccumulative, and toxic
PFA	Perfluoroalkoxy alkane

PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substance
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCA	Perfluoroalkyl carboxylic acid
PFEtS	Perfluoroethane sulfonic acid
PFMP	Perfluoro-2-methyl-3-pentanone
PFPrA	Perfluoropropanoic acid
PFPrS	Perfluoropropane sulfonic acid
PFSA	Perfluoroalkyl sulfonic acid
PTFE	Polytetrafluoroethylene
QC	Quality control
RPLC	Reversed phase liquid chromatography
SFC	Supercritical fluid chromatography
STP	Sewage treatment plant
TFA	Trifluoroacetic acid
TFMS	Trifluoromethane sulfonic acid
TfOH	Triflic acid
WAX-SPE	Weak anion exchange solid-phase extraction

Table of Contents

1.	INTRODUCTION.....	9
1.1.	Ultra-short-chain PFAAs	10
1.1.1.	Sources of ultra-short-chain PFCAs	11
1.1.2.	Sources of ultra-short-chain PFSAs	12
1.2.	Environmental fate	13
1.3.	Human health and environmental concerns	14
1.4.	Analytical challenges	15
2.	AIM AND OBJECTIVES	17
3.	METHODS.....	18
3.1.	Sampling sites	18
3.1.1.	Screening for potential point sources	18
3.1.2.	Seasonal variation, sources and distribution in the Arctic ..	19
3.1.3.	Mass balance in Lake Vättern	20
3.2.	Sample collection.....	24
3.3.	Sample preparation and instrumental analysis.....	25
3.3.1.	Sample extraction for analysis of ultra-short-chain PFAAs.	25
3.3.2.	Analysis of ultra-short-chain PFAAs.....	26
3.3.3.	Analysis of sodium and chloride ions in surface snow	27
3.4.	Quality assurance and quality control	27
3.5.	Mass balance calculations	28
3.5.1.	Input pathways.....	28
3.5.2.	Output pathway	29
3.5.3.	Inventory in the water basin	29
3.6.	Air mass trajectories and solar radiation in the Arctic	29
3.7.	Statistical analysis.....	30
4.	RESULTS AND DISCUSSION.....	31
4.1.	Analytical challenges	31
4.1.1.	Blank contamination	31
4.1.2.	Analysis of TFA without mass-labelled standard.....	32
4.1.2.1.	<i>Extraction efficiency</i>	32
4.1.2.2.	<i>Direct injection analysis</i>	33
4.1.3.	Analysis of TFA with mass-labelled standard	35
4.2.	Environmental occurrence of ultra-short-chain PFAAs.....	36
4.2.1.	Ultra-short-chain PFAAs in precipitation	36
4.2.1.1.	<i>Seasonal trends of TFA and PFPrA in precipitation</i>	37

4.2.1.2.	<i>Discovery of TFMS in precipitation</i>	40
4.2.2.	Potential point sources of ultra-short-chain PFAAs	41
4.2.2.1.	<i>Firefighting training sites</i>	42
4.2.2.2.	<i>Landfills</i>	43
4.2.2.3.	<i>Hazardous waste management facility</i>	43
4.3.	Mass balance of Lake Vättern	44
4.3.1.	Input of ultra-short-chain PFAAs to Lake Vättern.....	45
4.3.1.1.	<i>Input of TFA and PFPrA to Lake Vättern</i>	47
4.3.1.2.	<i>Input of TFMS, PFEtS, and PFPrS to Lake Vättern</i>	48
5.	CONCLUSIONS	50
6.	FUTURE PERSPECTIVE	52
7.	ACKNOWLEDGEMENTS	53
	REFERENCES	57

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) is a group of anthropogenic compounds that are ubiquitously found in the environment. Common applications using PFASs include surface-repellent coatings (e.g., food contact material, outdoor clothing, camping equipment, and cooking equipment) and surfactants (e.g., firefighting foams and mist suppressants).¹ PFASs comprise a large and diverse group of substances and are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom.² Aliphatic, fully fluorinated PFASs with an acid functional group are referred to as perfluoroalkyl acids (PFAAs) and they are commonly referred to as protonated acids despite that many are strong acids and dissociated in environmental matrices.³ PFAAs, including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), occupy most of the published research on PFASs due to the concerns being raised partly because of their high environmental persistence and toxic effects. In this thesis, PFAAs will hereby refer to PFCAs and PFSAs.

PFAAs have been divided into short- and long-chain compounds depending on the length of their carbon backbone. Long-chain PFCAs and PFSAs are defined as those containing at least eight and six carbon atoms or more, respectively.² The term ultra-short-chain PFAAs have been used to describe PFCAs and PFSAs with a chain length of 2–3 and 1–3 carbon atoms, respectively. The length of the carbon backbone of PFAAs not only determines their potential for bioaccumulation, but also their water solubility and mobility in the environment, and thereby their environmental fate. After being introduced to the environment from a contamination source, long-chain PFAAs may be retained by soil and sediment by hydrophobic interactions,⁴ while more polar substances, such as ultra-short-chain PFAAs, can be transported long distances from the source.⁵

In the past, environmental research has mainly focused on long-chain PFAAs due to their potential to bioaccumulate. A common criterion used in risk assessment of environmental contaminants is that a substance should be persistent, bioaccumulative, and toxic (PBT). It has recently been suggested that persistence alone should be a sufficient basis for regulation of potentially harmful substances as the effect of contamination by a persistent substance is poorly reversible and it might be challenging and costly to reverse the contamination once an adverse effect is identified.⁶ Concern has been raised on persistent and mobile substances, including

ultra-short-chain PFAAs, as these have a potential to contaminate drinking water supplies.⁷

Access to safe drinking water is of high importance for human health. One of the Sustainable Development Goals set by the European Commission aims to ensure availability and sustainable management of water and sanitation for all by 2030. In January 2021, the revised version of the Drinking Water Directive of the European Parliament on the quality of water intended for human consumption entered into force (Directive (EU) 2020/2184). The directive requires that member states should take the necessary measures to ensure that water intended for human consumption is free from any substances that constitute a potential danger to human health. The directive also states that necessary measures should be taken to reduce the level of purification treatment required in the production of water that is aimed for human consumption. To meet this goal, there is an urgent need of identifying substances that may accumulate in drinking water supplies and pose a risk to human health, and to subsequently reduce the contamination with these.

1.1. Ultra-short-chain PFAAs

Ultra-short-chain PFAAs include trifluoroacetic acid (TFA), perfluoropropanoic acid (PFPrA), trifluoromethane sulfonic acid (TFMS), perfluoroethane sulfonic acid (PFEtS), and perfluoropropane sulfonic acid (PFPrS). The mutual properties of these substances are their high polarity and persistence to degradation. The polarity is a result of a short perfluorinated backbone and an acidic functional group with pKa values below 1.4, meaning that all molecules will be charged at environmental pH values.

Ultra-short-chain PFAAs have recently gained attention, partly due to their persistence to degradation and expected accumulation in aquatic environments, but also because they are more frequently reported in the environment^{5, 8-12} after recent advances in analytical techniques for the analysis of highly polar substances.^{13, 14}

TFA occupy most of the published data on ultra-short-chain PFAAs. Up to date, data presenting the environmental occurrence and levels of ultra-short-chain PFAAs other than TFA are scarce, and little is known about their sources and environmental distribution.

1.1.1. Sources of ultra-short-chain PFCAs

Ultra-short-chain PFCAs include TFA and PFPrA. They consist of a carboxylic acid attached to one and two fully fluorinated carbons, respectively (Figure 1). The environmental distribution of TFA has been studied and documented since the 1990s. The increased attention was a result of the implementation of the Montreal protocol in 1989, which aimed at phasing out ozone depleting chlorofluorocarbons (CFCs) used as refrigerants and blowing agents. CFCs were replaced with hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), which degrade in the troposphere to form TFA. The introduction of HFCs and HCFCs as replacements to CFCs was motivated by the fact that these do not result in ozone depletion and have a lower global warming potential compared to those of CFCs. By that time, the toxicity and health impacts of oxidation products from HFCs and HCFCs, including TFA, were not considered to be of significance.¹⁵

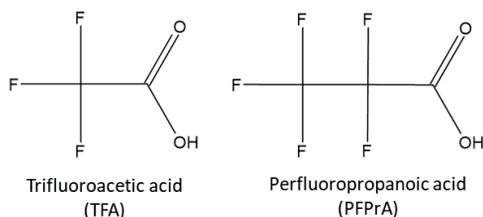


Figure 1. Chemical structures of TFA and PFPrA.

The atmospheric degradation of HFCs and HCFCs were initially considered as the only major source of TFA to the environment, but measurement of TFA, mainly in precipitation and surface waters, has indicated that additional sources exist.¹⁶ Various other sources have been identified, and natural sources have been investigated. TFA has been reported at evenly distributed concentrations in ocean water (150–200 ng/L), even at depths that represent pre-industrial water,^{17, 18} and deep-sea vents have been suggested as possible natural sources of TFA.¹⁸

TFA is formed by thermolysis of fluoropolymers^{19, 20} and by atmospheric oxidation of precursor compounds such as *n*:2 fluorotelomer alcohols (FTOHs),²¹ *N*-ethyl perfluorobutane sulfonamide (N-EtFBSE),²² and *N*-methyl perfluorobutane sulfonamidoethanol (N-MeFBSE).²³ TFA has been widely reported in precipitation,^{10, 16, 24-33} and seem to be ubiquitous in

precipitation even at very remote sites.^{26, 27} A recent study on Arctic ice cores shows an increased deposition of TFA since 1990.³⁴

The environmental occurrence of PFPrA has not been as well documented as for TFA. Similar sources and fate may be expected due to the structural similarities of these two compounds with PFPrA containing an additional CF₂-compartment between the trifluoromethyl moiety and the carboxylic group, compared to TFA. Similarly, formation of PFPrA can occur via oxidation of precursor compounds such as HFCs and HCFCs³⁵ as well as n:2 FTOHs,²¹ N-EtFBSA,²² and N-MeFBSE.²³ PFPrA has been reported in atmospheric precipitation worldwide³⁶ and was recently reported in Arctic ice cores.³⁴ In the same way as for TFA, an increase of PFPrA in the Arctic ice core since 1990 was observed, suggesting that CFC replacements play an important role in the deposition of PFPrA.

While the described atmospheric sources result in diffuse contamination, local contamination in surface waters as a result of discharge from point sources has also been observed. Releases from industries have been identified as potentially relevant point sources of TFA²⁵ and PFPrA⁸ and elevated concentrations of TFA were recently measured in surface water downstream a chemical industry.⁵ TFA has been identified as a main metabolite of pesticides containing a trifluoromethylphenyl structure.^{37, 38} The number of potential precursor compounds that can degrade into TFA and PFPrA in the environment may be large. TFA has been recognized as a substance of multiple sources, but there are still many sources that are not yet known and the relevance between them needs to be further assessed to establish appropriate countermeasures for the environmental contamination.

1.1.2. Sources of ultra-short-chain PFSA

Ultra-short-chain PFSA include TFMS, PFEtS, and PFPrS. They consist of a sulfonic acid attached to one, two, and three fully fluorinated carbons, respectively (Figure 2). Ultra-short-chain PFSA differs from PFCAs because they are used in different applications and thus, their sources and fate are different.

TFMS was recently reported in the environment for the first time.¹¹ There is no data available about potential sources of TFMS to the environment. TFMS, also known as triflic acid (TfOH), is a superacid widely used in organic synthesis.³⁹ The lithium salt of TFMS is commonly used in lithium-ion batteries.⁴⁰

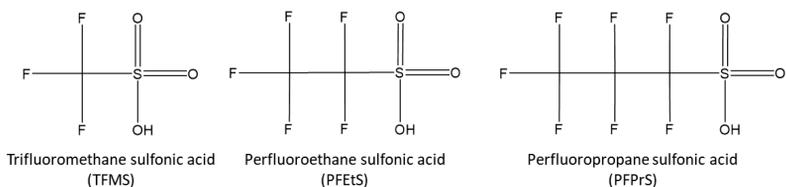


Figure 2. Chemical structures of TFMS, PFEtS, and PFPrS.

PFEtS and PFPrS have been reported in municipal and industrial wastewater.⁸ They were recently reported at concentrations up to 13 mg/L and 270 mg/L, respectively, in aqueous film forming foams (AFFFs) and at concentrations up to 75 µg/L and 63 µg/L, respectively, in groundwater connected to military training sites where AFFFs have been used for fire-fighting training purposes.⁹ This suggests that they are present as byproducts and/or a degradation products of other compounds used in AFFF formulas.

There is no evidence on formation of ultra-short-chain PFSAs from precursor compounds. One study has investigated the formation of the C₄ PFSAs, perfluorobutane sulfonic acid (PFBS), from the atmospheric degradation of N-MeFBSE²³ but there are no available data about the formation of TFMS, PFEtS, or PFPrS from volatile precursors. The potential sources and the environmental fate and distribution of these substances are not yet well understood. However, with respect to their high polarity and high persistence, contamination in water may be expected after release to the environment.

1.2. Environmental fate

Atmospheric deposition of TFA and PFPrA, from the degradation of HFCs and HCFCs as well as other volatile precursors, result in diffuse contamination globally. The distribution depends on the atmospheric lifetime of the precursor compound. TFA and PFPrA are formed by hydrolysis of intermediate degradation products after being incorporated into water droplets and are then deposited with precipitation. Atmospheric deposition, along with surface water inflow, was found to be an important pathway for short- and long-chain PFCAs to the Baltic Sea.⁴¹ The same formation of ultra-short-chain PFSAs from volatile precursors has not been documented and little is known about their spatial distribution. As

discussed, most of the available information only concern TFA and far too little attention has been paid to other ultra-short-chain PFAAs.

The high persistence and polarity of ultra-short-chain PFAAs is of concern because they can be transported in the environment and accumulate in aquatic systems.^{24, 25, 42} Once they are released into the environment, ultra-short-chain PFAAs can be transported long distances from their source and may contaminate drinking water. TFMS has been reported in surface water and groundwater far from primary environmental emission points.¹² TFA was discovered in a German river which led to high concentrations in drinking water even at large distances (300 km) from the identified point source.⁵ The same study also showed that TFA is not removed from drinking water by currently used purifying techniques. Removal of ultra-short-chain PFAAs from drinking water will likely be a challenging and costly project, since the removal rate of persistent and mobile substances from water is poor even with advanced technologies.⁴³

TFA is poorly retained by most soils. However, some soils, e.g. soils with high organic content, or mineral soils, may exhibit strong retention of TFA and the retention depends on the soil type, organic content, pH, and inputs of competing anions.^{44, 45} TFA and PFPrA can accumulate in plants^{42, 44, 46, 47} and a recent study discovered high concentrations of TFA in plant-based beverages.⁴⁸

While PFAAs with a longer carbon backbone might be retained by soil after being deposited over land, ultra-short-chain PFAAs are mobile and can be transported long distances in the aquatic system, depending on the properties and nature of the catchment area and soil composition and content. This means that the size of the catchment area might be an important factor for the contamination with ultra-short-chain PFAAs in a water body, compared to short- and long-chain PFASs, which are to a greater extent retained in the soil compared to ultra-short-chain PFAAs.

