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food science

Master Thesis 2016
60 credits

Selected perfluorinated compounds in the sediment of an arctic freshwater lake: A case study at Kapp Linnè

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“The red dust comes from southern lands
And ends up in our food.
Belive you me, it´s bad for tea
And more than spoils my mood.

I understand your tummy aches,
You poorly little bear.
it´s crystal clear it´s comming here:
Red dust is bad, beware!”

-Mrs. Walrus

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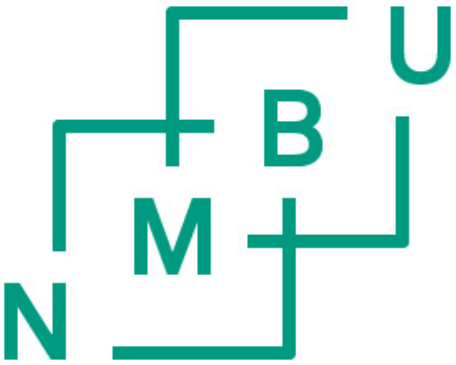
This thesis was written at the Department of Chemistry, Biotechnology and Food Science at the Norwegian University of Life Sciences (NMBU) in Ås, Norway. The work was done in collaboration with the Department of Technology at the University Centre in Svalbard (UNIS) in Svalbard.



Acknowledgements

During my bachelor program I got the opportunity to study on Svalbard. I fell in love with the place, so when I had to find a master thesis I started to look for something related to the Arctic. I found this topic, and have not regretted it for a second. The last year has been challenging, but I have loved every minute of it.

I would first like to thank my supervisor, Roland Kallenborn, for giving me the opportunity to do research in the Arctic, also for helpful discussions and guidance throughout the project.

I would also like to thank Jøran Solnes Skaar, whom I worked alongside with from the planning phase to the writing, due to similar topics on our thesis. We have had many discussions that have helped me a lot. Thanks for the cooperation Jøran.

I would also like to thank the people that helped me along the way. Thanks to Eirk Ræder for helping with the method development and instrumental analysis. Thanks to Tatiana Drotikova for all the help at UNIS. I would also like to thank Lutz Ahrens, Siri Alexson and Jelena Rakovic for accompanying Jøran and me for the field work. Also a big thanks to the logistics department at UNIS for all the help planning routs, equipment and the safety during the fieldwork.

This project was conducted in collaboration between the Norwegian University of Life Sciences (NMBU) and the University Centre in Svalbard (UNIS), Department of Arctic Technology in Longyearbyen. Financial support for this project was provided from the NMR/AMAP

funded project: Combined effects of Climate and pollutants in the Arctic as well as from UNIS funds.

Abstract

After their discovery in the environment in the early 2000s, polyfluorinated alkylated substances and perfluorinated alkylated substances (PFASs) received much attention because of their persistence, bioaccumulation potential, and possible adverse effects in organisms. Concentrations have been monitored in the biotic and abiotic environment. Due to atmospheric and oceanic transport PFAS have been unambiguously distributed in the environment, also in the Arctic.

Linnévatnet is a remote lake located on the west coast of Nordenskíold land, Spitsbergen, Svalbard. The aim of this thesis is to determine the levels of selected PFASs in the sediment of Linnévannet with an emphasis on the short chained compounds, and examine some possible point source locations on Svalbard. To examine this, a modified method meant for biota was used. An aim will be to se how the method performs, and if it is suitable for sediment analysis.

The sampling was carried out at Linnévatnet in June of 2015. Samples where taken with a grab sampler from a rubber boat or from the ice. The samples where transported to the field station and stored in a freezer until transport back to UNIS. At UNIS the samples where dried and packed, then sent to NMBU where the rest of the extraction and clean up were carried out. The extracts where analyzed at campus Adamsstuen, at the Institute for Food Safety and Infection Biology (MatInf, NMBU).

The recoveries where found to be to low, giving the results a significant uncertainty. The results where comparable with other studies conducted at similar sites in the Canadian Arctic. PFCAs and PFOS where found in Linnévatnet at low concentrations. The airport where identified as a possible local source, where high levels of PFSAs and PFCAs where found, suggesting fire fighting foam as a possible source from the associated fire training site.

Sammendrag

Etter at de ble oppdaget i miljøet tidlig på 2000-tallet har perfluoroalkyl og polyfluoroalkyl forbindelser fått mye vitenskapelig oppmerksomhet. De har blitt vist og være lite nedbrytbare, ha potensiale til og bioakkumulere, og ha negative effekter i organismer. Konsentrasjoner har blitt overvåket i biotiske og abiotiske prøver. På grunn av atmosfærisk og oseanisk transport er PFAS påvist i de fleste miljøer, også i Arktis.

Linnévatnet er en avsidesliggende innsjø på vestkysten av Spitsbergen, Svalbard. Målet med denne oppgaven er å undersøke konsentrasjonene av PFASs i sediment i Linnévatnet, og se om det er noen lokale kilder i nærheten. For å undersøke dette har en metode for biota blitt modifisert for og analysere sediment. Dette har bli vurdert hvor godt denne metoden fungerer for sediment.

Prøvetakingen har blitt utført ved Linnévatnet i juni 2015. Prøvene ble tatt med en grab sampler fra båt og fra isen. Prøvene ble transportert til felt stasjonen og lagret i en fryser (-20°C) til transport tilbake til UNIS. På UNIS ble prøvene tørket og pakket, slik at de kunne sendes til NMBU hvor prøvene ble ekstrahert og renset. Ekstraktene ble analysert på Campus Adamstuen, Institutt for Matsikkerhet og Infeksjonsbiologi (NMBU)

Gjenvinningen av intern standardene var generelt for lave, noe som bidra betydelig til metodeusikkerheten. Konsentrasjonene var sammenlignbare med resultater fra andre studier fra Canada. PFCA og PFOS ble funnet i Linnévatnet i lave konsentrasjoner. Flyplassen

ble også identifisert som en punkt kilde, der PFSA og PFCA ble funnet, noe som kan hinte om at brann skum er en mulig kilde.

Abbreviations

10:2 FTS - 10:2 Fluorotelomer sulfonate
6:2 FTS - 6:2 Fluorotelomer sulfonate
8:2 FTS - 8:2 Fluorotelomer sulfonate
A -Areal
APCI - Atmospheric pressure chemical ionization
C - Carbon
cm – Centimeter
DNA - Deoxyribonucleic acid
ECF - Electro chemical fluorination
ESI - Electrospray ionization
EU – European Union
F - flour
FOSA - Perfluoro octansulfonamide
FT - Fluor telomere
FTOHs - Fluorotelomer alcohols
FTS - Fluorotelomer sulfonates
g - Gram
GC/MS - Gas chromatography/mass spectrometry
HF - Hydrogen fluorite
HPLC – High pressure liquid chromatography
IKBM - Department of Chemistry, Biotechnology and Food Science
ISTD - Internal standard
Kd - sediment–water partition coefficient
LD 50 - lethal dose 50%
LOAEL - Lowest observed adverse effect level
LOD – Limit of detection
LOQ - Limit of quantification
LRT- Long Range Transport
m - Mass
MDL - method detection limit
MQL – Method quantification limit
MeFOSE - N-methyl perfluorooctane sulfonamido ethanol
mm - Millimeter
MQL - Method Quantification Limit
MS - Mass spectrometry
MSD- Mass Selective Detector
MS/MS - Tandem mass spectrometry
n - number of carbon atoms
N-EtFOSA-M - N-ethylPerfluoro-1-octaneSulfonamide
N-EtPFOSE - 2(N -ethyl perfluorooctane sulfonamido)ethanol
NMBU - Norwegian University of life Sciences
N-MeFOSA-M - N-Methylperfluoro-1-octanesulfonamide
N-MeFOSE-M - 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol
NA - Not available
NEtFOSE-M - 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol

ng - Nano gram
NMBU – Norwegian University of Life Sciences
NOAEL - No observed adverse effect level
NPI - Norwegian Polar institute
PCB – polychlorinated biphenyls
PFAS - Perfluorinated alkylated substances or Polyfluorinated alkylated substances
PFBA - Perfluorobutanoic acid
PFBS - Perfluorobutane sulfonate
PFCAs - Perfluorinated carboxylate acids
PFDA - Perfluorodecanoic acid
PFDoA - Perfluorododecanoic acid
PFHpA - Perfluoroheptanoic acid
PFHxA - Perfluorohexanoate
PFHxS - Perfluorohexane sulfonate
PFNA - Perfluorononanoic acid
PFOA - Perfluorooctanoic acid
PFOS - Perfluorooctan sulfonate
PFOSA - Perfluorooctane sulfonamide
PFPeA - Perfluoropentanoic acid
PFSAs - Perfluoroalkylsulfonic acid / perfluoroalkylsulfonates
PFTeA - Perfluorotetradecanoic acid
PFTrA - Perfluorotridecanoic acid
PFUnA - Perfluoroundecanoic acid
pg - pico gram
POP - Persistent organic pollutants
PP - Polypropylene
Q - Quadrupole
QQQ- triple quadropole
REACH - Registration, Evaluation, Authorization and Restriction of Chemicals
RFF- relative response factor
RSTD - Recovery standard
SLU - Swedish University of Agricultural Sciences
T4 - thyroxin
TFE - Tetra flour ethylene
TTR - transthyretin
UNIS - University Centre on Svalbard
US EPA – United States environmental protection agency
µm – Micrometer

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1. Aim

Based on the results of the master thesis of Garsjø (2013), high levels of selected short-chained perfluorinated compounds was found in Arctic char *(Salvelinus alpinus)* from lake Linnévatnet, Nordenskiold land, Spitsbergen, Svalbard. Some of these compounds are not known to bioaccumulate, therefore this might indicate high concentrations of these compounds also in the sediment. In the present study, a slightly modified version of the method used by Garsjø (2013) will be used to extract and clean up the samples. This method has not to my knowledge been used for sediment before.

The aim of this study was to determine the levels of perfluorinated alkylated compounds in the sediment of lake Linnévannet with an emphasis on the short-chained compounds, and examine some possible point-source locations on Svalbard. Another aim was to evaluate the performance of the analytical procedure and its suitability for sediment analysis.

2. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) is a family of anthropogenic compounds, with similar chemical properties, which have a completely or partially fluorinated alkyl backbone (Bossi et al. 2015; Buck et al. 2011). Production of PFAS started in the 1950s and had a considerably increase during the 1970s, due to high demand and widespread use in both industrial and consumer products (Ahrens, Lutz et al. 2011; Buck et al. 2011; Lyu et al. 2015; Nøst et al. 2014). Production and use of these products have lead to a substantial (Ahrens, L. et al. 2011; Buck et al. 2011; Butt et al. 2010), and PFAS are today detected in river water, oceans, sediment, soil, and tissues of wildlife and humans (Ahrens & Bundschuh 2014; Bossi et al. 2015; Braune & Letcher 2012; Butt et al. 2010; Cousins 2015; Dietz et al. 2008; Garsjø ; Haukas et al. 2007).

After the detection of PFASs in abiotic and biotic environmental samples in the early 2000s, they received much scientific attention because of their persistence, bioaccumulation potential, and possible adverse effects in organisms (Braune & Letcher 2012; Butt et al. 2010; Giesy & Kannan 2001). Some of the PFASs in this group have been tested for toxicological effects and have shown adverse effects in the environment, but the effect of all the compounds or a mixture is not known (Dietz et al. 2008; Giesy & Kannan 2001; Johansson et al. 2009; Pedersen et al. 2015; Verreault et al. 2005). Chemicals of the PFAS group have also been found in the Arctic, both in abiotic and biotic samples, which show that they are capable of long range transport, via the atmosphere and the ocean (Ahrens & Bundschuh 2014; Braune & Letcher 2012; Butt et al. 2010; Dietz et al. 2008). In

the beginning the focus was on the C-8 components (PFOS/PFOA), but in recent years the focus have been put on other related fluorinated components as well (Vierke et al. 2014).

2.1 Persistent Organic Pollutants

Since 1962 when Silent Spring by Rachel Carson (Carson 1962) where published, POPs have been a subject of significant scientific interest. When looking for background environmental levels, scientists turned to the Arctic, discovering that the concentrations here where higher than expected for many contaminants. POPs are classified by the Stockholm convention as persistent, potentially toxic, bioaccumulative and with the potential for long-range transportation (LRT) (Stockholm-Convention). Because of few local sources in the Arctic, the levels of POPs found are mostly considered to be transported from industrialized areas by atmospheric and oceanic currents.

The Stockholm Convention has set criteria for the priority properties that classify a compound as a POP. Persistence is determined by evidence of half-life of the chemical in water greater than two mounts, half-life in soil or sediment larger than six months. Detectable levels of POPs in remote areas such as the Arctic are a clear indicator of their persistence and their mobility in the environment (Stock et al. 2007).

Potential for bioaccumulation is determined by showing that the bioaccumulation factor for aquatic species are greater than 5000 or in absence of bioaccumulation factor, that the octanol water partitioning coefficient are greater than 5. Monitoring data showing

elevated concentrations in species high in the food chains might also be enough.

LRT is determined by showing elevated levels in locations distant from sources. Properties or model results showing potential for LRT trough air, water or biota, with potential to be transferred to the food web. For chemicals prone to be transported trough the air, a half-life should be greater than 2 days in the air. Prove of adverse effects to human health or the environment determines toxicity studies (Stockholm-Convention).

Some PFASs that have proven to exhibit adverse effects, are found in the Arctic, and are persistent in the environment. One difference between PFAS and traditional POPs are that PFAS tends to bioaccumulate in protein rich tissue, and not in lipids. Nevertheless, PFOS and its salts are already listed in annex B in the Stockholm-Convention, and PFOA and its salts are under consideration (Stockholm-Convention).

2.2 Arctic conditions

The Arctic experiences extreme changes in environmental factors like temperature and light condition. The variation of light makes photochemistry possible only during some parts of the year, making air concentrations varying with the seasons. This makes the persistence in air higher than in temporal areas. Also the low temperature affects the properties. The Arctic food webs are also rich in lipids, making bioaccumulation along the trophic levels more effective.

2.3 Terminology

Perfluoroalkyl substances are defined as aliphatic substances where all the hydrogen atoms, except the ones found in a functional group (ex. OH, COOH), have been replaced with fluorine and can be described by this formula: C_nF_{2n-1} (Buck et al., 2011). A polyfluoroalkyl substance is defined as an aliphatic substance where all the hydrogen atoms bound to one or more (not all) carbons in the chain have been replaced with fluorine. This means that a compound that has a scattered fluorination (ex. $CH_2FCHFCHFCH_2OH$) will not belong to the PFAS group, but if there is a grouped substitution (ex. $CF_3CF_2CH_2COOH$) and they have at least one perfluorinated moiety, it is considered a part of the PFAS group (Buck et al., 2011). Both subgroups have varying chain length and functional groups, which affects properties.

In the literature PFAS are often referred to as "long-chained" or "short-chained". To avoid confusion, Buck et al., 2011 encourages all literature to use the definition provided by the Organization for Economic Co-operation and Development (OECD). This definition differ long and short chains based on their toxicity and bioaccumulation potential (OECD 2011). For perfluorinated carboxylic acids (PFCA) this means that all compounds in this group with 7 or more fluorinated carbon atoms is considered as long-chained. For perfluorinated sulfonic acids (PFSA) a chain of six or more carbons are considered a "long-chained" PFAS (OECD 2011). Although the OECD definition does not include any other functional groups, one may consider that a perfluoroalkyl chain with 7 or more carbon atoms as long-chained (Buck et al. 2011).

2.4 Production

There are many estimates of production and release of PFAS , which are generally uncertain, but give an idea of how much is produced. In 2006 Prevedouros et al. (2006) estimated that 3200–7300t of PFCA was produced in 2005, accounting for approximately 80 % of the total world production (Prevedouros et al. 2006). For PFSAs the global production between 1970 and 2002 was estimated to be 122500t, where almost 30 000t was unused manufacturing wastes. Fluorotelomer (FT) production has increased steeply between 1995 and 2004, reaching 5000 tons year (Ellis et al. 2004; Krafft & Riess 2015). There is two main processes used to commercially produce PFAS: Telomerization and electrochemical fluorination (ECF).

2.4.1 Electrochemical fluorination

ECF involves the replacement of hydrogen atoms with fluorine atoms in a hydrocarbon chain. This happens trough electrolysis of an organic raw material, in the presentence of anhydrous hydrogen fluoride (HF). This process replaces the hydrogen atoms in the molecules, except the ones in functional groups, with Fluorine. Due to the free-radical nature of this process, the end product is a mixture of homologs, linear and branched isomers of the raw material (Buck et al. 2011).

2.4.2 Telomerization

In this Process pentafluoroethyl iodide, C_2F_5I, is reacted with tetrafluoroethylene, $CF_2{-}CF_2$ (TFE) to yield a mixture of perfluoroalkyl iodides that have a longer carbon chain length than the raw materials. A compound with the desired functional group is

reacted to give the perfluorinated carbon chain its functional group. (Buck et al. 2011). This method is widely used for production of fluorotelomer compounds like 6:2 FTOH, and are the reason that even numbered carbon chain lengths are more common for PFAS.

2.5 Properties

The C-F bonds are the strongest bond observed in organic chemistry (Garsjø 2013; Krafft & Riess 2015). This gives PFAS a high thermal and chemical stability, because it takes high energy to brake C-F bonds (Braune & Letcher 2012). This makes it resistant to hydrolysis, photolysis, biodegradation, and metabolism (Yeung et al. 2013; Zhu et al. 2014). PFAS can be heated to 400 °C without significant decomposition, retain their properties both in high and low temperatures, and resist to UV radiation (Krafft & Riess 2015). PFASs are amphiphilic. These properties have made sure that PFAS can be found in many products with grease and water repellent properties = amphiphilic (Krafft & Riess 2015; Zhu et al. 2014).

The unique physicochemical properties of PFAS have made them popular for many applications, and because of their widespread use they are ubiquitously distributed in the environment. They are generally persistent against typical environmental degradation processes, are bioaccumulative, and have potential toxic effects on organisms (Ahrens & Bundschuh 2014; Butt et al. 2010; Cousins 2015; Giesy & Kannan 2001; Johansson et al. 2009; Zhu et al. 2014).

2.6 Applications

PFASs have been widely used in numerous industrial and commercial applications, and have since the 1950 been applied in a wide range of

products due to the properties described in section 2.5 (Buck et al. 2011; Herzke et al. 2012). Their thermal stability makes them ideal for machinery working in extreme environments, like hydraulic fluid in aircrafts or coating on space shuttles (Krafft & Riess 2015). This combined with their properties and chemical inertness makes them ideal for non sticky cook wear (Leat et al. 2013). Aquatic fire fighting foam (AFFF) containing PFAS have been widely used on offshore oil platforms and are still used by many companies (Dietz et al. 2008). These foams often contain PFCA, PFOS and some fluorotelomer alcohols and sulfonates.

They are also used as surface coatings due to their amphiphilic properties, and can be found in outdoor clothing and other textiles, paints, paper electronics, lab wear (Buck et al. 2011; Butt et al. 2010; Herzke et al. 2012; Krafft & Riess 2015; Prevedouros et al. 2006). Some examples are FTOHs which are used to treat paper and textiles, particularly for waterproofing outdoor clothing (Herzke et al. 2012).

2.7 Sources

PFAS have thus been a growing group of high volume production chemicals with a wide range of applications. PFAS production also has a significant economic value; for example the market for stain repellents alone is around 1000 million USD (Ahrens & Bundschuh 2014).

Since they are found in many different products, there are also many different sources or pathways to the environment. It was suggested by Buck et al 2011 that the direct source of PFAS is release

throughout a product's life cycle, from manufacture, to use, and disposal, including emissions from a product in which the PFAS is present as an impurity. Indirect sources are classified as specific PFAS occurring through the transformation of precursor substances in the abiotic environment, wildlife, or humans (Buck et al. 2011).

The direct sources release into the aquatic systems throughout their life cycle, and its suspected that 95% of release ends up in the aquatic environment, and only 5% is released into the atmosphere (Ahrens and Bundschuh, 2014). Historically it is estimated between 3200 and 7300 tons of PFAS were produced in a 50 year period starting in the 1950s (Ahrens & Bundschuh 2014)

There are a number of point and diffusive secondary sources. Examples of point sources for PFASs are landfills, manufacturing plants, application of PFAS-containing products at a concentrated area (airports that used AFFF containing 6:2 FTS and sewage treatment plants. Examples of diffusive secondary sources are use of outdoor clothes, ski wax (Ahrens & Bundschuh 2014).

Braun and Letcher also describes the difference in direct and indirect sources, where production, use and disposal are considered direct sources, and degradation from volatile precursor compounds are considered indirect sources (Braune & Letcher 2012).