1.3. Human health and environmental concerns

The toxicity of TFA has been evaluated in algae, higher plants, fish, animals, and humans and was considered very low.⁴⁹ The lowest threshold level for one strain of algae was 0.12 mg/L and levels below 0.1 mg/L has been considered safe for aquatic organisms.⁵⁰ Little is known about the toxicity of ultra-short-chain PFAAs other than TFA and more research is needed in order to assess the potential hazards for humans and the environment. Due to the high polarity of these substances, the potential for bioaccumulation is low. However, the high persistence of these substances

will result in environmental accumulation, especially in aquatic environments. This makes them a potential threat to our drinking water. In addition to exposure via drinking water, plant-based beverages have been suggested to contribute with a considerable share of the total intake of TFA.⁴⁸ Very little is currently known about human exposure to ultra-short-chain PFAAs and only a recent study has reported TFA in human blood.⁵¹

The concentration of TFA in the environment, resulting from the atmospheric degradation of HFCs and HCFCs, has been considered to pose no risk for humans and the environment.⁴⁹ Reported concentrations of TFA in surface waters are usually below 500 ng/L,^{16, 24-26, 29, 52} yet concentrations up to 0.14 mg/L has been reported downstream a chemical industry.⁵

Environmental levels of TFA are expected to increase in the future as a result of the Kiagali amendment to the Montreal Protocol, which aims at protecting the climate by phasing out the use of HFCs. HFCs are not ozone depleting chemicals but they are greenhouse gases. HFCs are now being replaced with hydrofluoroolefins (HFOs) and a suggested replacement to HFC-134a (1,1,1,2-tetrafluoroethane), a common cooling agent used in automobile air conditioners, is HFO-1234yf (2,2,2,3-tetrafluoropropene). The shift to HFO-1234yf is motivated by the lower global warming potential of HFO-1234yf, because of the shorter atmospheric lifetime, compared to HFC-134a. The atmospheric lifetime of HFO-1234yf, with respect to reaction with hydroxyl radicals, is ~12 days,⁵³⁻⁵⁵ which is considerably shorter than the atmospheric lifetime of HFC-134a of ~14 years.⁵⁶ The concentrations of TFA in air and atmospheric deposition have been estimated to increase in the future, and become more localized,⁵⁷⁻⁵⁹ as a result of the shorter atmospheric lifetime of HFO-1234yf in combination with a higher conversion rate to TFA (~91%)⁵⁴ compared to HFC-134a (7–20%).⁶⁰

1.4. Analytical challenges

Data on ultra-short-chain PFAAs in the environment are scarce. This is partly due to the analytical challenges of highly polar substances using conventional analytical techniques such as gas chromatography (GC) and reversed phase liquid chromatography (RPLC). In Paper I, existing analytical techniques for the analysis of ultra-short-chain PFAAs were reviewed and discussed. Separation with GC often require additional sample preparation such as derivatization and the analytical run time is long (30–40 min),^{61, 62} whilst separation using RPLC is limited due to poor retention of

polar substances.³¹ Successful separation of ionic PFASs has been obtained using ion-exchange chromatography, but the analytical run time is long (30 min).³¹ Methods based on supercritical fluid chromatography (SFC) have shown to be promising and efficient, with analytical run times of 8–15 min,^{12, 13} but the instrumentation is not frequently available in commercial and research laboratories and investments in new instrumentation comes with a cost. Other promising methods, also with relatively short analytical run times (8–16 min), are hydrophilic interaction liquid chromatography (HILIC) and mixed-mode liquid chromatography (MMLC),^{12, 14} which both combines the chemistries of RPLC and ion-exchange chromatography to increase the retention of polar and ionic substances.

One of the main problems associated with analysis of ultra-short-chain PFCAs, especially TFA, is background contamination.^{14, 31, 61-63} Laboratory equipment made of perfluoroalkoxy alkane (PFA) and polytetrafluoroethylene (PTFE) have been shown to leach TFA.⁶² Several efforts have been made to identify and reduce the background contamination, but without eliminating TFA.¹⁴ Thus, the method detection- and quantification limits often depend on the background contamination. Similar issues have not been reported for other ultra-short-chain PFASs and their identification in environmental samples is a result of nearby contamination sources or their long-range environmental transport.

2. Aim and objectives

The aim of the thesis was to assess ultra-short-chain PFAAs with respect to their potential contamination sources and distribution in the environment. The specific objectives were:

- Review existing analytical methods and the potential analytical challenges and improve the analytical method (Papers I and II).
- Summarize the current state of knowledge regarding potential sources and environmental occurrence (Paper I).
- Identify potential point sources (Paper II).
- Assess the seasonal deposition, geographical distribution, and the role of atmospheric oxidation of volatile precursors as a source of contamination (Papers III and IV).
- Examine the relevance of local and diffuse contamination sources to a freshwater lake in Sweden (Paper IV).

3. Methods

3.1. Sampling sites

A total of 172 samples have been analyzed during the work in Papers II, III, and IV, excluding field blanks, procedural blanks and quality control samples. The samples were collected at various locations in Sweden and on the island of Spitsbergen in the Norwegian Arctic, to cover the purpose of the thesis. The sampling locations and the samples are described in the following sections.

3.1.1. Screening for potential point sources

A screening study was conducted to identify potential point sources of ultra-short-chain PFAAs (Paper II). Water samples were collected at various locations with known or suspected PFAS contamination. Sampling was performed downstream the suspected contamination source and at some sites, a series of samples were collected further downstream to get an indication on the distribution and environmental fate of ultra-short-chain PFAAs. The sites included in the screening study were five firefighting training sites, three municipal and industrial landfills, and a hazardous waste management facility. Two of the five firefighting training sites were not actual training sites, but rock shelters equipped with sprinkler systems for fire extinguishing. The water samples collected at these sites were out-flowing water from the rock shelters, consisting of a combination of groundwater, stormwater, and surface water from nearby areas. Due to the suspected contamination source being fire protection agents, these sites will hereafter be referred to as firefighting training sites. At the other three firefighting training sites, surface water or groundwater samples were collected in the proximity to or downstream of the firefighting training site. The landfills included were nonactive, active non-hazardous waste, and active hazardous waste landfills. At the hazardous waste management facility, samples were collected from a stream at the outlet of the facility and further downstream, as well as from two receiving lakes. A more detailed description of the sites included in the screening study is provided in Paper II.

3.1.2. Seasonal variation, sources and distribution in the Arctic

In Paper III, surface snow samples were collected at several locations on the island of Spitsbergen in the Norwegian Arctic to assess the seasonal deposition, sources, and geographical distribution of ultra-short-chain PFAAs in the Arctic. Seven sampling locations were chosen, out of which three sites were sampled several times from January to August 2019. These three sites represent both potentially locally contaminated and background sites, whilst being easily accessible all year around and were in the settlement of Longyearbyen, up the hill from the Kjell Henriksen Observatory (KHO), and on the summit of Foxfonna ice cap (Figure 3). The site in Longyearbyen were chosen to represent local sources. The site at KHO was located uphill of the Kjell Henriksen Observatory and was chosen because of its proximity to the Foxfonna sampling site (4.7 km), allowing for comparison between the sites and to understand possible PFAA contamination from the active coal mine in Longyearbyen. The Foxfonna sampling site was chosen to represent a potential remote location due to its high altitude and position upwind from Longyearbyen with respect to the easterly prevailing winds.



Figure 3. Sampling locations in Longyearbyen, Kjell Henriksen Observatory (KHO), and Foxfonna ice cap. The map is based on toposvalbard.npolar.no, (Norwegian Polar Institute).

Four high elevation sites on glaciers around Svalbard were chosen for snow sampling at single events from February to April 2019, as these most likely represent background reference locations presumably receiving PFAA input solely from long range processes. These sites were Drønbreen, Lomonosovfonna, Grønfyordbreen, and Nordmannsfonna and are shown in Figure 4.

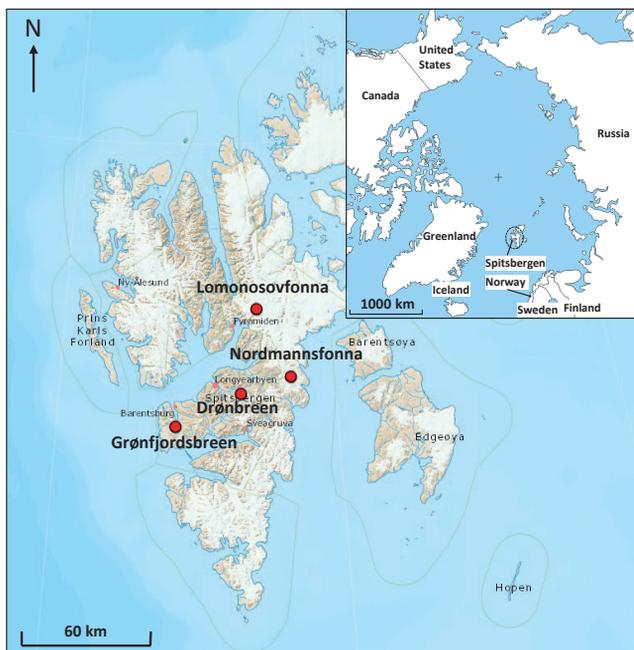


Figure 4. The reference snow sampling locations on Spitsbergen were Lomonosovfonna ($n=2$), Nordmannsfonna ($n=1$), Drønbreen ($n=1$), and Grønfyordbreen ($n=1$). The maps are based on toposvalbard.npolar.no (Norwegian Polar Institute) and d-maps.com.

3.1.3. Mass balance in Lake Vättern

In Paper IV, a mass balance of ultra-short-chain PFAAs was assembled for a freshwater lake to assess the relevance of local and diffuse sources. Lake Vättern is the second largest lake in Sweden and the sixth largest lake in Europe (1 900 km²). It is an important drinking water source, and the quality of the water is therefore of high importance. The lake has a large volume (74 km³), a relatively small catchment area (6 400 km²), and a

slow turnover (60–70 years), which makes the water quality stable, but also susceptible to pollution with persistent chemicals. An overview of the properties of Lake Vättern is provided in Table 1. Lake Vättern is surrounded by urban areas and is subject to anthropogenic impacts such as wastewater discharges, landfill leachates, and agricultural and industrial activity. In addition, two airports are located near Lake Vättern at which PFAA-containing AFFFs have been used and elevated concentrations of PFAAs in biota in Lake Vättern has previously been documented.⁶⁴ The relevance of different sources of PFAAs to Lake Vättern, including atmospheric deposition, is not known.

Table 1. Properties of Lake Vättern. Data were retrieved from the Swedish Meteorological and Hydrological Institute⁶⁵ and by oral communication with the water management association Vätternvårdsförbundet.

Surface area of Lake Vättern (km ²)	1885
Surface area of catchment area (km ²)	6376
Volume (km ³)	74
Average depth (m)	40
Maximum depth (m)	120
Turnover rate (years)	60–70
Average water flow (m ³ /s)	40*
Precipitation over the catchment area (mm/year)	650
Number of cities (>10 000 inhabitants)	3
Number of smaller towns (200 – 10 000 inhabitants) (>1 000)	42 (15)
Population (in the catchment area)	200 000

*The average water flow is based on measured and modelled data during 1940–2020. The average water flow has been lower since 2016 and was 18 m³/s during the year of the study (2019).

To establish the mass balance, samples were collected that represent the main input (inflowing streams, effluents, and atmospheric deposition), output (outflowing stream), and the lake inventory (water column). Atmospheric deposition samples were collected monthly on the island of Visingsö in Lake Vättern. Surface water were collected from streams representing the main inflow and outflow. The streams included in the study are subject to different anthropogenic impacts including sewage treatment plants, landfills, industries, firefighting training sites, agriculture as well as

stormwater from polluted areas (some with known PFAS pollution). Reference samples were collected from a stream upstream from the study area and downstream from a lake that is not a recipient of any known local contamination. Effluent water samples were collected from a sewage treatment plant and a paper mill that discharges directly into Lake Vättern. All surface water samples from streams and effluent samples were collected at four occasions representing four different seasons. Surface water samples were collected from two locations in Lake Vättern at two occasions representing spring, when the water column is mixed, and during summer when the lake is stratified. The sampling locations are shown in Figure 5. Information of potential contamination sources, annual flow rate and catchment area for each stream are listed in Table 2. Detailed information about the samples included in the mass balance is provided in Paper IV.

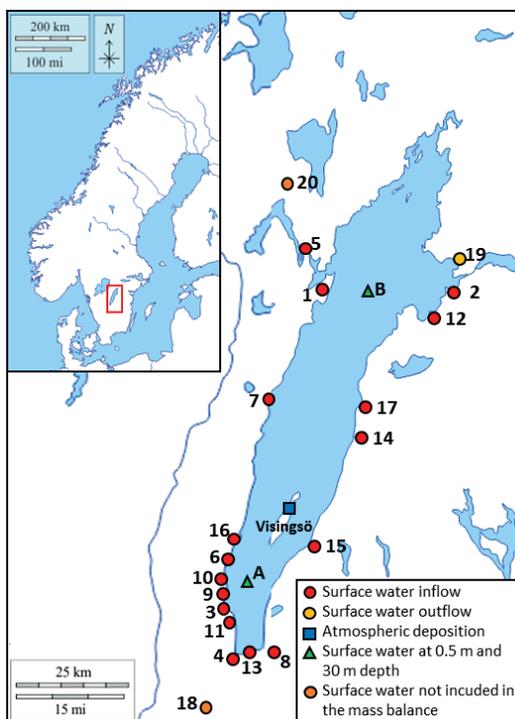


Figure 5. Geographical location and sampling sites in and around Lake Vättern. Maps are based on d-maps.com.

Table 2. Sampling locations, known potential contamination sources, catchment area (km²) and annual flow rate (m³/yr) of streams connected to Lake Vättern. “Other contamination” refers to sites with known contamination with metals and/or organic pollutants other than those defined as PFASs.