2.8 PFAS in the biota

Many Studies have demonstrated occurrence of PFAS in Arctic biota. The predominant PFAS reported are PFOS and PFOA, but also PFHxS, PFOSA, and 9-15 carbon chain length PFCAs have been reported

(Leat et al. 2013; Martin, Jonathan W. et al. 2004; Verreault et al. 2005). These PFASs have been shown to biomagnify between trophic levels in the food web (Butt et al. 2010; Martin, Jonathan W. et al. 2004)

There are little or no information available on adverse effect in Arctic biota. However, the toxic potency of various PFAS have been demonstrated in laboratory animals. The adverse effects observed in controlled animal experiments are likely to occur in Arctic animals if exposed to harmful. In a laboratory study with rats, the no-adverse-effect level (NOAEL) of PFOS in liver was 358 µg/g in males and 370 µg/g in females. Other investigations indicate lower effect levels. In a two-generation reproductive toxicity study of PFOS in rats, pup survival in the first generation was significantly decreased in the two highest dose groups, receiving 1.6 and 3.2 (mg/kg)/day. It is uncertain if Arctic animals tolerate less or more PFOS compared to laboratory mammals (Dietz et al., 2008).

2.8.1 Accumulation

PFAS is generally detected in low concentrations in Arctic biota. Arctic studies show that various PFASs biomagnify in food chain resulting in elevated concentrations in the organisms at the upper tropic level (Butt et al. 2010). A study by Haukas et al (2007) showed a significant increase between trophic levels and with calculated biomagnification factors, these had values >1 for PFHxS, PFNA, and PFOS in the majority of predator prey relationships (Haukas et al. 2007). The exact mechanism for the bioaccumulation is not fully understood, but generally it tends to accumulate in blood rich tissue, associated with protein, (blood, liver, brain, muscle)

rather than accumulating in the lipids, as many of the classical POPs tend to do (Bossi et al. 2015; Braune & Letcher 2012; Butt et al. 2010).

Bioaccumulation potential for PFAS depends on the physiochemical properties of the PFAS. It is also strongly dependent on the species, gender and reproductive status of the organism. There is also difference in bioaccumulation potential pending on chain length, structure (linear and branched) and also the functional group (Ahrens & Bundschuh 2014). The bioaccumulation potential increases with increasing chain length (Ahrens & Bundschuh 2014; Braune & Letcher 2012). The PFSA is more bioaccumulative than the PFCA, and there is also some data supporting a hypothesis that states that the odd numbered chains have a higher bioaccumulation potential than even numbered chains (Braune & Letcher 2012).

2.8.2 Toxicity

The interest of investigating the toxicology of PFSAs and PFCAs has increased the last two decades, and the main focus has been on PFOS and PFOA. In humans there was found an excess of bladder cancer among people occupationally exposed to high PFOS (Dietz et al. 2008). The health effects that give cause for concern are immunotoxicity, hormonal effects, neurobehavioral toxicity, developmental toxicity, hepatotoxicity, lung toxicity, reproductive toxicity, carcinogenic potential and weak genotoxic potential (Bytingsvik et al. 2012; Dietz et al. 2008; EFSA 2008; Pedersen et al. 2015; Verreault et al. 2005)

The effects of PFASs on wildlife are not well known, in particular for Arctic biota. Although the toxicities of PFOS and PFOA have been extensively studied, there is a lack of information for many of the other PFASs. It has recently been shown that 11- and 12 carbon PFCAs are equally potent inducers of stress response genes relative to PFOS and PFNA, and that the gene expression responses (oxidative damage, DNA damage, general cell lesions, membrane damage) were lower for the PFCAs than for the PFSAs. Studies also indicate that the effect of chain length is more important than the functional group (EFSA 2008; Leat et al. 2013).

Studies on polar bears and birds suggest that PFAS affect lipid metabolism and reproduction (Bytingsvik et al. 2012; Haukas et al. 2007; Verreault et al. 2005). PFOA has induced testis cancer, and reduces testosterone, increases estradiol. Observed developmental effects and higher motility of offspring of laboratory rats have also been observed for PFOA. PFOS and EtFOSE have induced liver cancer in experimental animals (Dietz et al. 2008; Martin, Jonathan W. et al. 2004). Because of its properties PFAS tend to not accumulate in fatty tissue like other legacy POPs, but rather bind to protein and accumulate in blood rich tissue (liver kidney, brain) (Braune & Letcher 2012; Dietz et al. 2008; Leat et al. 2013; Martin, Jonathan W. et al. 2004; Verreault et al. 2005)

PFAS are also of concern because of their ability to compete with thyroxin (T4) in binding to TH-transport proteins in blood such as transthyretin (TTR), and thereby decrease T4 levels in blood (Bytingsvik et al. 2012; Verreault et al. 2005). This is shown to influence growth and developmental processes. This may be a

problem especially for offspring in high tropic levels like the polar bear (Bytingsvik et al., 2012).

Laboratory tests on domestic chickens (*Gallus gallus*) estimated LD_{50} values for PFOS ranging from 4.9μg/g to 93μg/g, and based on reduced hatchability the LOAEL was estimated to 0.1 μg/g for PFOS in eggs (Leat et al., 2013). The observed effects ranged from decreased weight gain and increased liver mass to higher mortality, reduced hatchability, and liver histopathological changes (Leat et al., 2013).

2.9 Transport pathways

PFAS have been globally detected in various environmental matrices, even in remote areas like the Arctic (Butt et al. 2010; Dietz et al. 2008; Garsjø), but the fate and transport pathways are still not well understood, and have been subject of considerable scientific interest (Kwok et al. 2013). PFAS is a group of chemicals with different physiochemical properties that affect the transport. (Ahrens & Bundschuh 2014). Because of these differences there are multiple pathways and fates for the different subgroups of chemicals. There is two main processes that account for long-range transport (LRT) to remote areas: Oceanic transport and atmospheric transport, but the relative contribution remains unresolved (Bossi et al. 2015; Butt et al. 2010).

The transport mechanisms are pictured in Figure 1. In addition of these transport mechanisms, it is believed that local sources may account for some of the pollution. Airports, outdoors clothing, ski wax, waste burning is some examples of local sources.

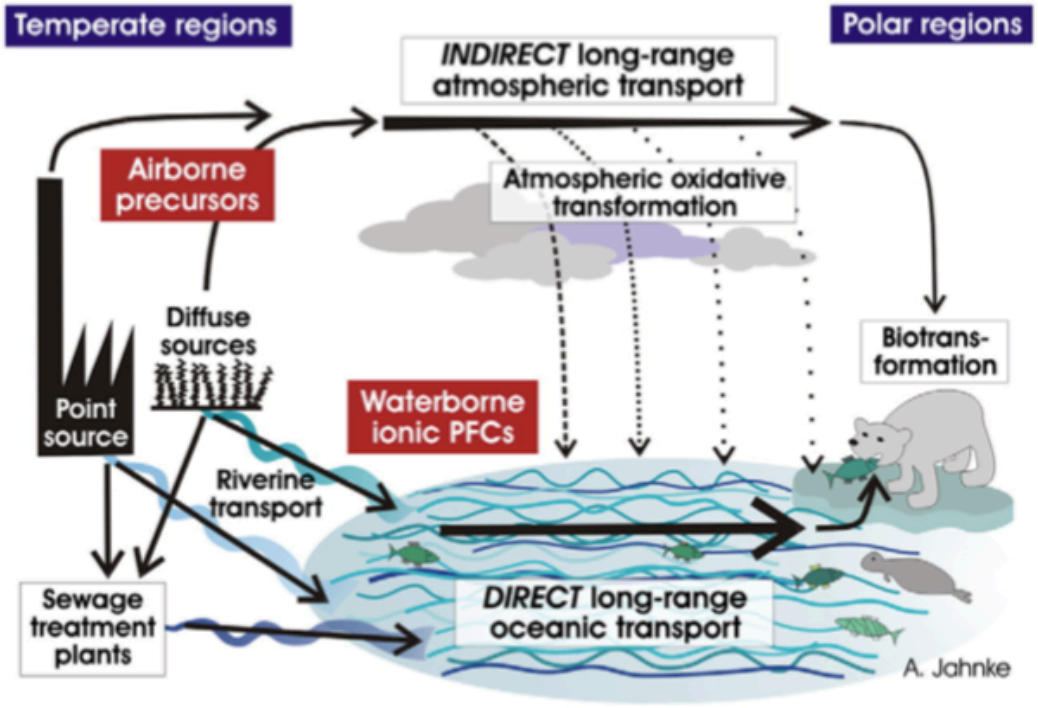

Figure 1: A schematic of the different transport pathways for PFAS to the Artic made by Annika Jahnke (Butt et al. 2010)

2.9.1 Oceanic transport

Oceanic transport involves the transport of directly emitted ionic PFASs via oceanic currents to the Arctic marine environment (Butt et al. 2010). This is the most important transport route for water soluble, highly stable and less volatile contaminates of the PFASs. They will be transported directly to the Arctic marine environment via ocean currents. Oceanic transport is compared to atmospheric transport a relatively slow transport, it may take decades before contaminants reach the Arctic from the mid-latitudes (Ahrens & Bundschuh 2014; Braune & Letcher 2012; Butt et al. 2010). Kwok et al (2013) reported that PFBS, PFOS and PFOA have been found in sea

surface and deep water samples collected from the Labrador Sea in the North Atlantic Ocean (Kwok et al. 2013).

2.9.2 Atmospheric transport

The first hypothesis of atmospheric transport of PFAS suggested that they where transported on particles. The physico-chemical properties of PFAS did not suggest any LRT (Dreyer et al. 2009; Haukas et al. 2007). Since this was expected to be a minor contribution compared to the oceanic transport, little focus was put on this transport pathway. The research then shifted towards shorter-chain PFCAs and PFSAs as well as airborne precursors, such as fluorotelomer alcohols (FTOHs), fluorinated sulfonamides (FOSAs), and sulfonamide ethanol (FOSEs) (Bossi et al. 2015; Braune & Letcher 2012; Ellis et al. 2004; Taniyasu et al. 2005; Young et al. 2007).

Atmospheric transport is a much faster transport pathway then oceanic, and can transport contaminants to the Arctic from mid latitudes within days or weeks (Bossi et al. 2015; Dietz et al. 2008). Air sampling in temperate regions has detected the volatile precursors in the atmosphere. Smog chamber tests have also shown that the lifetime of these compounds in the atmosphere is sufficient to complete mixing in the northern hemisphere and reach the Arctic (Ellis et al., 2004a; Stock et al., 2007; Young et al., 2007). Episuite (Estimation Programs Interface Suite Windows v4.11) was used to give an indication of the atmospheric lifetime of 8:2 FTOH and 6:2 FTOH. This model reported an estimated half-life in air of 30.695 h and a OH radical reaction rate of 4.1815 x 10^{-10} cm^3/molecule sec (US-EPA 2016).

Volatile precursors

The Volatile precursors have sufficient half-life in air to reach remote areas in the Arctic, but are not as bioaccumulative or toxic (Vierke et al. 2013). Some half-lifes have been determined, by using a smog chamber test, to be 10-20 days in air for FTOH and 20-50 Days for PFSA (Cai et al. 2012; Ellis et al. 2004) This might explain why FTOHs in general are found in gas phase and not particle face during sampling (Cai et al., 2012; Styler et al., 2013). OH radicals in the atmosphere will oxidize precursors either in the gas-phase, on atmospheric particles, or on ground surfaces such as snow and ice. PFCAs and PFSAs have been shown to be formed trough aldehyde, unsaturated aldehyde and carboxylic acid intermediate (Jackson et al. 2013; Styler et al. 2013; Taniyasu et al. 2013). Intermediates from this decomposition have already been found in environmental samples (Li et al. 2011).

Results for air sampling campaigns confirmed that the volatile precursors are capable of reaching the Arctic (Stock et al., 2007). A study by Shoeib et al. (2006) found detectable concentrations in atmospheric samples collected during a crossing of the North Atlantic and Canadian archipelago. Another study by Young et al. (2007) reported discovery of PFSA and PFCA on glacial ice caps, which is believed to only get contamination from the atmosphere. They concluded that atmospheric oxidation of volatile precursors is a primary source of PFSAs and PFCAs. This was strengthen when a positive correlation was found between PFOA and PFNA, suggesting

that PFOA and PFNA share similar transportation pathways (Kwok et al. 2013). Young et al (2007) found sodium concentrations that indicated that they were not a result of marine chemistry (Young et al. 2007). Another result that indicates that atmospheric transport is occurring is the detection of PFDA and PFUnA, neither, of which have any significant commercial production. The presence of these compounds is most likely a result of atmospheric oxidation. The concentrations of PFOA and PFNA were in agreement with modeling estimates of volatile precursors (Young et al., 2007).

Deposition

Due to high water solvability and low Henrys law constant PFOS and PFCA are susceptible for wet deposition (Cai et al. 2012). This is supported by notable concentrations of PFAS detected in wet deposition (Cai et al. 2012; Ellis & Mabury 2003; Ellis et al. 2004). A study by Tanlyasu et al. (2013) found PFBA, PFNA and PFOA in rainwater samples. The highest flux of PFASs was found in the first 1 mm of deposition, and decreased gradually (Taniyasu et al. 2013). It is interesting to note that short chain PFCAs were deposited rapidly within the first 3-mm deposition. The longer chain acids used longer to be totally deposited (Taniyasu et al. 2013).

Tanlyasu et al also collected and analyzed the PFAS content of snow. The concentrations ranged from 3.04 to 40.5ng/L in the different locations. The concentrations and compositions of the samples where then compared from fresh snow to one week old snow. On interesting result here was that they did not find long chained acids or PFOS in the fresh snow samples, but did find them in one-week-

old snow (Taniyasu et al. 2013). This might be an indication of transformation on the ice and snow surface.

2.10 Legislation

Due to reports showing that some PFAS bioaccumulate, have toxic properties (Butt et al. 2010; Dietz et al. 2008; Haukas et al. 2007), are persistent, and can be long range transported (Butt et al. 2010; Nøst et al. 2014). PFOS, PFOA, and their salts where voluntary phased out and restricted in most countries (Lyu et al. 2015). In 2000 one of the largest producers of these chemicals (3M Company), announced the phase-out of its PFOS based chemicals (Bossi et al. 2015)

In 2008 the EU approved regulation on PFOS (REACH) and a year later PFOS was added to Stockholm Convention on POPs (Herzke et al. 2012). The US EPA also restricted use (Bossi et al. 2015; Nøst et al. 2014). However, the restrictions still allow the use of PFOS in many of the applications for which they were used prior to the regulation, like aviation hydraulic fluids, semi-conductors and ceramic filters production, and photo imaging. Other applications that used PFOS have started using different types of PFAS (Bossi et al. 2015).

2.11 Concentrations found in the Arctic

PFAS are found globally, and have been found to be ubiquitous in water, sediment, wildlife and humans (Butt et al. 2010; Giesy & Kannan 2001; Higgins & Luthy 2006; Nøst et al. 2014). Residual PFASs continue to be detected today because of their environmental persistence and bioaccumulative nature (Ahrens, L. et al. 2011; Dietz et al. 2008; Krafft & Riess 2015; Lyu et al. 2015). Also in the

Arctic PFASs are detected in most media, Figure 2 shows concentrations detected in different matrices in six different high Arctic Canadian lakes (Lescord et al. 2015).

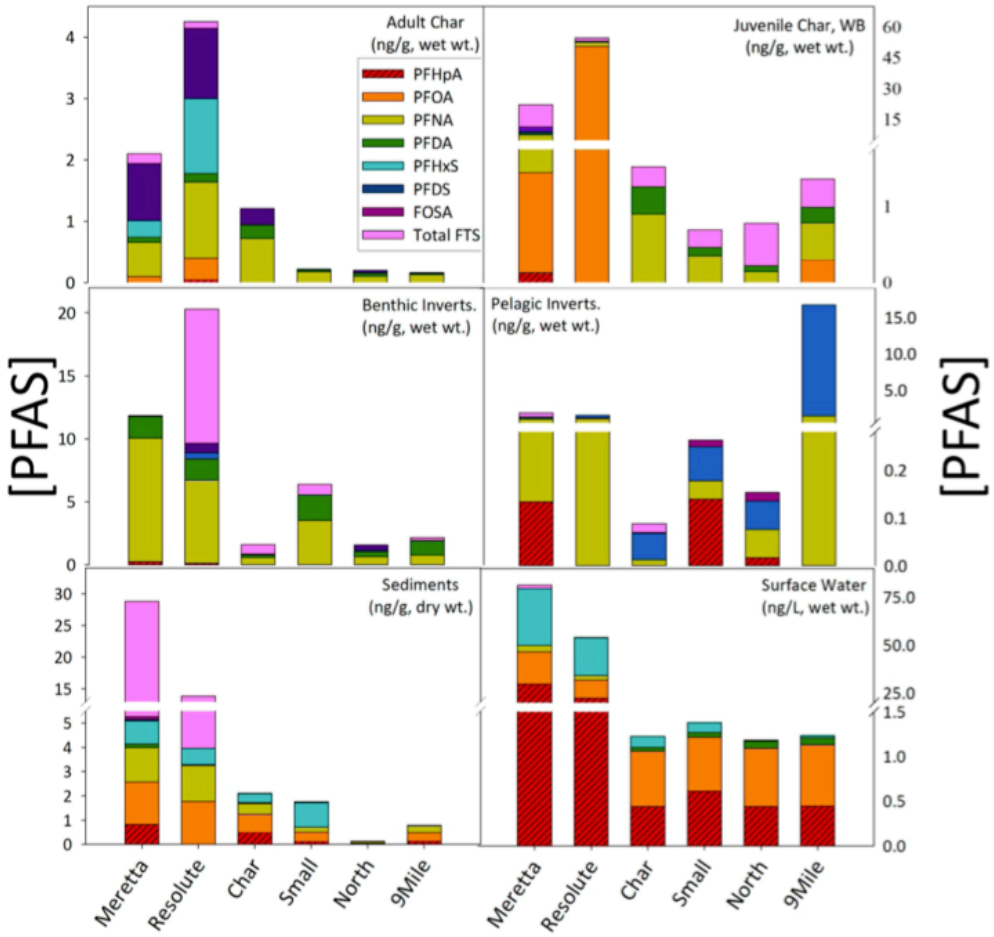

Figure 2: PFAS profiles in different biotic and abiotic compartments in six different Canadian lakes. Data are presented as ng/g ww., except water (ng/L) and sediments (ng/g, dw.). WB = whole body homogenates; Inverts. = Invertebrates. (Lescord et al. 2015)

2.11.1 Biotic

Historically, the focus on PFAS in wildlife have been on PFCA and PFSA, although some studies have shown their precursors also can be found (Braune & Letcher 2012). Food web studies in marine ecosystems suggest that some PFCAs and PFSAs can be biomagnified,

(Braune & Letcher 2012; Martin, Jonathan W. et al. 2004; Martin, Jonathan W et al. 2004). ΣPCBs for similar samples have been found to be comparable to ΣPFOS for polar bears, Arctic fox, mink, and various fish species, whereas ΣPCBs was much higher than either PFOS or ΣPFCAs in ringed seals, lake trout, and birds (Martin, Jonathan W. et al. 2004).

The polar bear (*Ursus maritimus*) is a top predator in the Arctic food web, and have a lipid rich diet. This means that it has accumulated high levels of contaminants. Studies on polar bears have indicated an increase in PFAS in the period from 1982 to 2002, and PFAS concentrations in polar bears are the highest measured in any species to date (Dietz et al., 2008). Some of the longer chains PFCAs have the potential to cross the blood brain barrier and from mother to cub, in a process that resembles the transport of free fatty acids, and it has been shown that the PFCAs and PFSAs can affect the nervous system, causing effects in behavior, motor function, memory, and learning capabilities in rodents (Johansson et al., 2009). In the analyzed polar bear brains, the sum of the concentrations of the PFSA in the different regions was determined to be 25 ng/g ww, where PFOS was the biggest contributor, over 90%. The sum of the concentrations of the PFCA was 25 ng/g ww where the C_{11}- C_{13} acids accounted for almost 80% (Pedersen et al., 2015).

PFAS have been found in birds, and have shown to be transferred to the egg during hatching (Braune and Letcher, 2012). A study by Braune and Letcher, have shown an increasing trend in ΣPFCA levels between 1975 and 2011 in the fulmar and thick billed murre

eggs from Prince Leopold Island. The same increasing trend have been seen in herring gull eggs from the Great Lakes between 1990 and 2010, in herring gull eggs from northern Norway between 1983 and 2003, and in Brünnich guillemot eggs from northern Norway and Svalbard from 1993 to 2003 (Braune and Letcher, 2012)

PFAS have been detected in fish from Arctic lakes in multiple studies (Bossi et al. 2015; Garsjø 2013). A study by Garsjø (2013) found multiple PFASs in samples from Arctic char caught in lake Linnévatnet. In this study PFBS, PFOS, and 6:2FTS where detected in the highest concentrations (Garsjø 2013).