Stream	Sampling location	Potential contamination sources	Catchment area (km ²)	Flow rate (m ³ /yr)
1	Kärnebäcken	FFTS	NA	326 000
2	Hamrabäcken	Landfill	NA	932 000
3	Domneån	Other contamination	66	15 300 000
4	Dunkehallaån	FFTS, industry, stormwater	26	6 840 000
5	Forsviksån	Other contamination	840	167 000 000
6	Gagnån	STP, Industry	29	7 560 000
7	Hjoån	Other contamination, stormwater, individual sewers	63	9 340 000
8	Huskvarnaån	PFAS contamination, landfill, STP, stormwater	660	139 000 000
9	Hökesån	FFTS, industry, stormwater	69	17 900 000
10	Knipån	Individual sewers	53	14 000 000
11	Lillån	STP, other contamination	35	8 400 000
12	Mjölnaån	Agriculture, individual sewers	420	25 200 000
13	Munksjön	FFTS, STP, stormwater, industry	240	124 000 000
14	Orrnäsaån	Agriculture	64	9 980 000
15	Röttleån	Individual sewers	220	9 180 000
16	Svedån	No known impact	49	13 500 000
17	Ålebäcken	Agriculture	84	11 500 000
18	Sandserydsån ^a	FFTS	NA	NA
19	Motala ström ^b	NA	6 400	576 000 000
20	Unden ^c	No known impact	NA	NA

Abbreviations: Fire-fighting training site (FFTS); Sewage treatment plant (STP); Not available (NA).

^aNot included in mass balance calculations. The stream discharges into a small lake, which is connected to Lake Vättern via stream number 13.

^bSurface water outflow.

^cReference sample collected upstream the study area.

3.2. Sample collection

For the work in Paper II, surface water, groundwater, landfill leachate and stormwater samples were collected from various locations with known or suspected PFAS contamination from February 2017 to May 2018 ($n=34$).

In Paper III, surface snow samples were collected at several locations on the island of Spitsbergen in the Norwegian Arctic from January to August 2019 ($n=32$). The sampling was conducted as soon as possible after a chosen precipitation event (typical <1 day–12 days, average 4.8 days), such that each snow sample represents a single precipitation event whereby post depositional processes have been minimized. A pre-cleaned aluminum shovel was used to collect 0–5 cm surface snow into a barrel. When collecting the surface snow samples, the site was approached by ski or snowmobile, with the final approach to the sampling site undertaken from downwind on foot.

In Paper IV, surface water samples were collected at four occasions representing four different seasons from streams that discharge into (streams 1–17) or represent the main outflow (stream 19) from Lake Vättern from March to December 2019 ($n=72$). Surface water samples ($n=8$) were collected from two additional streams that were not included in the mass balance. One of these streams (stream 18) passes near an airport with known PFAAs contamination and discharges into a small lake that are connected to Lake Vättern via stream 13 (included in the mass balance). The other stream (stream 20) is located upstream from the study area and downstream from a lake that is not a recipient of any known local contamination. Surface water samples were collected from two locations in Lake Vättern at 0.5 m depth in April 2019, when the water column is mixed, and at 0.5 m and 30 m depth in July or August, when the water column is stratified ($n=6$). Surface water, groundwater, landfill leachate, and stormwater were grab samples. Atmospheric deposition samples were collected monthly during July 2018 to June 2019 on the island of Visingsö in Lake Vättern ($n=12$). Rain samples were collected using polyethylene funnels (diameter: 248 mm) connected to polyethylene containers and snow samples were collected in polypropylene boxes. All atmospheric deposition samples were collected 1–1.5 m above the ground in an open field. Effluent water samples were collected at four occasions from March to December 2019 from a paper mill and a sewage treatment plant that discharges directly into Lake Vättern ($n=8$). These were composite samples.

All sample containers were rinsed three times with the sample matrix before collecting the samples. After sampling, the sample containers were sealed and transported to the laboratory. Snow samples were melted and transferred to pre-cleaned polyethylene containers. All samples were stored at 4 °C until processing. Detailed information about the sample collection can be found in Papers II, III, and IV.

3.3. Sample preparation and instrumental analysis

3.3.1. Sample extraction for analysis of ultra-short-chain PFAAs

In Papers III and IV, the pH of the samples was adjusted to 4 by addition of acetic acid before further sample preparation. In Papers II, III, and IV, surface water, groundwater, landfill leachate, stormwater, and surface snow samples were filtered with glass microfiber filters (1.2 µm, Grade GF/B, Whatman) prior to extraction. In Paper II, the particle phase was excluded in further processing. In Papers III and IV, the filters were extracted three times with methanol by ultrasonication for 30 min followed by centrifugation at 8000 rpm for 5 min. The filter extract was combined with the sample prior to extraction. Atmospheric deposition samples (Paper IV) were not filtered prior to extraction. The samples were extracted by weak anion exchange solid-phase extraction (WAX-SPE) using Oasis WAX cartridges (150 mg, 6 mL, 30 µm, Waters Corporation, Milford, USA) following the ISO25101 method with some modifications.

In Paper II, analysis of TFA was performed by direct injection of filtered water samples after 1:1 dilution in methanol.

All samples were spiked with mass-labelled internal standard prior to sample preparation. A general overview of the analytical workflow used in Papers II, III, and IV is provided in Table 3. For detailed information of the sample preparation methods, see Papers II, III, and IV.

Table 3. Overview of the analytical workflow used in Papers II, III, and IV.

	Paper II		Paper III	Paper IV	
Sample matrix	Surface water, groundwater, landfill leachate and stormwater		Surface snow	Surface water, industrial- and municipal effluent	Atmospheric deposition
Target analyte(s)	PFPrA, TFMS, PFEtS, PFPrS	TFA	TFA, PFPrA, TFMS, PFEtS, PFPrS	TFA, PFPrA, TFMS, PFEtS, PFPrS	
Sample volume (mL)	5–500	0.25	2 200	500–1 000	200
Sample preparation	Filtration, WAX-SPE	Filtration, dilution in methanol (1:1)	Adjust pH to <4, filtration, extraction of filters, WAX-SPE	Adjust pH to <4, filtration, extraction of filters, WAX-SPE	Adjust pH to <4, WAX-SPE
Particle- and/or dissolved phase analyzed	Dissolved phase		Particle- and dissolved phase	Particle- and dissolved phase	

3.3.2. Analysis of ultra-short-chain PFAAs

Separation and quantification were performed using SFC coupled to tandem mass spectrometry (MS/MS) (Acquity Ultra Performance Convergence Chromatograph and Xevo TQ-S (Paper II) or Xevo TQ-S micro (Papers III and IV), Waters Corporation, Milford, MA, USA). An SFC Torus DIOL column (3.0 mm i.d., 150 mm length, 1.7 µm particle size, Waters Corporation, Milford, MA, USA) was used to achieve chromatographic separation. The mobile phase consisted of carbon dioxide (A) and 0.1% ammonium hydroxide in methanol (B). Gradient elution was used, and the total run time was 8–10 min.

The MS/MS was operated in negative electrospray ionization (ESI) mode. Two transitions were monitored for TFMS, PFEtS, and PFPrS. Only one transition was monitored for TFA and PFPrA. For detailed information about the chromatographic methods, source parameters, and the monitored transitions, see Papers II, III, and IV.

3.3.3. Analysis of sodium and chloride ions in surface snow

Concentrations of Na⁺ and Cl⁻ in surface snow were determined by ion chromatography using Dionex ICS-4000 Integriion anion and cation systems. See Paper III for detailed information about the ion chromatography analysis.

3.4. Quality assurance and quality control

The performance of the SFC-MS/MS method was evaluated in terms of linear range and precision. The instrumental detection and quantification limit was set as the lowest calibration point with signal-to-noise of at least three and ten, respectively. The sample preparation method was assessed based on the extraction and analysis of quality control (QC) samples. The QC samples consisted of fortified MilliQ water to assess the extraction efficiency, or fortified test samples (e.g. surface water, landfill leachate, and atmospheric deposition) to evaluate matrix recovery. The repeatability of the methods was assessed based on repeated extractions of fortified test samples.

Field blanks were included to check for contamination during sampling. The field blanks were prepared as MilliQ water in precleaned polyethylene containers that were opened in the field during sampling. Procedural blanks were included in each batch of samples to check for contamination during sample preparation in the laboratory. Solvent blanks were injected to check for instrumental contamination and analyte carry over. The method limits of detection and quantification were calculated as the average concentration in repeated blank extractions plus three times the standard deviation. The instrumental limits of detection and quantification, set as the lowest calibration point with a signal-to-noise ratio of at least three or ten, were used as method detection and quantification limit for those analytes that were not observed in blank extractions.

Quantification was done by isotope dilution using mass-labelled standards that were added to the samples prior to sample preparation. In Paper II, mass-labelled standards for ultra-short-chain PFAAs were not available at the time of analysis. Mass-labelled standards for the C₄ homologues

perfluorobutanoic acid (PFBA) and PFBS were used for quantification. In Papers III and IV, a mass-labelled standard for TFA was used for quantification of TFA. For detailed information about the quality assurance and quality control measures in each study, see Papers II, III, and IV.

3.5. Mass balance calculations

A mass balance of ultra-short-chain PFAAs in Lake Vättern was assembled based on the calculated input, output, and inventory in the water column.

3.5.1. Input pathways

The input pathways considered were atmospheric deposition, surface water inflow, and municipal and industrial effluents that discharges directly into Lake Vättern. The input from atmospheric deposition (kg/year) was calculated based on the measured concentration in atmospheric deposition (kg/m³) in monthly samples and the amount of atmospheric deposition over Lake Vättern per month (m³/month). The input was calculated based on the assumption that that the composition and amount of atmospheric deposition were equal over the entire surface of Lake Vättern, according to:

$$N_{deposition} = \sum C_i \times Q_i$$

where C_i is the PFAA concentration (kg/m³) in atmospheric deposition collected during month i and Q_i is the amount of atmospheric deposition (m³) over Lake Vättern during month i . The amount of atmospheric deposition was calculated based on measurements by the Swedish Meteorological and Hydrological Institute.⁶⁶

The input from surface water inflow and effluent (kg/year) was calculated based on the median concentration (kg/m³) and the discharge rate per year (m³/year) according to:

$$N_{surface\ water/effluent} = \sum C_i \times Q_i$$

where C_i is the PFAA concentration (kg/m³) in stream or effluent i and Q_i is the discharge rate per year (m³/year) of stream or effluent i . The discharge rate per year for effluent was based on measured data. For surface water inflow, the discharge rate per year was retrieved from a database created by the Swedish Meteorological and Hydrological Institute and the Swedish Agency for Marine and Water Management and based on measured or modelled data.⁶⁷ If data was not available, the discharge rate per year was calculated based on flow rate measurements during the sampling

and calibrated against the modelled discharge rate per year from an adjacent catchment area. Low-bound estimates (LBE) and high-bound estimates (HBE) were calculated based on the lowest and highest concentrations measured, respectively.

3.5.2. Output pathway

Surface water outflow was assumed to be the dominating output and other output pathways such as transformation in water, volatilization, and sediment burial were not considered. The output via surface water outflow (kg/year) was calculated based on the median concentration (kg/m³) and the discharge rate per year (m³/year) for the stream that represents the main outflow, according to:

$$N_{Output} = C \times Q$$

where C is the PFAA concentration (kg/m³) in the outflowing stream and Q is the discharge rate per year (m³/year). The discharge rate per year was based on measured data obtained from the Swedish Meteorological and Hydrological Institute and the Swedish Agency for Marine and Water Management.⁶⁷ LBE and HBE were calculated based on the lowest and highest concentrations measured, respectively.

3.5.3. Inventory in the water basin

The concentrations of ultra-short-chain PFAAs in the water basin were in the same range at different locations and depths and did not differ between samples collected in April compared to those collected in July or August. Thus, the concentrations were considered equal in the entire water basin. The inventory of ultra-short-chain PFAAs in Lake Vättern (kg) was calculated based on the average concentration in the water basin (kg/m³) and the volume of water (m³), according to:

$$M_{Water} = C \times V$$

where C is the PFAA concentration (kg/m³) in the water basin and V is the volume of water in the water basin (m³).

3.6. Air mass trajectories and solar radiation in the Arctic

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model was used to assess whether solar radiation may be linked to precursor degradation, and hence the occurrence of ultra-short-chain PFAAs in the surface snow at the Foxfonna sampling site. A backwards air mass

trajectory was calculated for each of the 10 snow sampling events, with the trajectory ending at the same time as sampling. A 6-day backwards air mass trajectory was used since it was expected that atmospheric half-life of ultra-short-chain PFAAs with respect to wet- and dry deposition would be similar to that of nitric acid.⁶⁸ The National Center for Environmental Prediction's Global Data Assimilation System (GDAS) model was used for the meteorological data. This was used to calculate the amount of solar radiation each air mass parcel had been subject to that was associated with each snow sample. For detailed information, see Paper III.

3.7. Statistical analysis

Spearman rank correlations between the concentrations of ultra-short-chain PFAAs in atmospheric deposition and surface snow and the solar radiation, and between the concentration of ultra-short-chain PFAAs and the concentrations of sodium and chloride ions in surface snow, were calculated using Microsoft Excel version 2105.

4. Results and discussion

4.1. Analytical challenges

4.1.1. Blank contamination

Throughout the work in Paper II, several efforts were made to reduce blank contamination during sample preparation. All ultra-short-chain PFAAs were detected in the procedural blanks. The concentrations observed in the blanks varied between batches and within batches. Blank concentrations for PFETs and PFPrS were satisfactory (<0.03 ng/L for 500 mL sample volume). The concentrations of TFA, PFPrA, and TFMS were generally higher and varied over 1–2 orders of magnitude. There are several possible contamination sources in the laboratory, both laboratory consumables and the indoor air. A major contamination source for TFA and TFMS was suspected to be the storage and handling of concentrated TFA and TFMS (>99%) in the laboratory. This may cause contamination of the indoor air as well as contamination of consumables used during sample preparation. The blank levels were significantly reduced by removing TFA and TFMS from the laboratory, and by replacing consumables that might have been contaminated. The blank concentrations of TFMS were hereafter satisfactory and did not vary significantly (0.14–0.24 ng/L for 500 mL sample volume). The blank concentrations of TFA and PFPrA were still varying, and the reason for this was not further investigated. Since TFA and PFPrA are formed by atmospheric degradation of HFCs and HCFCs, these are likely present in the indoor air. The concentrations of TFA and PFPrA in the procedural blanks were hereafter satisfactory for the purpose of the study (0.79–3.2 ng/L and 0.10–8.8 ng/L for 500 mL sample, respectively).

During the work in Papers III and IV, the quantification was performed using a mass spectrometer which had been recently installed. Elevated background levels of TFA and PFPrA were observed. The background signals were thought to come from the MS/MS system, since the background levels were lower when the same chromatographic system was coupled to another mass spectrometer. The background of both TFA and PFPrA was reduced by a factor of 4 by leaving the system in operate for 14 days, and further reduced by a factor of 18 (TFA) and 4 (PFPrA) by flushing with mobile phase for seven days. No further decrease was observed with additional flushing and the background was constant when

the system was left in operate mode. If the system was left in standby but keeping the atmospheric pressure ionization (API) gas on, the background was kept constant. The gas tubing which delivers the API gas has a PTFE lining. It was hypothesized that short-chain PFCAs are leaching from the PTFE lining and may accumulate in the system when there is no gas flow in the tubing. The PFCAs are transferred to the ESI source once the gas flow is switched on, resulting in a high background signal which then decreases with time if the system is left in operate with the API gas on.

Opening the ion source and venting the instrument increased the background by a factor of 5 (TFA) and 2 (PFPrA), indicating that TFA and PFPrA are present in the indoor air. Yet the highest increase in background signal was observed after the system had been in standby for four months, without keeping the API gas on. This resulted in an increase of TFA and PFPrA by a factor of 16 and 8, respectively. Additional tests were performed and an increase in background was observed every time the system was left in standby without the API gas on.

4.1.2. Analysis of TFA without mass-labelled standard

4.1.2.1. Extraction efficiency

During the work in Paper II, varying and unsatisfactory extraction recoveries of TFA were obtained using WAX-SPE. The recovery varied from 7 to 42% in three selected test samples (landfill leachate, groundwater, and surface water). The recovery of PFBA, which was used as an internal standard for TFA as a mass-labelled TFA standard was not available, ranged from 94 to 111% in the same test samples, meaning that mass-labelled PFBA is not a suitable surrogate to compensate for losses of TFA during WAX-SPE. Large pH dependent variations in recovery of TFA during extraction by WAX-SPE have been observed and reported previously.⁶³

Lowering the pH increase the recovery of anionic analytes during WAX-SPE by protonating the functional groups of the sorbent, as well as reducing the extraction of competing anions such as bicarbonate. In the study by Janda et al.,⁶³ TFA recoveries in the range 94–114% were obtained over the pH range 3–5. In the present work, the recovery did not seem to depend only on the pH of the sample but rather the combination of the pH and sample matrix. Only 7% recovery of TFA was achieved during WAX-SPE of a surface water sample with pH 5. Lowering the pH from 5 to 4 by addition of acetic acid resulted in an increase in recovery

from 7 to 77%. In addition to reducing the effect of competing anions by lowering the pH, addition of an acid could increase the recovery of TFA by breaking up ion pairs between TFA and basic compounds. Strong ion-pairs are formed between TFA and basic compounds when TFA is used as a mobile phase additive for chromatographic separation of basic compounds causing signal suppression during mass spectrometric determination.⁶⁹

4.1.2.2. Direct injection analysis

In Paper II, a method based on direct injection analysis by SFC-MS/MS was applied for the analysis of TFA in aqueous samples, due to the unsatisfactory recoveries obtained by WAX-SPE. The same set of test samples as for the WAX-SPE method were used to assess the recovery (due to ion signal effects) of the direct injection method. The recovery of TFA in the test samples was $81 \pm 0.4\%$ (Figure 6). In addition to increased recovery of the direct injection method, less sample preparation results in reduced blank contamination. The detection limit of the WAX-SPE method is highly dependent on contamination in the procedural blanks and was in the range 0.79–3.2 ng/L (sample volume 500 mL, concentration factor 1000x). The detection limit of the direct injection method was 34 ng/L (sample volume 250 μ L, concentration factor 0.5x). A schematic overview of the direct injection and WAX-SPE methods is shown in Figure 7.

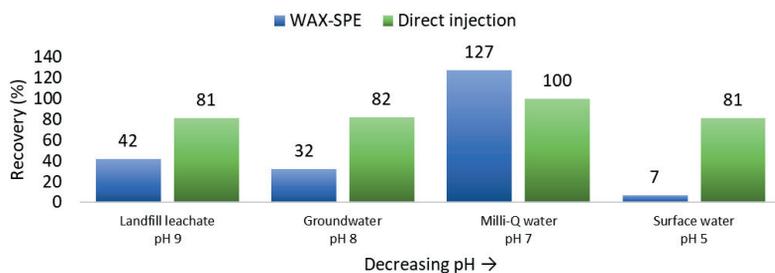


Figure 6. Extraction efficiency (%) of TFA in selected test samples during WAX-SPE and direct injection after 1:1 dilution in methanol.

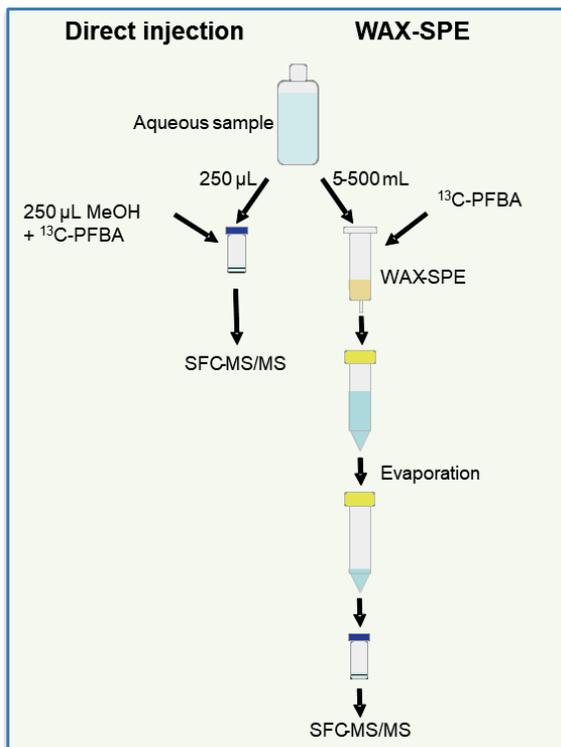


Figure 7. Schematic overview of the direct injection and WAX-SPE methods.

Both methods were applied on surface water, groundwater, and landfill leachate samples ($n=34$) from various locations connected to suspected point sources. The concentrations of TFA in the water samples observed by WAX-SPE and by direct injection are shown in Figure 8. The observed TFA concentrations by WAX-SPE were up to 600 times lower than the concentrations observed by direct injection. In addition, the detection frequency of TFA was 61% by direct injection and 30% by WAX-SPE. These results illustrate the drawbacks of WAX-SPE for the analysis of TFA in water samples resulting in both underestimation and lower detection frequency of TFA, when no corresponding mass-labelled internal standard is used.

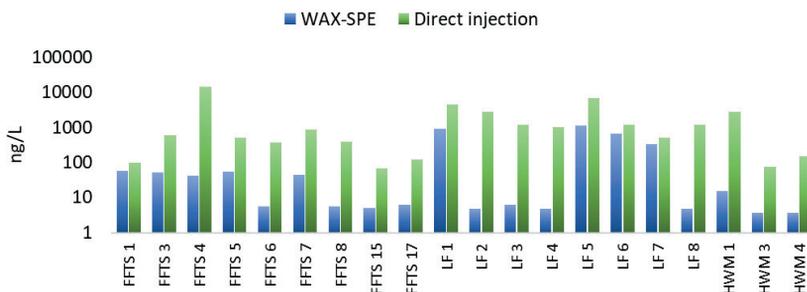


Figure 8. Concentrations of TFA in surface water and groundwater at firefighting training sites (FFTSs), in landfill leachate (LF) and in surface water receiving effluent from a hazardous waste management facility (HWMF), observed after extraction by WAX-SPE and direct injection after 1:1 dilution in methanol. Only samples in which TFA was detected above the detection limit are included.

4.1.3. Analysis of TFA with mass-labelled standard

During the work in Paper II, it was observed that the extraction of TFA from aqueous samples is highly dependent on the sample matrix and pH and that losses during extraction is not compensated for by using mass-labelled PFBA, which is often used as an internal standard when mass-labelled TFA is not available. A mass-labelled internal standard for TFA was desired for the continued work in Papers III and IV, as it is needed for accurate quantification of TFA when using WAX-SPE. The purity in terms of native TFA content were tested in two ^{13}C -labelled standards (+1 amu) and in one $^{13}\text{C}_2$ -labelled standard (+2 amu), all commercially available. The two ^{13}C -TFA standards contained significant amounts of ^{12}C -TFA (65% and 57% relative to ^{13}C -TFA) and only the $^{13}\text{C}_2$ -TFA was free from contamination (Figure 9). Moreover, for quantification using mass-labelled standards, a $^{13}\text{C}_2$ -TFA standard over a ^{13}C -labelled standard is preferred since the latter will produce biased results due to interference with the naturally occurring ^{13}C -TFA. The results in Paper II are based on direct injection analysis and the results in Papers III and IV are calculated by isotope dilution using $^{13}\text{C}_2$ -TFA.

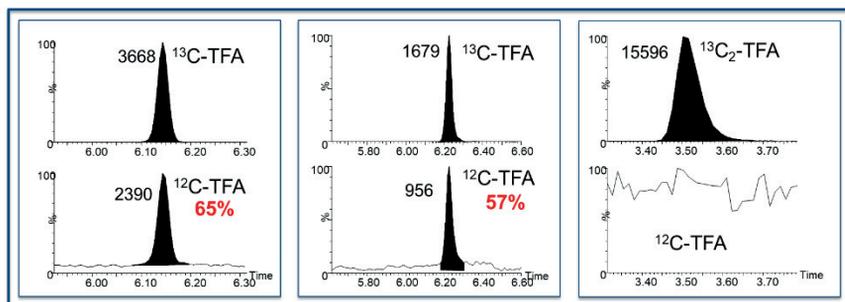


Figure 9. Chromatograms showing the ^{12}C -TFA content, based on peak area, in three different mass-labelled TFA standards.

4.2. Environmental occurrence of ultra-short-chain PFAAs

Atmospheric deposition is an important diffuse source of PFAAs and wet deposition is an effective scavenger for removal of PFASs from the atmosphere.⁷⁰ Atmospheric degradation of precursor compounds, such as FTOHs, has been identified as a route for global distribution of PFAAs.^{21, 71} Analyzing PFASs in atmospheric deposition can give information about temporal trends and spatial distribution. However, there might be some other potential sources of ultra-short-chain PFAAs.

4.2.1. Ultra-short-chain PFAAs in precipitation

Ultra-short-chain PFAAs were measured in surface snow collected over the period from January to August 2019 on the island of Spitsbergen in the Norwegian Arctic (Paper III), and in atmospheric deposition samples collected monthly from July 2018 to June 2019 on the island of Visingsö, Sweden (Paper IV), to assess their geographical distribution and seasonal variation. In Paper III, concentrations of ultra-short-chain PFAAs were measured in surface snow collected from different sites to represent both local (Longyearbyen) and diffuse sources.

TFA and PFPrA were detected in all samples analyzed, including surface snow samples collected at the four high elevation reference sites on the island of Spitsbergen (Drønbreen, Lomonosovfonna, Grønfjordbreen, and Nordmannsfonna), which are thought to represent input solely from long-range processes. The concentrations of TFA and PFPrA were in the range 18–300 ng/L and 0.92–3.7 ng/L in atmospheric deposition collected on the island of Visingsö, and 5.6–270 ng/L and 0.21–1.5 ng/L in surface snow collected on the island of Spitsbergen, respectively.

Among the ultra-short-chain PFSAs, TFMS was detected in two atmospheric deposition samples collected on the island of Visingsö (0.13–0.15 ng/L) and in all surface snow samples collected on the island of Spitsbergen (0.15–5.1 ng/L). PFPrS was not detected in any of the samples and PFETs was only detected in surface snow samples collected in or in the proximity to Longyearbyen. Environmental occurrence of PFBS in the area has previously been linked to local sources such as firefighting training sites and landfills,^{72, 73} and PFETs has been associated to similar sources.⁹

On the island of Spitsbergen, the concentrations of ultra-short-chain PFAAs at a potential remote location (Foxfonna) were in the range 7.3–270 ng/L (TFA), 0.29–1.5 ng/L (PFPrA), and 0.29–5.1 ng/L (TFMS). Similar concentrations of TFA have previously been reported in precipitation in remote locations.²⁷ Positive correlation was observed between the concentration of TFA and PFPrA ($r=0.98$, $p<0.01$) suggesting that they share similar atmospheric sources and fate in remote Arctic environments. No correlation was observed between the concentration of TFMS with neither TFA nor PFPrA.

4.2.1.1. Seasonal trends of TFA and PFPrA in precipitation

PFASs have been shown to be effectively scavenged from the atmosphere by wet deposition and most of the PFAS removal is expected to occur at the beginning of a rainfall.⁷⁰ Thus, the PFAS concentration in samples from a month with large rainfall is expected to be diluted compared to samples from a month with less rainfall. As expected, in Paper IV, the higher concentrations were generally observed in samples collected during months with little rainfall, and *vice versa*. Therefore, a better way of presenting the occurrence of PFASs in atmospheric deposition, as suggested by Taniyasu et al.,⁷⁰ especially when looking at seasonal variations and correlation with solar radiation, is as flux, which is the amount per square meter (ng/m^2). The fluxes of TFA and PFPrA in atmospheric deposition on the island of Visingsö were in the range 300–16 000 ng/m^2 and 16–260 ng/m^2 , respectively. For both PFCAs, the highest flux was observed in July and the lowest flux was observed in January (Figure 10). This observation is in accordance with the results in a previous study.³³ The occurrence of ultra-short-chain PFAAs in surface snow (Paper III) were presented as concentration (ng/L) because data to calculate the flux were not available.

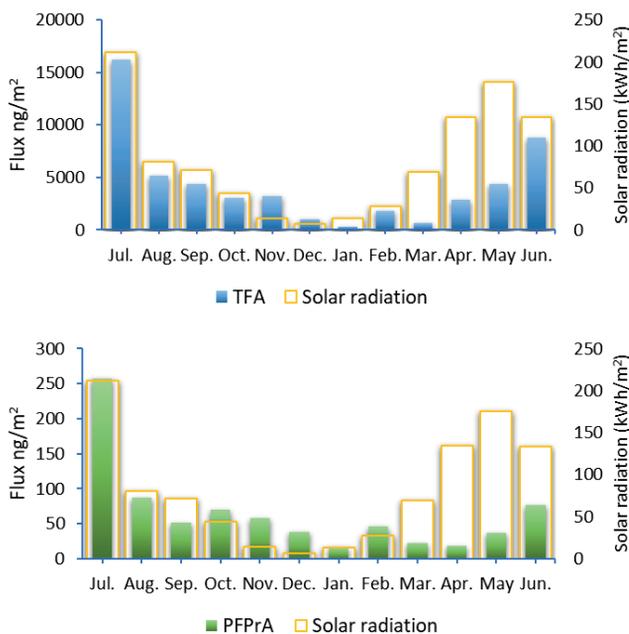


Figure 10. Seasonal variation of TFA and PFPrA fluxes (ng/m²) and solar radiation (kWh/m²) on the island of Visingsö, Sweden based on concentrations in atmospheric deposition samples collected monthly from July 2018 to June 2019.