2.11.2 Abiotic

Atmosphere

Air measurements have shown a widespread occurrence of PFAS in the Arctic. This is mostly the volatile precursors, and PFCA and PFSA hanging onto particles (Butt et al. 2010; Shoeib et al. 2006; Stock, Naomi L. et al. 2007). Shoeib et al. (2006) sampled air during a cruise across the North Atlantic Ocean and Canadian Archipelago (Figure 3). The samples measured the total air concentration (sum of particle bound and gas phase) of some PFASs. They found 8:2 FTOH, 10:2 FTOH, and MeFOSE in detectable quantities in all samples, and 6:2 FTOH and EtFOSE where high enough to be quantified in half of the samples. The highest concentration they reported where of 8:2 FTOH (5.8-26 pg/m^3), 10:2 FTOH (1.9-17 pg/m^3). 8:2 FTOH represents 50-70% of the total FTOHs in the samples (Shoeib et al. 2006)

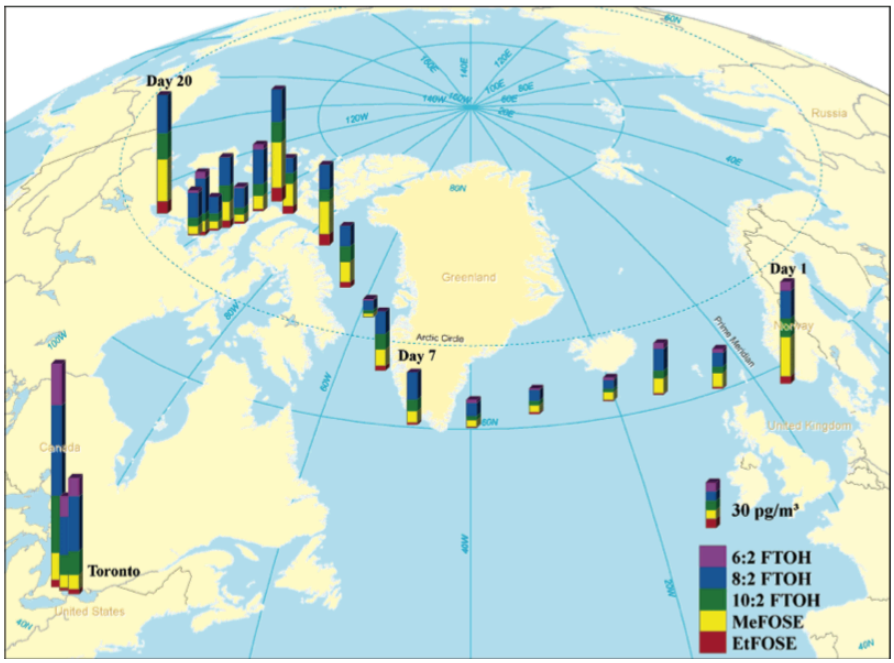

Figure 3: This figure shows the total air concentrations (sum of gas phase and particle phase) for FTOHs and PFASs across the North Atlantic Ocean and Canadian Archipelago (Shoeib et al. 2006)

Another study by Stock et al. (2007) measured PFASs in the atmosphere at Cornwallis Island in the summer of 2004. They sampled air and particles. The results are presented in Figure 4. FTOHs where detected in 80% of the air samples collected, mostly in gas phase. They reported mean value concentrations of FTOHs ranging from 2.8 pg/m^3 (10:2 FTOH) to 14 pg/m^3 (8:2 FTOH) (Stock et al., 2007).

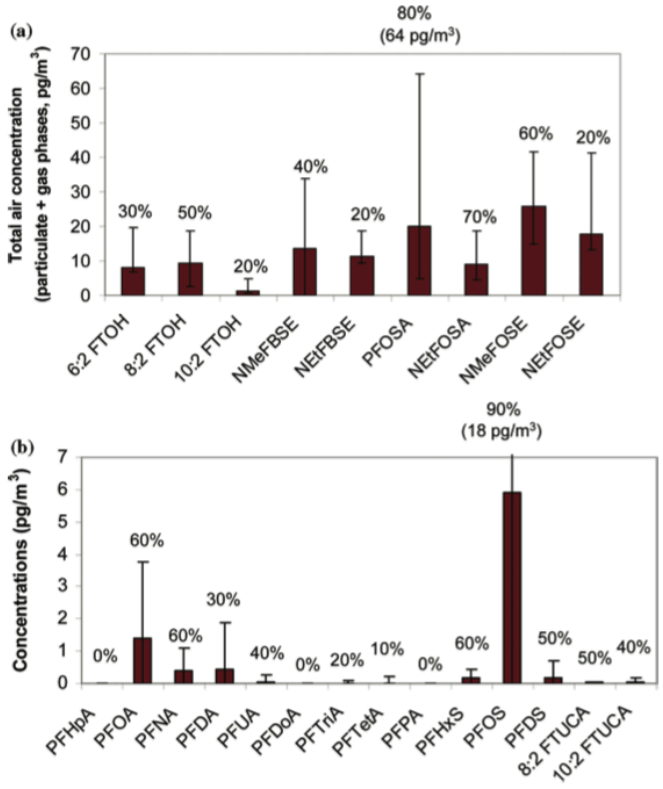

Figure 4: Mean values of (a) total concentrations and (b) particle concentrations collected on Cornwallis island in the summer of 2004 (Stock, Naomi L. et al. 2007). Frequency of detection is also indicated.

A study by Dreyer et al (2009) used a high volume air sampler and sampled on a cruise from Europe to the Antarctic and found similar results. Neutral volatile and semi volatile PFASs were detected almost exclusively in the gas phase. Total gas-phase concentrations of samples ranged from 4.5 pg/m^3 in the Southern Ocean to 335 pg/m^3 in source regions. 8:2 FTOH where observed in the highest concentrations ranging 1.8 to 130 pg/m ^{3}. In the particle face, mostly ionic PFAS was found. PFBS, PFHxS, PFOS, PFBA, PFPA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, and PFTriDA were detected. Most frequently, PFOS, PFBA, PFHxA, PFOA, PFNA, and PFDA where the ones found in high enough concentrations for quantification (Dreyer et al. 2009).

Glacier ice and snow

PFAS have been found in air samples from the Arctic (Shoeib et al. 2006; Stock, Naomi L et al. 2007) and its hypothesized that they are deposited from the air into the environment. A study by Kwok et al (2013) investigated the PFAS levels in ice cores from Longyearbreen, a glacier close to Longyearbyen, Svalbard.

Total PFAS concentrations were 94.8 pg/L and 165.8 pg/L in the different ice cores. The sample pattern of PFOS and PFCA where observed in the two ice core and the major compounds in the samples where PFBA (39%), PFOA (17%) and PFNA (11%). There was observed a peak in concentrations of PFOA, PFNA and PFOS in the layers corresponding to the period where the production of these where highest 1997-2000 (Kwok et al. 2013).

Concentrations of PFAS in snow have been measured to get a better understanding of deposition. In the Canadian Arctic PFOS and PFCA was found in all samples in concentrations ranging from 1.4–4.6 pg/L for PFOS, 13.1–53.7 pg/L for PFOA, 5.0–12.1 pg/L for PFNA, 1.5–4.5 pg/L for PFDA and 1.1–5.1 pg/L for PFUnA (Young et al. 2007). In surface snow from the study of Longyearbreen PFHxS, PFOS, and PFCAs from C_4 to C_{12} were detected, PFOS and PFOA was the major PFAS present in the surface snow samples, the concentrations where found to be 2.6-86 pg/L for PFOS, 12-147 pg/Lfor PFOA; 5.0-246 pg/L for PFNA; <LOQ to 22 pg/L for PFDA; and <LOQ to 27 pg/L for PFUnA. (Kwok et al. 2013). These concentrations are 2-3 orders of magnitude lower than those measured in precipitation at lower

latitudes, and have similar composition of components (Butt et al. 2010; Kwok et al. 2013; Young et al. 2007)

Some indicators of atmospheric transport where observed in these samples. There was an annual flux in concentrations that corresponded to the annual flux in precipitation. The presence of PFDA and PFUnA on the ice cap indicated atmospheric oxidation. Ratios of PFAS to sodium concentrations were highly variable, signifying PFAS concentrations on the ice cap were unrelated to marine chemistry (Young et al. 2007).

Sediment

The expected concentrations of PFAS in sediments strongly depend on the position of the lake, relative position compared to the inlet and outlet, and what transport mechanisms that are supplying contaminants (Butt et al., 2010).

Lake Ontario, Canada has been the site for multiple studies on PFAS. A Study by Mayer's et al (2012) found total PFCA concentrations in open lake sediments ranging from 2 to 18 ng/g in the different sampling sites. Among the 4 different basins sampled there was similar proportions of the PFCA, and the long chain PFAS where most abundant. PFOS was the dominant PFSA observed in sediments, with the highest concentrations present sites ranged from 4.4 to 49 ng/g (Myers et al. 2012). Similar results where reported by Yeung et al (2013) who reported that long-chain PFCAs were over 80% of total PFCAs, and Short-chain PFCAs only accounted for 0–21% of total PFCAs (Yeung et al. 2013).

Lescord et al (2015) analyzed sediment from 6 different lakes on Cornwallis Island, where four are atmospherically supplied and two are downstream from a local airport. The highest concentration for PFAS in the two lakes downstream from the airport where 57 ± 10 ng/g, dry wt. and 64 ± 6.6 ng/g wt. compared to the four remote lakes (range from 0.19 ± 0.03 to 2.7 ± 0.18 ng/g, dry wt.). The highest concentrations detected in sediment from the high-contaminated lakes were PFOS, FTSs, PFOA, and PFNA, and the profile were dominated by PFOS (~57%), while PFCAs were less abundant (~9%). The four atmospherically supplied lakes had a different profile dominated by PFCAs (70%) (Lescord et al. 2015).

A study by Stock et al (2007) analyzed samples from some of the same lakes as Lescord et al (2015) and found similar results with respect to concentrations and profiles (Figure 5). Resolute Lake is one of the lakes downstream from the airport, and Char lake and Amituk Lake are atmospherically supplied (Stock, Naomi L et al. 2007). Figure 5 clearly show the difference between the profiles and concentrations between Resolute Lake which where contaminated by a local source and Char Lake and Amituk Lake which where atmospherically fed.