Since hydroxyl radicals are produced by incoming solar radiation into the atmosphere,⁷⁴ the solar radiation (kW/m²), retrieved from measurements by the Swedish Meteorological and Hydrological Institute,⁶⁶ was used to access the seasonal variations in hydroxyl radicals in the atmosphere over the island of Visingsö. Positive correlation was observed between the solar radiation and the flux of TFA ($r=0.73$, $p<0.01$). No correlation was observed between the solar radiation and the flux of PFPrA. The fluxes of both TFA and PFPrA were low, relative to the solar radiation, during March–June, compared to the rest of the year, which may explain the lack of correlation between solar radiation and flux of PFPrA. Positive correlation was observed between the solar radiation and the flux of PFPrA during July–February ($r=0.80$, $p<0.05$).

The lower flux of TFA and PFPrA relative to the solar radiation observed during March–June compared to July–August may be linked to a lower atmospheric concentration of volatile precursors during March–

June, which can be influenced by factors such as emission rates, temperature, aerosols, and the prevailing wind direction and speed. The production of TFA and PFPrA depends on the presence of water in the atmosphere and on the availability of hydroxyl radicals, which both vary seasonally. The rate of atmospheric oxidation is linked to the availability of hydroxyl radicals, which depends on the concentration of hydroxyl radicals in the atmosphere as well as the concentration of other volatile organic compounds that are oxidized by hydroxyl radicals. Since hydroxyl radicals are formed by solar irradiation on ozone molecules subsequent cleavage of gaseous water molecules, the concentration of atmospheric hydroxyl radicals over Sweden is expected to be slightly higher during summer when the absolute humidity is higher (10–11 g H₂O/m³ in July) compared to spring (4–5 g H₂O/m³ in March) (humidity data were retrieved from the Swedish Meteorological and Hydrological Institute⁶⁶). Thus, the formation rate of TFA and PFPrA by hydroxyl radical driven atmospheric oxidation of volatile precursors, relative to the solar radiation, could be expected to be slightly lower during spring, when the absolute humidity is low, compared to during summer. Another possible hypothesis would be that seasonal differences in automobile and domestic air conditioning result in larger local as well as seasonal differences in TFA flux, as a result of a shift from HFC-134a to HFO-1234yf, as the atmospheric lifetime with respect to oxidation by hydroxyl radicals is considerably shorter for HFO-1234yf (~12 days)⁵³⁻⁵⁵ compared to HFC-134a (~14 years).⁵⁶

On the island of Spitsbergen, the occurrence of ultra-short-chain PFAAs at the Foxfonna sampling site was thought to be explained by long-range processes due to its high elevation, up wind of Longyearbyen with respect to the prevailing winds. This was supported by the fact that the concentrations of TFA and PFPrA at the Foxfonna sampling site were in similar range (7.3–270 ng/L and 0.29–1.5 ng/L, respectively) as the concentrations observed at the reference sites (13–90 ng/L and 0.34–1.1 ng/L, respectively). Therefore, data from the Foxfonna sampling site were used to investigate seasonal variations in long range processes. The concentrations of TFA and PFPrA were higher in samples collected during the polar summer with 24-hour daylight (April–August), compared to the concentrations in samples collected during the polar night with 24-hour, or partial, darkness (January–March) (Figure 11). The correlation between the observed concentrations of ultra-short-chain PFAAs in the surface snow at the Foxfonna sampling site and solar radiation was examined to assess the relevance of the atmospheric degradation of volatile precursors as a pathway to

remote locations. A positive correlation was observed between the solar radiation and the concentration of TFA ($r=0.94$, $p<0.01$) and PFPrA ($r=0.96$, $p<0.01$).

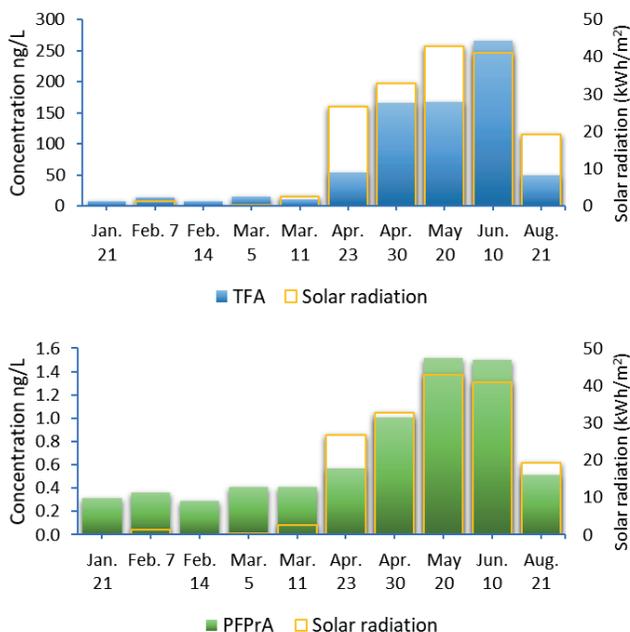


Figure 11. Concentration (ng/L) of TFA and PFPrA in surface snow samples collected at the Foxfonna ice cap from January 2019 to August 2019 and solar radiation (kWh/m²) along the 6-days air mass backwards trajectory.

4.2.1.2. Discovery of TFMS in precipitation

TFMS was detected both in atmospheric deposition samples collected on the island of Visingsö, Sweden, and in surface snow collected on the island of Spitsbergen in the Norwegian Arctic. TFMS was detected in all surface snow samples, including those collected at reference sites that are assumed to receive input only from long-range processes, at concentrations ranging 0.15–5.1 ng/L. The detection of TFMS at remote Arctic locations suggests that this compound is globally distributed.

No seasonal variation was observed for TFMS in surface snow and there was no correlation between the concentration of TFMS and solar radiation (Figure 12). There is no information on formation of ultra-short-

chain PFSA from the atmospheric degradation of volatile precursors. Formation of PFBS from the atmospheric degradation of N-MeFBSE has been illustrated in laboratory experiments.²³ Yet the findings in Paper III suggest that the occurrence of TFMS in surface snow may be a result of other processes rather than the hydroxyl radical initiated atmospheric degradation of volatile precursors alone.

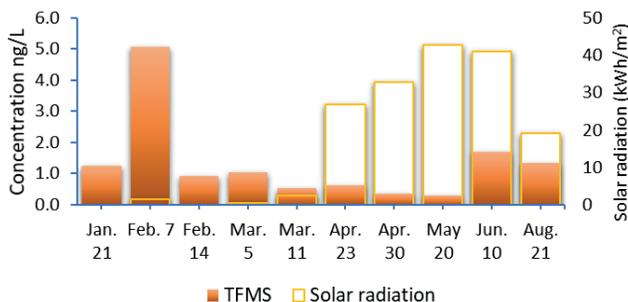


Figure 12. Concentration (ng/L) of TFMS in surface snow samples collected at the Foxfonna ice cap from January 2019 to August 2019 and solar radiation (kWh/m²) along the 6-days air mass backwards trajectory.

To further investigate potential sources of TFMS to the Arctic environment, the correlations between TFMS, sodium and chloride ions were studied in Paper III as these ions are tracers for marine aerosols. Positive correlation was observed between the concentration of TFMS and sodium ions ($r=0.64$, $p<0.05$) but not between TFMS and chloride ions. One sample, collected on February 7, contained higher concentration of TFMS (3–17 times) compared to other samples. This could be explained by several factors, including wind direction and the origin of the air mass. No correlation was observed between the concentration of TFMS with sodium or chloride ions when this sample was excluded. These findings suggest that neither atmospheric degradation of volatile precursors, nor the long-range oceanic transport are main sources of TFMS to the Arctic environment. However, it cannot be ruled out that both mechanisms are involved, alongside other transport mechanisms such as particle bound processes.

4.2.2. Potential point sources of ultra-short-chain PFAAs

In Paper II, a screening study was performed to identify potential point sources of ultra-short-chain PFAAs. Concentrations of ultra-short-chain

PFAAs were measured in water samples collected in areas highly contaminated or suspected to be highly contaminated with PFASs in Sweden. The sites included were at or in connection to five firefighting training sites ($n=20$), three landfills ($n=9$), and one hazardous waste management facility ($n=5$).

4.2.2.1. Firefighting training sites

Ultra-short-chain PFAAs were detected in water samples collected in connection to all firefighting training sites. The detection frequencies and concentrations ranges are listed in Table 4. The highest concentrations for all ultra-short-chain PFAAs were observed in water connected to two rock shelters with previous usage of AFFFs in sprinkler systems. PFEtS and PFPrS have previously been linked to the use of AFFFs for firefighting training purposes⁹ and the detection of these in the samples connected to firefighting training sites is not unexpected. Sources of TFMS have not been reported in the scientific literature, however; very few studies have attempted to include TFMS. Contamination with TFA and PFPrA has not been previously associated with the use of AFFF. Yet they were detected at concentrations up to 14 000 ng/L (TFA) and 53 000 ng/L (PFPrA) in water connected to the rock shelters. In addition, TFA and PFPrA are degradation products of HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) and perfluoro-2-methyl-3-pentanone (PFMP) that are used in fire suppression systems.^{75, 76} It is not known if HFC-227ea or PFMP have been used in these rock shelters, or if TFA and PFPrA are present in AFFFs as by-products and/or degradation products of other precursors. The notably high concentrations observed in outflowing water from rock shelters may indicate that sprinkler systems are major sources of ultra-short-chain PFAAs. It is important to bear in mind that the flow rates of water from these rock shelters are not known, and thus, the flux of ultra-short-chain PFAAs to the surrounding environment remains unknown.

The findings in Paper II show that firefighting training sites are point sources of ultra-short-chain PFAAs. In Paper IV (section 4.3), the input of ultra-short-chain PFAAs to a freshwater lake via surface water inflow was studied. Streams connected to areas with known usage of AFFFs, together accounting for 26% of the total water inflow to the lake, only accounted for 9.3–25% of the input of ultra-short-chain PFAAs via surface water inflow. This shows that point sources other than firefighting training sites also play an important role for the contamination with ultra-short-chain PFAAs in the lake.

Table 4. Detection frequency (%) and concentration range (ng/L) of ultra-short-chain PFAAs in samples collected at or in connection to firefighting training sites ($n=20$).

	Detection frequency (%)	Concentration range (ng/L)
TFA	45	<34–14 000
PFPrA	85	<5.1–53 000
TFMS	90	<1.8–940
PFEtS	90	<1.8–1 700
PFPrS	80	<0.009–15 000

4.2.2.2. Landfills

All ultra-short-chain PFAAs were detected in landfill leachate and stormwater. The detection frequencies (%) and concentration ranges (ng/L) are provided in Table 5. The highest concentrations were seen for TFA, followed by PFPrA and TFMS. TFA was more frequently detected at higher concentrations in landfill leachate and stormwater compared to in water connected to firefighting training sites. TFA concentrations ranging from 500 ng/L to 6 900 ng/L was observed in eight out of nine samples. As discussed in the previous section regarding firefighting training sites, the flux of ultra-short-chain PFAAs from landfill leachate and stormwater is not known.

Table 5. Detection frequency (%) and concentration range (ng/L) of ultra-short-chain PFAAs in landfill stormwater and leachate ($n=9$).

	Detection frequency (%)	Concentration range (ng/L)
TFA	89	<34–6 900
PFPrA	89	<7.2–800
TFMS	100	<13–500
PFEtS	44	<1.8–9.2
PFPrS	100	<2.8–90

4.2.2.3. Hazardous waste management facility

At the hazardous waste management facility, samples were collected at the outlet and in surface water downstream from the facility. The detection frequencies (%) and concentration ranges (ng/L) are provided in Table 6. PFPrA, TFMS, PFEtS and PFPrS were detected in surface water collected at the outlet. TFA was not quantified in the sample collected at the outlet but was observed at high concentration (2 700 ng/L) about 100 m downstream. All ultra-short-chain PFAAs were detected in the sample collected

100 m downstream from the outlet. TFA, TFMS, and PFPrS were all detected in samples collected further downstream, but PFPrA and PFEtS were not detected above the detection limit.

Table 6. Detection frequency (%) and concentration range (ng/L) of ultra-short-chain PFAAs in samples collected at the outlet of and downstream from a hazardous waste management facility (n=5).

	Detection frequency (%)	Concentration range (ng/L)
TFA*	75	<34–2 700
PFPrA	40	<3.1–9.9
TFMS	100	21–200
PFEtS	40	<1.8–3.6
PFPrS	100	0.74–13

*TFA was not quantified in the sample collected at the outlet and the data are based on four samples analyzed.

4.3. Mass balance of Lake Vättern

In Paper IV, a mass balance was assembled for ultra-short-chain PFAAs in Lake Vättern, based on measured concentrations in atmospheric deposition, inflowing surface water, effluents from a paper mill and a sewage treatment plant, and in the water column of the lake. Ultra-short-chain PFAAs were detected in all samples analyzed. The detection frequencies and concentrations in atmospheric deposition, surface water, and in the water column in the lake are summarized in Table 7. TFA, PFPrA, and TFMS were the most frequently detected ultra-short-chain PFAAs in atmospheric deposition, surface water inflow and in the water column of the lake. PFEtS and PFPrS were not detected in atmospheric deposition and only PFPrS was detected in the water column of the lake. Both PFEtS and PFPrS were detected in surface water from inflowing streams.

Table 7. Detection frequency (DF) (%) and concentration (ng/L) of ultra-short-chain PFAAs in atmospheric deposition, surface water inflow, and water column of Lake Vättern. The concentration in the water column is presented as average concentration \pm standard deviation.

	Atmospheric deposition		Surface water inflow		Water column	
	DF (%)	Conc. (ng/L)	DF (%)	Conc. (ng/L)	DF (%)	Average (ng/L)
TFA	100	18–300	89	30–820	100	34 \pm 5.2
PFPrA	100	0.92–3.7	71	0.60–2.9	100	0.5 \pm 0.04
TFMS	17	0.13–0.15	89	0.20–15	100	0.26 \pm 0.07
PFEtS	n.d.	<0.10	43	0.24–0.62	n.d.	<0.12
PFPrS	n.d.	<0.10	39	0.44–3.5	50	0.23 \pm 0.01

n.d. = not detected.

4.3.1. Input of ultra-short-chain PFAAs to Lake Vättern

The results of the mass balance of ultra-short-chain PFAAs in Lake Vättern is illustrated in Figure 13 and summarized in Table 8. Detailed information about the results of the mass balance is found in Paper IV. The highest input was observed for TFA (120–170 kg/yr) followed by PFPrA (1.3–2.0 kg/yr). The net mass fluxes of TFMS, PFEtS, and PFPrS were close to zero. Both atmospheric deposition and surface water inflow seem to be relevant sources for the input of ultra-short-chain PFCAs to Lake Vättern with atmospheric deposition accounting for approximately 57% (TFA) to 76% (PFPrA) of the total input based on median estimates of input via surface water inflow. For ultra-short-chain PFSAs, surface water inflow was the most important input pathway accounting for 94% (TFMS) and 100% (PFEtS and PFPrS) of the total input.

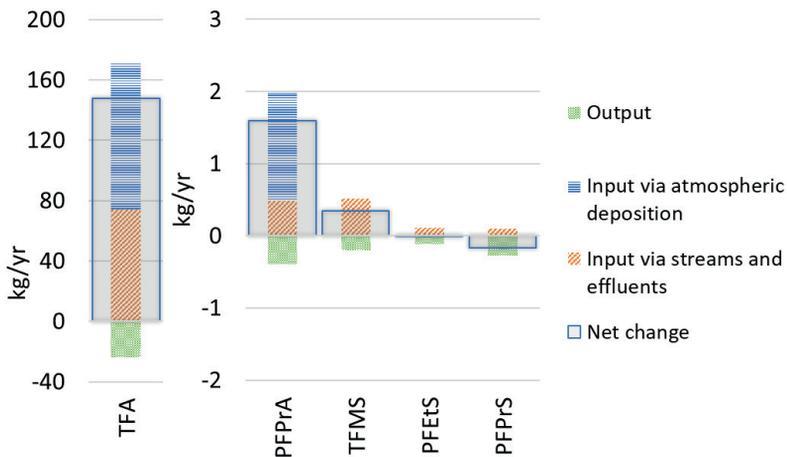


Figure 13. Net change (kg/yr) of ultra-short-chain PFAAs in Lake Vättern.

Table 8. Summary of ultra-short-chain PFAA mass balance in Lake Vättern based on ultra-short-chain PFAA inventory (kg), input from surface water inflow, effluents, and atmospheric deposition (kg/yr) and output via surface water outflow (kg/yr). Ranges are based on low- and high-bound estimates.

	TFA	PFPrA	TFMS	PFEtS	PFPrS
Inventory (kg)					
Water basin	2600	38	20	n.d.	17
Input (kg/yr)					
Surface water inflow and effluents	45–86	0.30–0.88	0.24–0.89	0.08–0.41	0.11
Atmospheric deposition	98	1.5	0.03	n.d.	n.d.
SUM Input	140–180	1.8–2.4	0.27–0.92	0.08–0.41	0.03–0.27
Output (kg/yr)					
Surface water outflow	17–28	0.36–0.54	0.12–0.37	0.07–0.16	0.07–0.16
Net change (kg/yr)					
Input-output (kg/yr)	120–170	1.3–2.0	-0.10–0.80	-0.08–0.34	-0.24–0.24

n.d. = not detected.

4.3.1.1. Input of TFA and PFPrA to Lake Vättern

Both atmospheric deposition and surface water inflow was found to be important input pathways for TFA and PFPrA to Lake Vättern. Among the surface water inflow, three streams (streams 5, 8, and 13) were found to be major input sources for both TFA and PFPrA (Figure 14). These streams together accounted for an input of 55% and 75% of the TFA and PFPrA input via surface water inflow, based on median estimates. The same streams were also the streams with the largest flow rate, and among the streams with the largest catchment area, together accounting for 74% of the surface water inflow. The input via these streams was in the same range relative to the flow rate, and potential contamination sources did not seem to have a large influence on the input. Two additional streams (streams 12 and 17) were also found to account for a relatively large fraction of the TFA input (22% and 7%). These two streams together only accounted for 6% of the surface water inflow. The reason for the relatively high input via these two streams, despite the lower flow rate, is not known. The two streams are surrounded by agricultural activity and a potential contamination source could be the use of pesticides with a tri-fluoromethyl structure.

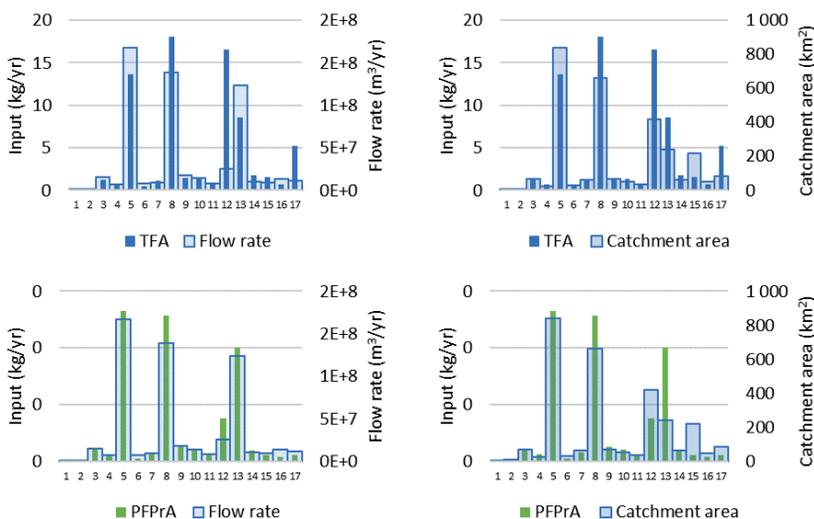


Figure 14. Input of TFA and PFPrA (kg/yr), flow rate (m^3/yr) and catchment area (km^2) for streams 1–17.

In general, a higher input for both TFA and PFPrA was observed from streams with a larger catchment area and a higher flow rate. Positive correlation was observed between the catchment area and the input of TFA ($r=0.96$, $p<0.01$) and PFPrA ($r=0.80$, $p<0.01$), and between the annual flow rate and the input of TFA ($r=0.85$, $p<0.01$) and PFPrA ($r=0.90$, $p<0.01$). The input of TFA and PFPrA via atmospheric deposition was 98 kg/yr and 1.5 kg/yr, respectively, based on the surface area of Lake Vättern of 1 900 km². Taking into consideration the size of the catchment area of Lake Vättern (6 400 km² including the lake surface), atmospheric deposition is likely an important source of TFA and PFPrA to Lake Vättern not only over the surface of the lake, but also via surface water inflow, as a result of their persistence and mobility.

4.3.1.2. Input of TFMS, PFEtS, and PFPrS to Lake Vättern

In contrast to ultra-short-chain PFCAs, surface water inflow was found to be the main input pathway for ultra-short-chain PFSAs. Similar as for PFCAs, the highest input of PFSAs was observed from streams with the largest catchment area and highest flow rate (streams 5, 8, and 13) (Figure 15). Stream 8 was found to be the main source of ultra-short-chain PFSAs, accounting for 46% (TFMS), 33% (PFEtS), and 64% (PFPrS) of the input via surface water inflow, based on median estimates. This stream runs through an urban area and is subject to different contamination sources, including landfills and sewage treatment plants. In addition, the stream receives water from a lake with known PFAS contamination located upstream.

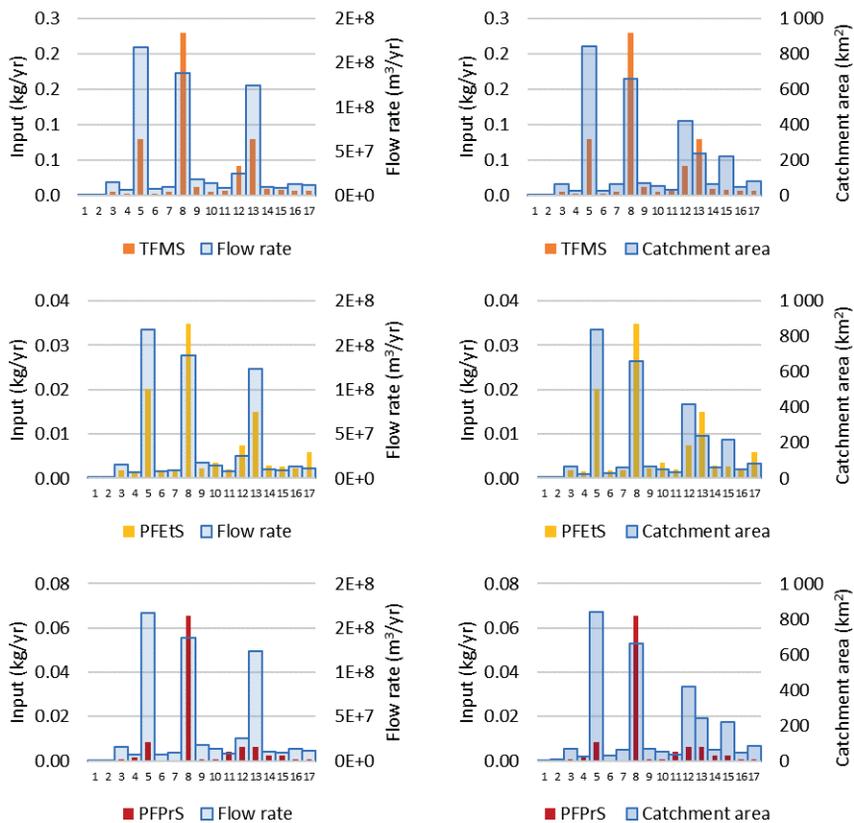


Figure 15. Input of TFMS, PFETs, and PFPrS (kg/yr), flow rate (m^3/yr) and catchment area (km^2) for streams 1–17.

5. Conclusions

This thesis has reviewed the analytical methods and summarized some of the major analytical challenges for analysis of ultra-short-chain PFAAs in aqueous samples.

Background contamination with ultra-short-chain PFAAs during sample preparation by WAX-SPE could be reduced by not storing or handling these as concentrated acids in the laboratory. TFA and PFPrA were detected at varying concentrations in the procedural blanks, and the indoor air could likely be a contamination source. The instrument background signal was increased when the mass spectrometer was vented. In addition, a major source contributing to the instrument background was found to be PTFE lining in the tubing delivering the API gas. The instrument background signal was increased each time the mass spectrometer was in standby with no API gas flow, which would allow for leached PFAAs to accumulate inside the tubing delivering the API gas to the ionization source. This resulted in an increased background signal once the mass spectrometer and the API gas flow was switched on, which then decreased with time. A constant API gas flow helped keeping the instrument background signal low.

TFA was poorly recovered by WAX-SPE and this can result in large underestimations of the TFA concentration in the samples. Using mass-labelled PFBA does not compensate for losses of TFA during the extraction. More adequate is direct injection analysis, or WAX-SPE using mass-labelled TFA, when analyzing TFA in water samples.

This thesis adds new information about contamination sources and environmental occurrence of ultra-short-chain PFAAs. Firefighting training sites, landfills, and hazardous waste management facilities were identified as point sources for all studied ultra-short-chain PFAAs. Yet diffuse atmospheric sources were found to play a major role in the contamination with TFA and PFPrA in Lake Vättern, compared to point sources. For TFMS, PFEtS, and PFPrS, surface water inflow was the most important input pathway to the lake.

The work in this thesis has shown that ultra-short-chain PFAAs, including TFMS, are globally distributed. This is the first time TFMS is reported at remote locations far away from potential point sources. The importance of hydroxyl radical initiated oxidation of volatile precursors for the global distribution and seasonal variation of TFA and PFPrA was demonstrated. The occurrence of TFMS in the Arctic environment could not be explained

neither by atmospheric oxidation of precursor compounds nor by long-range oceanic transport and the sources of TFMS to remote Arctic locations remains unknown.

The flux of TFA and PFPrA via atmospheric deposition varied seasonally and was correlated with the solar radiation but might also depend on factors such as atmospheric concentration of volatile precursors and the availability of hydroxyl radicals.

6. Future perspective

This thesis has shown that the concentrations of TFA, PFPrA, and TFMS in Lake Vättern are increasing and that diffuse sources of TFA and PFPrA play an important role. There is a need to identify major sources, and to subsequently reduce the emission of these. A first step could be to identify additional important precursor compounds by suspect screening in air and/or atmospheric deposition samples. This could be done in combination with atmospheric chemistry modelling studies to determine the rate of atmospheric oxidation and the TFA/PFPrA yield for selected precursor compounds.

The importance of atmospheric oxidation of volatile precursors as a source of TFA and PFPrA also implicates that the contamination is not caused by local emissions only. This means that measures to reduce the emissions of significant sources must be taken on a global scale. Assuming halogenated refrigerants and blowing agents contribute with a major fraction of TFA in atmospheric deposition, alternative substances, that do not contribute to TFA, should be considered. In the meantime, environmental monitoring should be continued.

There are limited data on potential toxic effects and exposure routes of ultra-short-chain PFAAs. In the work in this thesis, the observed concentrations of most ultra-short-chain PFAAs were considerably lower compared to TFA. Yet with no available data on potential toxic effects, precautionary measures should be taken. Levels in drinking water and in the environment should be monitored and major exposure routes and potential toxic effects need to be identified and evaluated.

This thesis reported concentrations of TFMS in surface snow at remote locations, showing that this substance is globally distributed. The formation of TFMS by atmospheric degradation of volatile precursors or specific transport mechanisms to remote locations could not be confirmed and should be further examined.

Additional point sources of ultra-short-chain PFAAs than those pointed out in this thesis may be of importance, and the relevance of these should be further investigated. This becomes especially important if the currently observed concentrations are found to be harmful and/or if environmental concentrations are increasing.

7. Acknowledgements

I am grateful for the opportunity to do my PhD at MTM research centre and for the great working and learning environment it has offered. First, I would like to thank my three supervisors *Ingrid Ericson Jogsten*, *Anna Kärrman*, and *Leo Yeung*, for guiding me to become the researcher that I am today. Thank you for all your help and input, and for always being available whenever I needed guidance.

Ingrid, I am grateful for the opportunity you have given to me to work with this project and for all the things that we have learned and experienced together. I am truly thankful to you for your presence and for always keeping the door open for me to ask for advice. You do have a special gift in making me feel calm and proud of the work that I have done. I will never forget about those moments when I walk into your office with a question on my mind, and after clearing my head being able to answer it myself, without you saying a word. Thank you.

Anna, my rock. Thank you for being such a great and inspiring supervisor. You are a person that I really look up to. You have been part of my education already since I started Basåret in 2011, and it has been a long, exciting, and educational journey that would not have been the same without you. Thank you for being you, for being smart, wise, and fun.

Leo, thank you for being so inspiring and encouraging. I have really enjoyed working with you. You have so much knowledge and experience and I am truly grateful for everything you have taught me.