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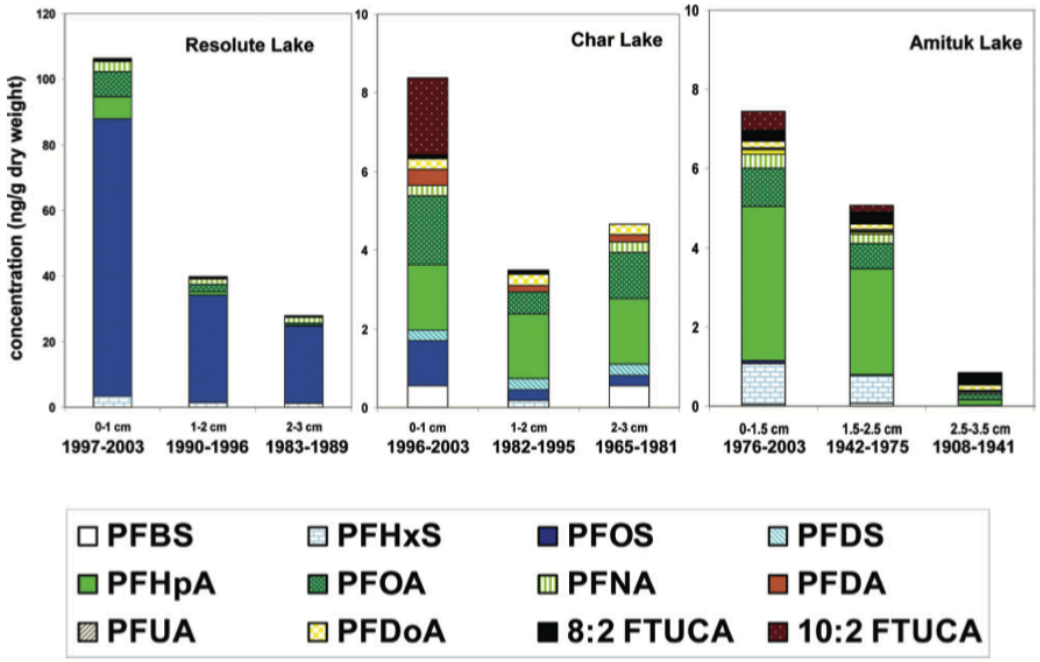

Figure 5: Concentrations in ng/g dw. from tree different lakes on Cornwallis Island (Stock, Naomi L. et al. 2007).

A study by Veillette et al. (2012) looked at 3 unnamed lakes located on the northwest coast of Ellesmere Island, Nunavut, Canada (Figure 6). They used a core sampler, and have looked at PFOS at different depths. The result was several orders of magnitude greater than those detected in the other studies. The results from one of the lakes are presented in Figure 6 (Veillette et al. 2012)

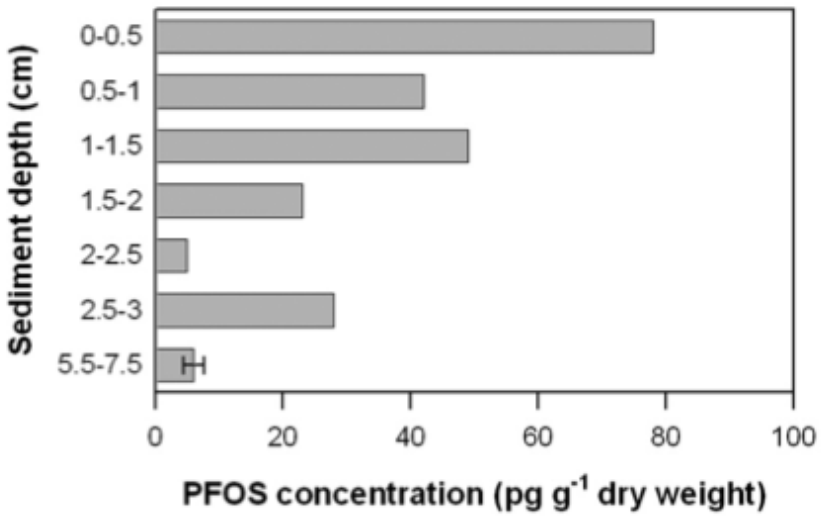

Figure 6: From an unnamed lake located on the northwest coast of Ellesmere Island, Nunavut, Canada, showing the PFOS decreasing with depth (Veillette et al. 2012).

Lake water

The studies by Lescord et al (2015) and Stock et al (2007) also analyzed surface water. As with sediment the lakes downstream from the airport had significantly higher concentration (153 ± 14 ng/L) compared to the atmospherically supplied (1.9 ± 0.42 ng/L). This suggests that the airport where a significant point source. The water samples were dominated by lower-chain PFCAs and PFSAs suggesting that the more hydrophobic long chains tend to partition to the sediment (Lescord et al. 2015),

2.12 High-Resolution chromatography mass Spectrometry

HPLC is a technique used to separate components in a mixture based on their different distribution between two phases. The stationary phase is bonded to fine particles packed inside a closed column and the mobile phase is forced through the column (Miller 2009).

HPLC coupled to a mass spectrometer is used to separate and detect compounds by studying the mass of compounds and fragments of compounds in a mass spectrum (Williams & Fleming 2008).

After leaving the HPLC and entering the MS, the sample enters the Ion source. In this study Electrospray Ionization (ESI) were used. ESI produces ions by applying high voltage to a liquid, making an aerosol. The aerosol is then accelerated into a mass filter where it is filtered using an electric field. They are detected in a detector according to their m/z, giving a signal to a computer that interpreters the results and presents them as a mass spectra (Hoffmann & Stroobant 2007). A mass spectrum show the intensity of ions whit the same m/z at a given time (Williams & Fleming 2008).

Liquid chromatograph connected to a tandem mass spectrometer (LC/MS-MS) is a sensitive instrument and it is therefore a suitable instrument-set up for environmental trace analysis.

3. Method

3.1 Overview

The sampling was carried out with a grab sampler from boat or on the ice. The samples where transported to the field station at Kapp Linné (78°3.77'N, 13°36.83'E) and stored in a freezer (-20 °C) until transport back to UNIS. At UNIS the sample where dried and packed, then sent to NMBU where the rest of the extraction and clean up was carried out. The extracts where analyzed at campus Adamstuen.

3.2 Study site

Svalbard is an archipelago located between 74° and 81° north latitude and between 10° and 35° east longitude. Spitsbergen, Nordaustlandet, Barentsøya, Edgeøya, Kong Karls Land, Prins Karls Forland, and Bjørnøya are the main islands of Svalbard (Figure 7). The study site, Kapp Linné is a cape on the west coast of Spitsbergen and is located on the outermost part of Isfjorden.

Figure 7: Map of Svalbard, except for Bjørnøya. The study is conducted on the west coast of the main island, Spitsbergen, close to Barentsburg. Map: Norsk Polarinstitutt

Linnévatnet is located just east of Kapp Linné and is approximately 4.7 km long and 1.3 km wide, about 10 meter above sea level, with a maximum depth of 35-40m (Snyder et al., 2000). The lake is located in the middle of Linnédalen valley. It is connected to Linnébreen glacier by Linnélva river ass seen in Figure 8 (Mangerud et al. 1992; Svendsen et al. 1987; Svendsen et al. 1989). Linnédalen valley covers a 36 km^2 catchment area.

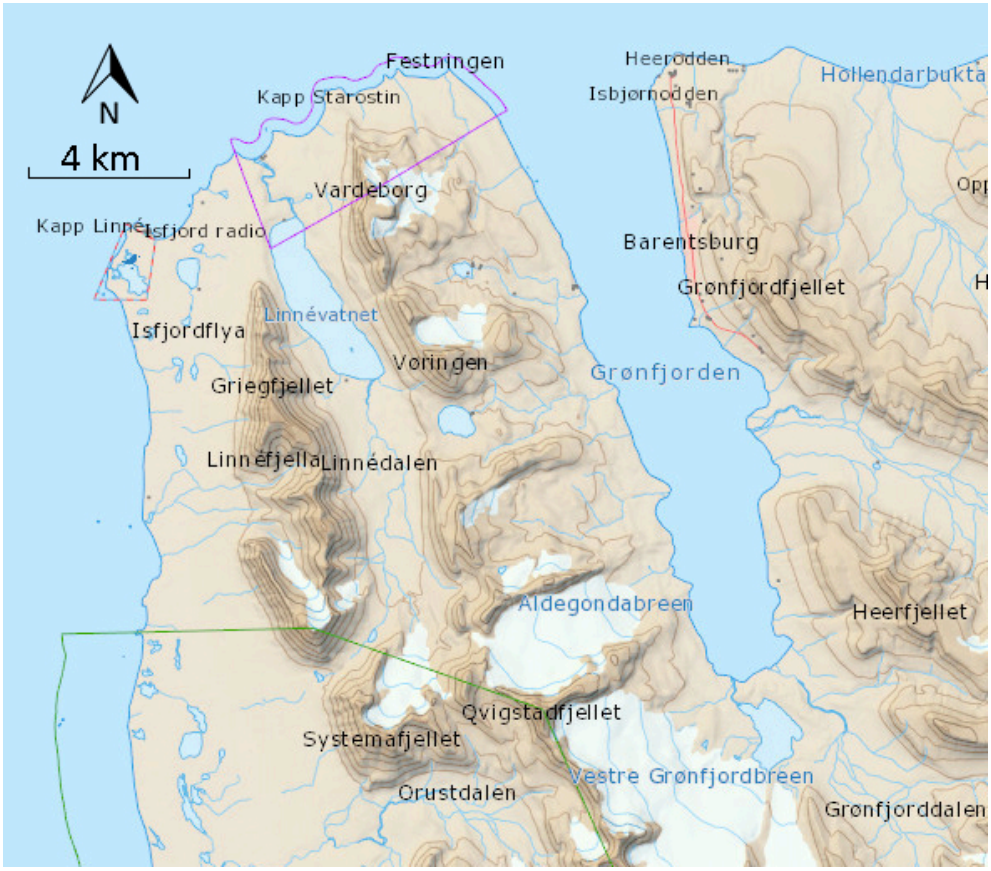

Figure 8: Map of Linnédalen and the surrounding area. Isfjord Radio is positioned on Kapp Linné, on the northwest corner. Linnévatnet is locates in the middle of the map in the end of Linnédalen. Barentsburg is located on the east side of Grønnfjorden. Map: Norsk Polarinstitutt

Previous studies have shown that Linnévatnet is an isocheimal and isothermal monomictic lake that remains at a temperature below 4°C throughout the year (Boyum & Kjensmo 1978). Linnévatnet is typically covered with ice, up to 2 m thick, from late September until July and sometimes into early August (Svendsen et al. 1989).

The main Source of sediment for Linnévatnet is the Linnéelva, which gathers water and sediment from a large portion of the catchment area (Snyder et al. 2000). The Linnébreen is the largest glacier in the

catchment. Linnébreen is a four km long retrieving valley glacier (Svendsen et al. 1989).