Some people have been involved in the work presented in this thesis, and their support and contribution are invaluable. I would like to thank my co-authors *William Hartz*, *Roland Kallenborn*, and *Jack Humby*, for the great collaboration in Paper III. A special thanks to *William* and *Roland* for hosting me at University Centre in Svalbard, for all the good work and interesting discussions, and for all the great memories. Thanks to *Måns Lindell* and *Friederike Ermold* at Vätternvårdsförbundet, for all the good discussions, assistance with planning the sampling campaign in Paper IV and for collecting part of the surface water samples. Thanks to *Ingemar Zander*, *Dan Björk*, *Anna-Karin Pålsson*, and *Martin Liungman* for the assistance with collecting some of the samples for the work in Paper IV, and to *Kenneth Nilsson* at campus services for assisting with shipments of material and samples between Örebro, Visingsö and Longyearbyen. Thanks to the laboratory engineers *Per Lindström*, *Joakim Larsson*, and *Anders Crommert* for the assistance with constructing the sampling

equipment, and a special thanks to *Per* for not only being a good colleague, but also being a good and supporting friend.

I would like to thank the people that have made Örebro University such a good workplace. A special thanks to my Queen Team *Felicia Fredriks-son*, *Mio Skagerkvist*, and *Daniel Duberg* for all the fun during these years. The three of you have truly meant a lot to me and I will forever be grateful for your support and for all the treasure hunts, pranks, and all other memories that we share. *Felicia*, systra mi, thank you for being the best office mate and for always being available when I needed a hug or someone to talk to (π^{173} times and counting). Your support throughout these years is invaluable. *Mio*, the best assistant I could have wished for, always there with a lame joke when I needed one. *Daniel*, thank you for being a good friend and for always making sure I am awake at work. No one will ever make my heart beat as you and your bubbelplast. I would also like to thank *Samira Salihovic*, who have been like a big-sis to me, always supportive and encouraging, *Rudolf “bree” Aro*, for always being there with your positive energy, and *Ulrika Eriksson* for all the help in the lab and with troubleshooting instruments, and for spreading so much positive vibes around you. *Luis Morales*, gracias por tu apoyo y las conversaciones durante los coffee breaks. A big thank you to my office mates *Jordan Stubleski*, *Filip Bjurlid*, and *Ingrid Rijk*, who have made my time joyful by sharing life, laughter and wisdom in the office. *Jordan*, I will never forget how much you laughed every time I accidently lowered my chair, thank you for all the fun times and awesome hugs!

Thanks to all my fellow PhD candidates, *Greta Nilén*, *Tim Sinioja*, *Florian Dubocq*, *Monika Lam*, *Christine Schönlaui*, *Mélanie Blanc*, *Kristina Åhlgren*, *Josefine Persson*, *Lisanna Sinisalu*, and *Ayan Au Musse*, for all the fun during these years.

Thanks to all my current and former colleagues at Örebro University, some of them are *Steffen Keiter*, *Tuulia Hyötyläinen*, *Anna Rotander*, *Heideloire Fiedler*, *Victor Castro Alves*, *Manon Fallet*, *Syed Akhtar*, *Andi Alijagic*, *Arslan Hashmi*, *Cathrin Veenaas*, *Carl Lemon*, *Sofia Francois*, *Cissi Carlsson*, *Dawei Geng*, *Ivan Titaley*, *Fangfang Chen*, *Breanne Holmes*, *David Wigren*, *Danielle Ydstål*, *Siamak Sobhanei*, *Abeer Baabish*, and *Mohammad Sadia*.

A special thanks to *Thanh Wang*, *Maria Larsson*, *Viktor Sjöberg*, *Magnus Engwall*, *Mattias Bäckström*, *Stefan Karlsson*, *Nikolai Scherbak*, *Alf Ekblad*, *Irina Kalbina*, *Jana Jass*, *Håkan Berg*, and *Ulla Stenlund*, you have all been part of my education prior to my PhD and you have played a

big role in my decision to continue my education after my BSc. I am grateful for all the inspiration and support that you have provided throughout my years at Örebro University.

In addition to the above-mentioned people, there some amazing persons that have made my time at Örebro University so joyful. Thanks to *Kristina Pettersson* and *Cajsa Gunnarsson* for all the breakfast laughs, and to *Jörgen Stenlund*, *Owe Persson*, *Erik Sjöstedt*, *Barbro Bergfeldt*, and *Bodil Sundberg* for all the fun and interesting lunch conversations.

Some people outside from Örebro University have also played an important role in this journey. A special thanks to my Svalbard crew *Helene Fiedler*, *Veerle van Winden*, and *Nora Gallarotti* and the members of the snow group *Marina Cerasa*, *Rémi Dallmayr*, and *Kalliroyi Sdougkou*, for making my time in Longyearbyen so much fun and unforgettable! Ski marathons, winter camping, or late study nights in the common kitchen watching the sun never set would not have been the same without you and your awesomeness!

I especially would like to acknowledge two persons that in one way or another always have provided me with support and inspiration. My warmest thanks to my dear friend and adventure partner *Jana Weiss*, for encouraging me to take the course at University Centre in Svalbard, thank you for all the memories that we share and for always being there to help, advise and support. To my amiga and former supervisor *Ana Ballesteros-Gómez*, thank you for inspiring me to take a PhD in the first place. Thank you for all the great memories, in Amsterdam, Córdoba, and in Örebro, and for all the support you have given me throughout the years I have known you.

I would like to thank all my friends outside of my PhD life, who have offered an environment in which I could let go of all the stress, blank contamination, and non-working instruments. To my friends *Marie Björklund*, *Karin Abrin*, *Natalie Järling*, *Evelina Hjälms*, *Therese Lindberg*, *Amanda Sletten*, *Sandra Hallin*, *Linda Abrahamsson*, and *Jessica Adolfs-son*, thank you for all the fun times and for your support throughout these years, it has meant more to me than you know. Thanks to my kitesurf and travel crew *Elin Nilsson*, *Elin Mattson*, *Naima Linderson*, *Astrid Sjögren*, and *Ricky Jansson*, for always being up for fun, travels and adventures. Thanks to my first ever university-buddy *Johanna Nystedt* and to my cousin *Jimmy Sohlman*, for always being up for having a good time.

I would also like to thank the people responsible for making my time in Örebro so much fun! To my Tower Beach crew, chasing the wind with

you has truly been the most efficient stress management tool one could have. Big thanks to my running and beer drinking buddies in Mikkeller Running Club, and to all members of LK Gränslöst for all the Thursday runs. Also, a big thank you to all coaches and members of CrossFit Örebro, I couldn't have had a better place to spend my evenings after a stressful day at work. A special thank you to *Coach Lucas* for introducing me to the Disney Princesses, their contribution to this thesis is significant.

I especially want to acknowledge my parents, *Björn* and *Kristina*, I could not have done this without you and your unconditional love and support. Thank you for always being there for me.

And last but most certainly not least, thank you to the one and only *Koira* <3

References

1. KEMI (Swedish Chemicals Agency) *Occurrence and use of highly fluorinated substances and alternatives*; 2015.
2. OECD (Organisation for Economic Co-operation and Development) *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance*; Series on Risk Management, 61, 2021.
3. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; J., v. L. S. P., Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr. Environ. Assess. Manag.* **2011**, *7*, (4), 513-541.
4. Sharifan, H.; Bagheri, M.; Wang, D.; Burken, J. G.; Higgins, C. P.; Liang, Y.; Liu, J.; Schaefer, C. E.; Blotvogel, J., Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone. *Sci. Total Environ.* **2021**, *771*.
5. Scheruer, M.; Nödler, K.; Freeling, F.; Janda, J.; Happel, O.; Riegel, M.; Müller, U.; Rüdiger Storck, F.; Fleig, M.; Lange, F. T.; Brunsch, A.; Brauch, H. J., Small, mobile, persistent: Trifluoroacetate in the water cycle - Overlooked sources, pathways and consequences for drinking water supply. *Water Res.* **2017**, *126*, 460-471.
6. Cousins, I. T.; Ng, C. A.; Wang, Z.; Scheringer, M., Why is high persistence alone a major cause of concern? *Environmental Science: Processes & Impacts* **2019**, *21*, 781-792.
7. UBA (German Environment Agency) *REACH: Improvement of guidance and methods for the identification and assessment of PMT/vPvM substances*; UBA TEXTE, 126/2019, 2019.
8. Zhang, W.; Zhang, Y.; Taniyasu, S.; Yeung, L. W. Y.; Lam, P. K. S.; Wang, J.; Li, X.; Yamashita, N.; Dai, J., Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants in economically developed areas of China. *Environ. Pollut.* **2013**, *176*, 10-17.
9. Barzen-Hanson, K. A.; Field, J. A., Discovery and implications of C2 and C3 perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. *Environ. Sci. Technol. Lett.* **2015**, *2*, (4), 95-99.
10. Zhai, Z.; Wu, J.; Hu, X.; Li, L.; Guo, J.; Zhang, B.; Hu, J.; Zhang, J., A 17-fold increase of trifluoroacetic acid in landscape waters of Beijing, China during the last decade. *Chemosphere* **2015**, *129*, 110-117.
11. Zahn, D.; Frömel, T.; Knepper, T. P., Halogenated methanesulfonic acids: A new class of organic micropollutants in the water cycle. *Water Res.* **2016**, *101*, 292-299.

12. Schulze, S.; Zahn, D.; Montes, R.; Rodil, R.; Quintana, J. B.; Knepper, T. P.; Reemtsma, T.; Berger, U., Occurrence of emerging persistent and mobile organic contaminants in European water samples. *Water Res.* **2019**, *153*, 80-90.
13. Yeung, L. W. Y.; Stadey, C.; Mabury, S. A., Simultaneous analysis of perfluoroalkyl and polyfluoroalkyl substances including ultrashort-chain C2 and C3 compounds in rain and river water samples by ultra performance convergence chromatography. *J. Chromatogr. A* **2017**, *1522*, 78-85.
14. Montes, R.; Rodil, R.; Placer, L.; Wilms, J. M.; Cela, R.; Quintana, J. B., Applicability of mixed-mode chromatography for the simultaneous analysis of C1-C18 perfluoroalkylated substances. *Anal. Bioanal. Chem.* **2020**, *412*, 4849-4856.
15. Wallington, T. J.; Schneider, W. F.; Worsnop, D. R.; Nielsen, O. J.; Sehested, J.; Debruyn, W. J.; Shorter, J. A., The environmental impact of CFC replacements - HFCs and HCFCs. *Environ. Sci. Technol.* **1994**, *28*, (7), 320-326.
16. Jordan, A.; Frank, H., Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFCs. *Environ. Sci. Technol.* **1999**, *33*, (4), 522-527.
17. Frank, H.; Christoph, E. H.; Holm-Hansen, O.; Bullister, J. L., Trifluoroacetate in ocean waters. *Environ. Sci. Technol.* **2002**, *36*, 12-15.
18. Scott, B. F.; Macdonald, R. W.; Kannan, K.; Fisk, A.; Witter, A.; Yamashita, N.; Durham, L.; Spencer, C.; Muir, D. C. G., Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans. *Environ. Sci. Technol.* **2005**, *39*, 6555-6560.
19. Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G., Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. *Nature* **2001**, *412*, 321-324.
20. Cui, J.; Guo, J.; Zhai, Z.; Zhang, J., The contribution of fluoropolymer thermolysis to trifluoroacetic acid (TFA) in environmental media. *Chemosphere* **2019**, *222*, 637-644.
21. Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J., Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316-3321.
22. Martin, J. W.; Ellis, D. A.; Mabury, S. A., Atmospheric Chemistry of Perfluoroalkanesulfonamides: Kinetic and Product Studies of the OH Radical and Cl Atom Initiated Oxidation of N-Ethyl Perfluorobutanesulfonamide. *Environ. Sci. Technol.* **2006**, *40*, (3), 864-872.
23. D'eon, J.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A., Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol,

- C4F9SO2N(CH3)CH2CH2OH: kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* **2006**, *40*, 1862-1868.
24. Wujcik, C. E.; Cahill, T. M.; Seiber, J. N., Determination of trifluoroacetic acid in 1996-1997 precipitation and surface waters in California and Nevada. *Environ. Sci. Technol.* **1999**, *33*, (10), 1747-1751.
25. Berg, M.; Müller, S. R.; Mühlemann, J.; Wiedmer, A.; Schwarzenbach, R. P., Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. *Environ. Sci. Technol.* **2000**, *34*, (13), 2675-2683.
26. Scott, B. F.; Mactavish, D.; Spencer, C.; Strachan, W. M. J.; Muir, D. C. G., Haloacetic acids in canadian lake waters and precipitation. *environ. Sci. Technol.* **2000**, *30*, (20), 4266-4272.
27. Von Sydow, L. M.; Grimvall, A. B.; Borén, H. B.; Laniewski, K.; Nielsen, A. T., Natural background levels of trifluoroacetate in rain and snow. *Environ. Sci. Technol.* **2000**, *34*, (15), 3115-3118.
28. Scott, B. F.; Spencer, C.; Martin, J. W.; Barra, R.; Bootsma, H. A.; Jones, K. C.; Johnston, A. E.; Muir, D. C. G., Comparison of haloacetic acids in the environment of the northern and southern hemispheres. *environ. Sci. Technol.* **2005**, *39*, 8664-8670.
29. Zhang, J.; Zhang, Y.; Li, J.; Hu, J.; Ye, P.; Zeng, Z., Monitoring of trifluoroacetic acid concentration in environmental waters in China. *Water Res.* **2005**, *39*, 1331-1339.
30. Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G., Poly and perfluorinated carboxylates in North American precipitation. *Environ. Sci. Technol.* **2006**, *40*, (23), 7167-7174.
31. Taniyasu, S.; Kannan, K.; Yeung, L. W. Y.; Kwok, K. Y.; Lam, P. K. S.; Yamashita, N., Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2-C4) in precipitation by liquid chromatography-tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C5-C8). *Anal. Chim. Acta* **2008**, *619*, 221-230.
32. Wang, Q.; Wang, X.; Ding, X., Rainwater trifluoroacetic acid (TFA) in Guangzhou, South China: Levels, wet deposition fluxes and source implication. *Sci. Total. Environ.* **2014**, *468-469*, 272-279.
33. Freeling, F.; Behringer, D.; Heydel, F.; Scheurer, M.; Ternes, T. A.; Nödler, K., Trifluoroacetate in Precipitation: Deriving a Benchmark Data Set. *Environ. Sci. Technol.* **2020**, *54*, 11210-11219.
34. Pickard, H. M.; Criscitiello, A. S.; Persaud, D., Spencer, C.; Muir, D. C. G.; Lehnerr, I.; Sharp, M.; De Silva, A. O.; Young, C. J., Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations. *Geophys. Res. Lett.* **2020**, *47*, 1-11.