Linnévatnet is divided into three basins: the west, the east and the main basin. The main basin is about 35 m deep and the west and east basins about 10-15m (Svendsen et al. 1989). The east basin accumulates sediment from Linnéelva, which is carrying sediment from glaciers to the south. However, a bathymetric ridge prevents the western basin from receiving sediment from Linnéelva.

The Location of Svalbard gives it a cold climate with little precipitation, creating a polar desert. Snow is the dominant form of precipitation, varying between 200 – 600 mm water equivalency per year (Arnold 2009).

Past projects have indicated that sedimentation cycles occur annually throughout Linnévatnet with fine grained material being deposited in both the fall and winter, and larger-grained material being deposited in the spring and into the summer (McKay 2009). A study by Coleman (2010) showed that in five sedimentation years, the sediment trap collected a cumulative total of 83.65 cm of sediment, giving an average of 16.73 cm per year. Average grain size 17,47 µm in diameter (Coleman 2010).

3.3 Sediment

A Study on PFAS concentrations and biomagnification in the lake Ontario food web found significantly higher concentrations in the benthic invertebrate, (*Diporeia spec.)*, compared to a pelagic feeder, (*Mysis spec.*.) These findings suggest that sediment was a major

source of PFAS to this food web compared to water (Martin, Jonathan W. et al. 2004).

Sediment is an important sink and reservoir of POPs and has a large impact on their distribution, transport, and fate in the aquatic environment. Some studies consider sediment and Transport to the deep oceans to be the only significant environmental sink for PFOA and PFOS (Zhu et al. 2014).

The sediment–water partition coefficient (Kd), are necessary to predict their environmental fate. PFASs with a low Kd will mostly exist in a dissolved phase, and will be rapidly dispersed. The PFASs with a high Kd will hang on to particulate matters and accumulate in the sediment. This will in terms also have an impact on the bioavailability. Sediment water distribution is a complex process, depending on the physicochemical characteristics of the compounds and the sediment nature (ex. organic carbon content) (Ahrens et al., 2010b; Zhao et al., 2012). In a study by Vierke et al (2014) they found that the short chained components where less retained in the sediment than the longer chained once (Vierke et al. 2014).

3.4 Sampling

The sampling was carried out in June of 2015 at Linnévatnet. From Longyearbyen a polar circle boat was used to get to Kapp Linné. Isfjord radio, a hotel located on Kapp Linné, was used as a field station for the work. From Isfjord radio, there is a 4 km walk to get till Linnédalen and the start of Linnévannet. All equipment needed was carried out, and a bike was used to drag the heaviest of the equipment.

At Linnévatnet four sample locations along the lake were used (Table 1, location S04-S07). The ice measured around 1,20m, a motorized drill (with a 200mm cut) and ice saws was used to make a hole big enough for the grab sampler. The grab sampler was lowered into the bottom of the lake and pulled up. Sediment samples where put in pre-cleaned aluminum boxes (methanol and sample cleaned), covered with aluminum foil, and put in a plastic bag. After transport back to Isfjord radio (field station) the sample where kept in a freezer (-20 °C) until pre treatment started.

Between Longyearbyen and Kapp Linné marine sediment samples where taken (Table 1, location S01-S03 and S07-S09) using a grab sampler and the on board winch. Samples where put in pre cleaned aluminum boxes (Methanol and sample cleaned), covered with aluminum foil, put in a plastic bag. After transport back to UNIS the sample where kept in a freezer until pre-treatment started.

In Longyearbyen close to the airport (Table 1, location S10), a small creak running down from the fire training area that belongs to the airport where sampled. The sample was collected using an aluminum container. The sample was dried, and sieved trough a cleaned sewer with a 1mm grid. The sample where kept in a freezer until pre treatment started

Table 1: Table showing coordinates, depth and a description of every sampling location

Sample location	Latitude	Longitude	Depth [m]	Notes
S01	78°14'35.2	15°39'50.0	59	Waste water Outlet
S02	78°15.08,9	15°29'48.0	20,5	Airport Outlet
S03	78°06.51,3	14°56'49.5	30	Coalsbukta
S04	78°02'03.1	13°51'16.3	13	Linnévatnet
S05	78°02'23.0	13°49'37.5	33	Linnévatnet
S06	78°02'52.9	13°48'05.3	36	Linnévatnet
S07	78°03'36.0	13°46'20.5	28	Linnévatnet
S08	78°00'25.0	14°16'40.8	50	Barentsburg/Grønnfjorden
S09	78°04'01.6	13°37'54.8	13	Randvika/Kapp Linné
S10	78°14'25.0	15°32'13.0	0,2	Stream from airport fire training site

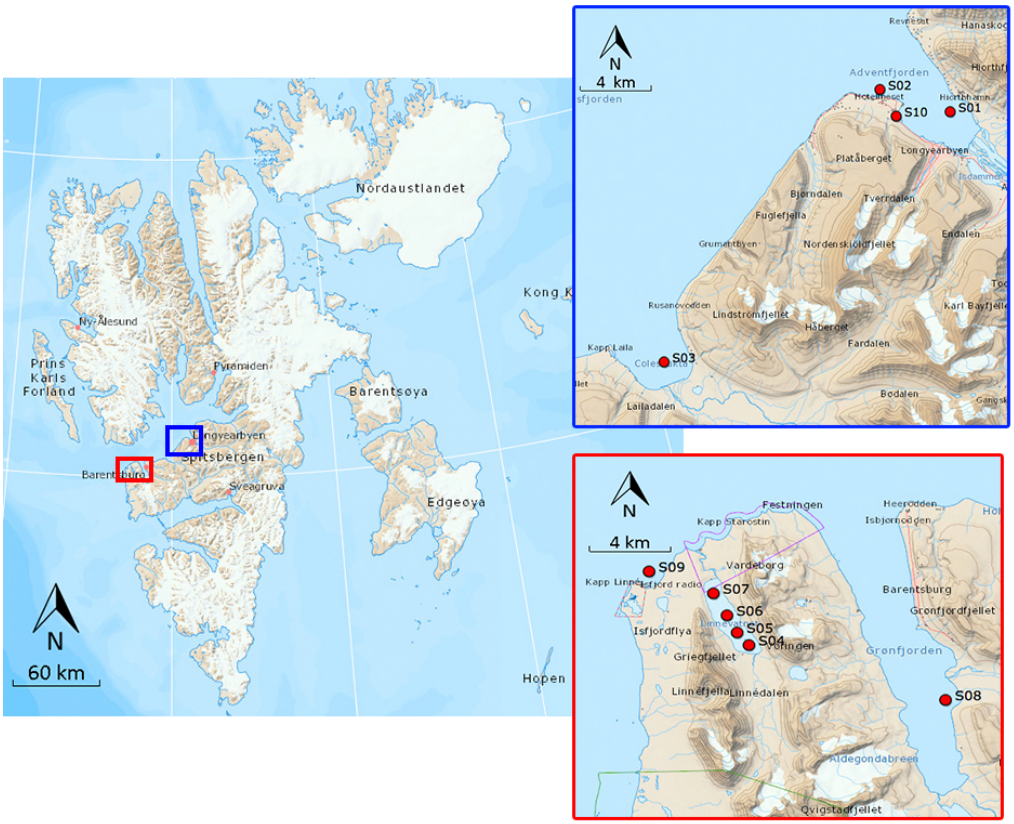

Figure 9: The map shows the sampling locations Map: Norsk Polarinstitutt

3.5 Chemicals and standards

All solvents used in this project were of Chromasolv® grade (Table 2). In the extraction of the sediment samples methanol was used. For the clean up process Super clean ENVI-Carb was used together with glacial acetic acid. Methanol and Acetone where used for cleaning equipment.

Table 2: Chemicals used in the method

Chemical	CAS #	Producer	Lot #	Purity
ENVI-Carb		Supelco	4015103V	
Acetic Acid	64-19-7	Sigma Aldrich	SZBE1130V	99,8
Acetone	67-64-1	Sigma Aldrich	STBF4530V	99,5
Methanol	67-56-1	Sigma Aldrich	SZBE230CV	99,9

There were used two different ISTD mixes. ISTD1 had a concentration of 200pg/µL, of M_5PFHxA, M_4PFHpA, MFHET, d-N-Mesas-M and d7-N-MeFOSE-M, where M represents the number of ^{13}C labeled carbons in the molecule. These certified standards were obtained from Greyhound Chromatography and Allied Chemicals (Merseyside, United Kingdom) and produced by Wellington Laboratories Inc. Guelph, Ontario, Canada (Appendix A) ISTD2 was a premixed IS-mixture named PFAC-MXA obtained from Greyhound Chromatography and Allied Chemicals (United Kingdom). This was diluted to 200pg/µL. This mixture contained M_4PFBA, M_2PFHxA, M_4PFOA, M_5PFNA, M_2PFDA, M_2PFUnDA, M_2PFDoA, $^{18}O_2$PFHxS and M_4PFOS.

M_8PFOA was dissolved in methanol to a final concentration of 0.1 ng/µL. This was obtained from Greyhound Chromatography and Allied Chemicals (Birkenhead, Merseyside, United Kingdom) and used as recovery standard (RSTD).

3.6 Laboratory method

All equipment used in this project was cleaned with ultra pure solvents (Methanol, acetone) before usage. The list of all equipment used in this project is provided in Appendix I. Before the extraction method was carried out, the sediment samples were thawed for ca. 1-2 hours in a ventilation cabinet.

3.6.1 Pre treatment

A thin layer of sample was put on a prewashed (Acetone x 3, Methanol x 3) aluminum container. The container was then covered with aluminum foil, with a little opening so vapor could escape. The container was then put in a oven at 35°C until it was completely dry (can 48h). To evaluate if the sample was completely dry, it was weighted after reaching room temperature, then put in the oven again. This proses was repeated after an hour. When the mass was stable (±0.5% difference between weights) it was considered completely dry. The water loss where then determined gravimetrically.

After drying the sample was sieved trough a 0.5mm mesh size sieve, and the <0.5mm fraction was collected. The samples were kept in freezer until extraction.

3.6.2 Extraction

10 g of samples were weighed on a fine scale and transferred into a 50 mL PP-centrifuge tube. The samples were spiked with 50 µL of each of the ISTD mixes using a 20-100µL pipette. 10µL of methanol was added to each sample. The centrifuge tubes were capped and vortexed thoroughly with a vortex mixer.

The 45 mL centrifuge tubes were placed in an ultrasonic bath for three exposures of 15min duration. The samples were vortexed in between.