35. Burkholder, J. B.; Cox, R. A.; Ravishankara, A. R., Atmospheric degradation of ozone depleting substances, their substitutes, and related species. *Chem. Rev.* **2015**, *115*, 3704–3759.
36. Kwok, K. Y.; Taniyasu, S.; Yeung, L. W. Y.; Murphy, M. B.; Lam, P. K. S.; Horii, Y.; Kannan, K.; Petrick, G.; Sinha, R. K.; Yamashita, N., Flux of perfluorinated chemicals through wet deposition in Japan, the United States, and several other countries. *Environ. Sci. Technol.* **2010**, *44*, (18), 7043-7049.
37. EFSA (European Food Safety Authority) *Reasoned opinion on the setting of MRLs for saflufenacil in various crops, considering the risk related to the metabolite trifluoroacetic acid (TFA)*; 2014.
38. EFSA (European Food Safety Authority) *Peer review of the pesticide risk assessment of the active substance flurtamone*; 2016.
39. Kazakovaa, A. N.; Vasilyeva, A. V., Trifluoromethanesulfonic acid in organic synthesis. *Russ. J. Org. Chem.* **2017**, *53*, (4), 485–509.
40. Aravindan, V.; Gnanaraj, J.; Madhavi, S.; Liu, H. K., Lithium-ion conducting electrolyte salts for lithium batteries. *Chem. - Eur. J.* **2011**, *17*, 14326 – 14346.
41. Filipovic, M.; Berger, U.; S. McLachlan, M., Mass Balance of Perfluoroalkyl Acids in the Baltic Sea. *Environ. Sci. Technol.* **2013**, *47*, 4088-4095.
42. Cahill, T. M.; Thomas, C. M.; Schwarzbach, S. E.; Seiber, J. N., Accumulation of trifluoroacetate in seasonal wetlands in California. *Environ. Sci. Technol.* **2001**, *35*, 820-825.
43. Agency, U. G. E. *Protecting the sources of our drinking water: The criteria for identifying persistent, mobile and toxic (PMT) substances and very persistent and very mobile (vPvM) substances under EU Regulation REACH (EC) No 1907/2006*; UBA TEXTE, 127/2019, 2019.
44. Likens, G. E.; Tartowski, S. L.; Berger, T. W.; Richey, D. G.; Driscoll, C. T.; Frank, H. G.; Klein, A., Transport and fate of trifluoroacetate in upland forest and wetland ecosystems *Proc. Natl. Acad. Sci.* **1997**, *94*, 4499–4503.
45. Richey, D. G.; Driscoll, C. T.; Likens, G. E., Soil retention of trifluoroacetate. *Environ. Sci. Technol.* **1997**, *31*, 1723-1727.
46. Rollins, A.; Barber, J.; Elliott, R.; Wood, B., Xenobiotic monitoring in plants by ¹⁹F and ¹H nuclear magnetic resonance imaging and spectroscopy. *Plant Physiol.* **1989**, *91*, 1243-1246.
47. Zhang, L.; Sun, H.; Wang, Q.; Chen, H.; Yao, Y.; Zhao, Z.; Alder, A. C., Uptake mechanisms of perfluoroalkyl acids with different carbon chain lengths (C2-C8) by wheat (*Triticum aestivum* L.). *Sci. Total. Environ.* **2019**, *654*, 19–27.

48. Scheurer, M.; Nödler, K., Ultrashort-chain perfluoroalkyl substance trifluoroacetate (TFA) in beer and tea – An unintended aqueous extraction. *Food Chem.* **2021**, *351*, 129304.
49. Boutonnet, J. C.; Bingham, P.; Calamari, D.; de Rooij, C.; Franklin, J.; Kawano, T.; Libre, J. M.; McCulloch, A.; Malinverno, G.; Odom, J. M.; Rusch, G. M.; Smythe, K.; Sobolev, I.; Thompson, R.; Tiedje, J. M., Environmental risk assessment of trifluoroacetic acid. *Hum. Ecol. Risk Assess.* **1999**, *5*, (1), 59-124.
50. Berends, A. G.; Boutonnet, J. C.; De Rooij, C. G.; Thompson, R. S., Toxicity of trifluoroacetic acid to aquatic organisms. *Environ. Toxicol. Chem.* **1999**, *18*, (5), 1053-1059.
51. Duan, Y.; Sun, H.; Yao, Y.; Meng, Y.; Li, Y., Distribution of novel and legacy per-/polyfluoroalkyl substances in serum and its associations with two glycemic biomarkers among Chinese adult men and women with normal blood glucose levels. *Environ. Int.* **2020**, *134*.
52. Scott, B. F.; Spencer, C.; Marvin, C. H.; Mactavish, D. C.; Muir, D. C. G., Distribution of haloacetic acids in the water columns of the Laurentian Great Lakes and Lake Malawi. *Environ. Sci. Technol.* **2002**, *36*, 1893-1898.
53. Nielsen, O. J.; Javadi, M. S.; Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Singh, R., Atmospheric chemistry of CF₃CF=CH₂: Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O₃. *Chem. Phys. Lett.* **2007**, *439*, 18-22.
54. Hurley, M. D.; Wallington, T. J.; Javadi, M. S.; Nielsen, O. J., Atmospheric chemistry of CF₃CF=CH₂: Products and mechanisms of Cl atom and OH radical initiated oxidation. *Chem. Phys. Lett.* **2008**, *450*, 263-267.
55. Orkin, V. L.; Martynova, L. E.; Ilichev, A. N., High-Accuracy Measurements of OH Reaction Rate Constants and IR Absorption Spectra: CH₂=CF-CF₃ and trans-CHF=CH-CF₃. *J. Phys. Chem. A* **2010**, *114*, 5967-5979.
56. WMO (World Meteorological Organization) *Scientific Assessment of Ozone Depletion: 2010*; Global Ozone Research and Monitoring Project, 52, Geneva, Switzerland, 2011.
57. Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Brunner, D.; O'Doherty, S.; Buchmann, B., Future emissions and atmospheric fate of HFC-1234yf from mobile air conditioners in Europe. *Environ. Sci. Technol.* **2012**, *46*, (3), 1650-1658.
58. Kazil, J.; McKeen, S.; Kim, S. W.; Ahmadov, R.; Grell, G. A.; Talukdar, R. K.; Ravishankara, A. R., Deposition and rainwater concentrations of trifluoroacetic acid in the United States from the use of HFO-1234yf. *J. Geophys. Res. Atmos.* **2014**, *119*, 14059-14079.

59. Wang, Z.; Wang, Y.; Li, J.; Henne, S.; Zhang, B.; Hu, J.; Zhang, J., Impacts of the degradation of 2,3,3,3-tetrafluoropropene into trifluoroacetic acid from its application in automobile air conditioners in China, the United States, and Europe. *Environ. Sci. Technol.* **2018**, *52*, 2819–2826.
60. Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen, O. J., Role of Excited CF₃CFHO Radicals in the Atmospheric Chemistry of HFC-134a. *J. Phys. Chem.* **1996**, *100*, 18116-18122.
61. Scott, B. F.; Alaei, M., Determination of Haloacetic acids from Aqueous Samples Collected from the Canadian Environment Using an In Situ Derivatization Technique. *Water. Qual. Res. J.* **1998**, *33*, (2), 279-293.
62. Wujcik, C. E.; Cahill, T. M.; Seiber, J. N., Extraction and Analysis of Trifluoroacetic Acid in Environmental Waters. *Anal. Chem.* **1998**, *70*, 4074-4080.
63. Janda, J.; Nödler, K.; Brauch, H. J.; Zwiener, C.; Lange, F. T., Robust trace analysis of polar (C₂-C₈) perfluorinated carboxylic acids by liquid chromatography-tandem mass spectrometry: method development and application to surface water, groundwater and drinking water. *Environ. Sci. Pollut. Res.* **2018**.
64. Berger, U.; Glynn, A.; Holmström, K. E.; Berglund, M.; Halldin Ankarberg, E.; Törnkvist, A., Fish consumption as a source of human exposure to perfluorinated alkyl substances in Sweden – Analysis of edible fish from Lake Vättern and the Baltic Sea. *Chemosphere* **2009**, *76*, 799-804.
65. SMHI (Swedish Meteorological and Hydrological Institute). *Fakta om Vättern*. <https://www.smhi.se/kunskapsbanken/hydrologi/de-stora-sjoarna/fakta-om-vattern-1.4730> (accessed 2021-08-06).
66. SMHI (Swedish Meteorological and Hydrological Institute). *Meteorological observations*. <https://www.smhi.se/data> (accessed 2021-08-06).
67. SMHI (Swedish Meteorological and Hydrological Institute). *Vattenwebb*. <https://vattenwebb.smhi.se> (accessed 2021-08-06).
68. Kotamarthi, V. R.; Rodriguez, J. M.; Ko, M. K. W.; Tromp, T. K.; Sze, N. D., Trifluoroacetic Acid from Degradation of HCFCs and HFCs: A Three-Dimensional Modeling Study. *J. Geophys. Res. Atmos.* **1998**, *103*, 5747-5758.
69. Mallet, C. R.; Lu, Z.; Mazzeo, J. R., A study of ion suppression effects in electrospray ionization from mobile phase additives and solid-phase extracts. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 49–58.
70. Taniyasu, S.; Yamashita, N.; Moon, H. B.; Kwok, K. Y.; Lam, P. K. S.; Horii, Y.; Petrick, G.; Kannan, K., Does wet precipitation represent

local and regional atmospheric transportation by perfluorinated alkyl substances? *Environ. Int.* **2013**, *55*, 25-32.

71. Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Sulbaek Andersen, M. P., Formation of C7F15COOH (PFOA) and Other Perfluorocarboxylic Acids during the Atmospheric Oxidation of 8:2 Fluorotelomer Alcohol. *Environ. Sci. Technol.* **2006**, *40*, 924-930.

72. Skaar, J. S.; Raeder, E. M.; Lyche, J. L.; Ahrens, L.; Kallenborn, K., Elucidation of contamination sources for poly- and perfluoroalkyl substances (PFASs) on Svalbard (Norwegian Arctic). *Environ. Sci. Pollut. Res.* **2019**, *26*, 7356-7363.

73. Ali, A. M.; Langberg, H. A.; Hale, S. E.; Kallenborn, K.; Hartz, W. F.; Mortensen, Å. K.; Ciesielski, T. M.; McDonough, C. A.; M., J. B.; Breedveld, G. D., The fate of poly- and perfluoroalkyl substances in a marine food web influenced by land-based sources in the Norwegian Arctic. *Environ. Sci.: Processes Impacts* **2021**, *23*, 588-604.

74. Rohrer, F.; Berresheim, H., Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation. *Nature* **2006**, *442*.

75. Banks, R. E.; Clarke, E. K.; Johnson, E. P.; Sharratt, P. N., Environmental aspects of fluorinated materials: part 31 Comparative life-cycle assessment of the Impacts associated with fire extinguishants HFC-227ea and IG-541. *Process Saf. Environ. Prot.* **1998**, *76*, (3), 229-238.

76. Jackson, D. A.; Young, C. J.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A., Atmospheric Degradation of Perfluoro-2-methyl-3-pentanone: Photolysis, Hydrolysis and Hydration. *Environ. Sci. Technol.* **2011**, *45*, 8030-8036.

PUBLICATIONS *in the series*
ÖREBRO STUDIES IN CHEMISTRY

1. Bäckström, Mattias, *On the Chemical State and Mobility of Lead and Other Trace Elements at the Biogeosphere/Technosphere Interface*. 2002.
2. Hagberg, Jessika, *Capillary zone electrophoresis for the analysis of low molecular weight organic acids in environmental systems*. 2003.
3. Johansson, Inger, *Characterisation of organic materials from incineration residues*. 2003.
4. Dario, Mårten, *Metal Distribution and Mobility under alkaline conditions*. 2004.
5. Karlsson, Ulrika, *Environmental levels of thallium – Influence of redox properties and anthropogenic sources*. 2006.
6. Kärrman, Anna, *Analysis and human levels of persistent perfluorinated chemicals*. 2006.
7. Karlsson Marie, *Levels of brominated flame retardants in humans and their environment: occupational and home exposure*. 2006.
8. Löthgren, Carl-Johan, *Mercury and Dioxins in a MercOx-scrubber*. 2006.
9. Jönsson, Sofie, *Microextraction for usage in environmental monitoring and modelling of nitroaromatic compounds and haloanisoles*. 2008.
10. Ericson Jogsten, Ingrid, *Assessment of human exposure to per- and polyfluorinated compounds (PFCs). Exposure through food, drinking water, house dust and indoor air*. 2011.
11. Nilsson, Helena, *Occupational exposure to fluorinated ski wax*. 2012.
12. Salihovic, Samira, *Development and Application of High-throughput Methods for Analysis of Persistent Organic Pollutants in Human Blood*. 2013.
13. Larsson, Maria, *Chemical and bioanalytical characterisation of PAH-contaminated soils. Identification, availability and mixture toxicity of AhR agonists*. 2013.

14. Kalaitzaki, Argyro, *Biocompatible microemulsions: formulation, encapsulation of bioactive compounds and their potential application*. 2014
15. Saqib, Naeem, *Distribution and chemical association of trace elements in incinerator residues and mining waste from a leaching perspective*. 2016
16. Chatzidaki, Maria, *Formulation and characterization of W/O nano-dispersions for bioactive delivery applications*. 2016
17. Geng, Dawei, *Gas Chromatography-Atmospheric Pressure Chemical Ionization-Tandem Mass Spectrometry Methods for the Determination of Environmental Contaminants*. 2016
18. Eriksson, Ulrika, *Contribution of polyfluoroalkyl phosphate esters (PAPs) and other precursor compounds to perfluoroalkyl carboxylates (PFCA) in humans and the environment*. 2016
19. Riddell, Nicole, *Packed Column Supercritical Fluid Chromatography: Applications in Environmental Chemistry*. 2017
20. Bjurlid, Filip, *Polybrominated dibenzo-p-dioxins and furans: from source of emission to human exposure*. 2017
21. Stableski, Jordan, *Assessing the longitudinal trend of POP concentrations in humans using high-throughput sample preparation methods developed for low-volume samples*. 2018
22. Persson, Josefin, *Indoor air quality and chemical emissions of organic compounds in newly built low-energy preschools*. 2018
23. Schönlaug, Christine, *Microplastics in the marine environment and the assessment of potential adverse effects of associated chemicals*. 2019
24. Mullin, Lauren, *Advances in Mass Spectrometry for the Analysis of Emerging Persistent Organic Pollutants*. 2019
25. Koch, Alina, *Characterization of PFASs and Organofluorine in Freshwater Environments - Transfer from water to land via emergent aquatic insects*. 2020
26. Dubocq, Florian, *Optimizing nontarget workflows for identification of organic contaminants in various matrices*. 2020
27. Åhlgren, Kristina, *Environmental impact of alum shale mining in Kvarntorp, Närke, Sweden*. 2020

28. Aro, Rudolf, *Organofluorine Mass Balance and Per- and Polyfluoroalkyl Substance Analysis of Environmental Samples and Human Blood*. 2021
29. Björnsdotter, Maria K. *Ultra-short-chain perfluoroalkyl acids: Environmental occurrence, sources and distribution*. 2021