The samples where centrifuged for 15min at 2500rpm. The supernatant gained after sedimentation in PP-vials were transferred to TurboVap-glasses with Pasteur pipettes and concentrated to approximately 0,5 mL using the sensor function on the TurboVap.

3.6.3 Clean up

A 1.5 mL Eppendorf centrifuge tube was filled with 25 mg ENVI-carb, 50µL Glacial Acetic Acid. Then the concentrate made in the TurboVap was transferred to the centrifuge tube using a pasture pipette. The samples were vortexed thoroughly, and centrifuged at 10.000rpm for 10 min. The supernatants where then transferred to a SpinX centrifuge filter and filtered in a centrifuge at 2500rpm for 3min. The filtrate was then transferred to an auto injector vial and added 100µL RSTD (0,1 ng/µL) and capped for final quantification.

3.7 Instrumental analysis

The PFAS compounds were analyzed by an ultra-high pressure liquid chromatography triple quadrupole mass spectrometer (UHPLC-MS/MS). The analytes, ISTD and RSTD can be seen in Table 3. Agilent 6460 triple quadrupole mass spectrometers were used for the analysis of PFAS. The sample separation was conducted by injection of 10 µL on an Agilent Eclipse plus C18 separation column (2,1 X 150mm 3,5µm) equipped with a Supelco supelguard discovery 18 (2cm x 2,1mm 55µm). Agilent jet stream ESI where used as ion source. To achieve separation, 2 mM NH_4OAc in 90:10 methanol/water (A) and 2 mM NH_4OAc in methanol (B) was used as the mobile phases at a flow rate of 0,2 mL/min. More information on the instrumental settings is avalible in Appendix D.

The Retention time, quantifier transition and a qualifier transition was used to be sure what compounds where detected. For some of the analytes there was not found any usable qualifier transition. A full list of transitions and instrumental settings can be found in attachment 2 and 3.

Table 3: Overview of analytes forted by their sub groups. ISTDs and RSTD can be seen at the bottom of the table. The structures of the analytes are available in appendix B

Group	CAS#	Acronym	Name
PFCA			
	375-22-4	PFBA	Perfluorobutanoic acid
	2706-90-3	PFPA	Perfluoropentanoic acid
	307-24-4	PFHxA	Perfluorohexanoic acid
	375-85-9	PFHpA	Perfluoroheptanoic acid
	335-67-1	PFOA	Perfluorooctanoic acid
	375-95-1	PFNA	Perfluorononanoic acid
	335-76-2	PFDcA	Perfluorodecanoic acid
	4234-23-5	PFUnA	Perfluoroundecanoic acid
	307-55-1	PFDoA	Perfluorododecanoic acid
	72629-94-8	PFTrA	Perfluorotridecanoic acid
	376-06-7	PFTeA	Perfluorotetradecanoic acid
PFSA			
	3872-25-1	PFBS	Perfluorobutane sulfonate
	432-50-7	PFHxS	Perfluorohexane sulfonate
	1763-23-1	PFOS	Perfluorooctane sulfonate
FT			
	27619-97-2	6:2 FTS	6:2 Fluorotelomer sulfonate
FOSA			
	31506-32-8	N-MeFOSA-M	N-Methylperfluoro-1-octanesulfonamide
	4151-50-2	N-EtFOSA-M	N-ethylPerfluoro-1-octaneSulfonamide
FOSE			
	24448-09-7	N-MeFOSE-M	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol
	1691-99-2	NEtFOSE-M	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol
ISTD			
	N.A	M_4PFBA	Perfluoro-n-[$^{13}C_4$]butanoic acid
	N.A	M_2PFHxA	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid
	N.A	M_4PFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid
	N.A	M_5PFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid
	N.A	M_2PFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid
	N.A	M_2PFUnDA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid
	N.A	M_2PFDoA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid
	N.A	$^{18}O_2$PFHxS	Sodium perfluoro-1-hexane[^{18}O]sulfonate
	N.A	M_4PFOS	Sodium perfluoro-1-[1,2,3,4-^{13}C]octanesulfonate
	N.A	dNMeFOSA-M	N-methyl-$^2H_3$-perfluoro-1-octanesulfonamide
	N.A	d7-N-MeFOSE-M	2-(N-methyl-$^2H_3$-perfluoro-1-octanesulfonamido)ethan-$^2H_4$-o l
RS			
	N.A	M_8PFOA	Perfluoro-n-[13C8]octanoic acid

3.8 Quality Control

Contamination of the samples is possible in every step of the analysis. Sources for contaminations may generally be classified as instrumental, sampling and procedural or analytical.

In order to monitor background levels and "carry over" effects, injections of methanol were done regularly during the analysis. The quality was checked with regularly analysis of one methanol sample in approximately every tenth sample.

Method blank samples underwent the same method, but do not contain biological matter. The purpose of these is to identify contamination during sample treatment and estimate background noise.

Blank samples were exposed during sampling and underwent the same method as the samples (field blank). These contained sodium sulfate (heated to 450°C for 6h) instead of sediment. The purpose of these was to identify contamination during all steps from sampling to analysis. These will be used to determine MLD/MQL since these are the worst-case contaminated blanks.

3.8.1 Quality Assurance and method validation

The recovery of every ISTD, in every sample, where monitored. The recoveries where calculated using Equation 1.

Equation 1 Calculation of the recovery of ISTD in samples (Oehme 2014).

$$RFF_g = \frac{M_{ISTD} \times A_{RSTD}}{M_{RSTD} \times A_{ISTD}}$$

$$R(\%) = \frac{M_{RSTD} \times A_{ISTD} \times RFF_g \times 100\%}{M_{ISTD} \times A_{RSTD}}$$

RFF_g = Response factor of the internal standard relative to the recovery standard.
M_{RSTD} = Amount of the recovery standard.
M_{ISTD} = Amount of the internal standard.
A_{RSTD} = Signal area of recovery standard.
A_{ISTD} = Signal area of the internal standard.
R(%) = Percentage recovery of the internal standard

3.8.2 identification and quantification

Compounds eluting from the chromatographic column were identified by retention time and characteristic ions from the mass selective detector (MSD), both quantifier and qualifier was used if available. The detection and integration of the peaks where done in Masshunter workstation software: quantitative analysis for QQQ (version B.07.00/build 7.0.457.0) The peak where considered detected when the S/N was above 3.

Response factors relative to internal standards were calculated for each target-compound *(*Equation *2)*. Amount of each compound were quantified using isotope-labeled ISTD (Equation 3), sample concentrations were calculated by dividing the amount in in the extracts by the weight of the extracted sediment. The RRFs were calculated from the linearity test.

Equation 2 Calculations of relative Response factors for target-analytes relative to the internal standards (Oehme 2014).

$$RFF_i = \frac{M_i \times A_{ISTD}}{M_{ISTD} \times A_i}$$

RFF_i = Response factor of analyte Pi relative to the ISTD.
M_i = Amount of the target analyte in standard solution.
M_{ISTD} = Amount of the internal standard.
A_i = Signal area of analyte.
A_{ISTD} = Signal area of the internal standard

Equation 3 Calculation of amount of analyte in samples (Oehme 2014).

$$M_i = \frac{M_{ISTD} \times A_i \times RFF_i}{A_{ISTD}}$$

M_i = Amount of analyte in sample.
RFF_i = Response factor of analyte relative to the ISTD.
M_{ISTD} = Amount of the internal standard added to the sample.
A_i = Signal area of analyte.
A_{ISTD} = Signal area of the internal standard

3.8.3 Detection and Quantification Limits

The instrumental detection limit where set to S/N=3.

The MDL and MQL where calculated for all compounds analyzed. Most compounds where not detected in the blank samples, and for these the lowest detected linear standard where used as MQL. For PFBA, PFOA and PFDoA there was found some contamination in the blank. For these equation 4 and 5 where used for calculation of MDL and MQL, respectively.

Equation 4 Calculation of MDL based on the Average blank value and Standard deviation

$$MDL = Blank + 3 \times SD$$

Equation 5 Calculation of MQL based on the Average blank value and Standard deviation

$$MQL = Blank + 5 \times SD$$

3.8.4 Blank samples

Field blank was brought to the field and underwent the same treatment as the samples. This will be used as worst case blank, and will be used to determine the MDL and MQL.

Method blank is methanol that underwent the clean up process describes in section 4.6.3

Methanol blank is pure methanol, that have been added ISTD and RSTD at the same time as the samples.

4. Results

4.1 Linearity

The linearity for all analytes had an R squared above 0,99, ranging from 0,9916 to 0,99954. The linear range for all components where from the lowest linearity standard 0,1 ng/mL to 100 ng/mL. One example of the linearity can be found below.

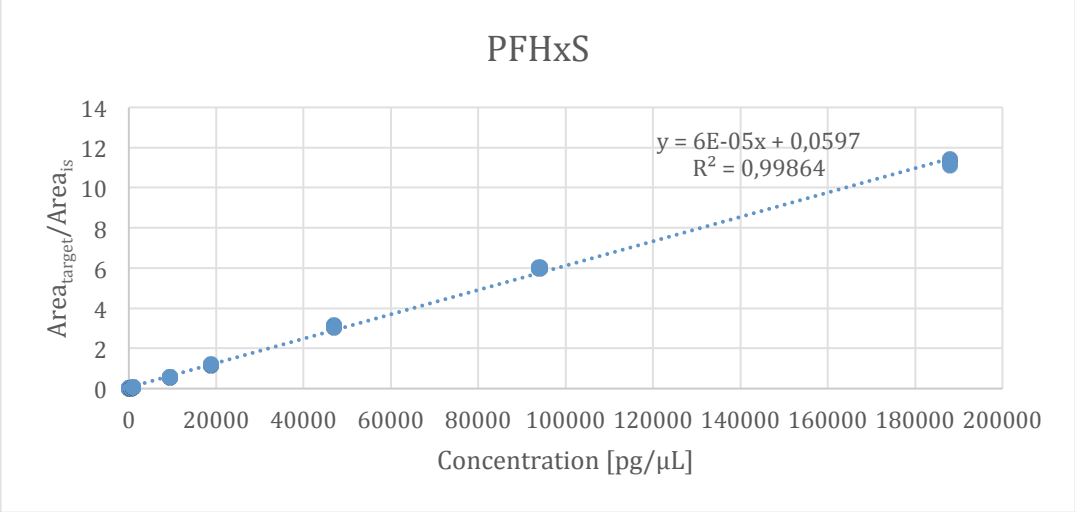

Figure 10 Linearity test for PFHxA

4.2 Recovery of ISTD

The recoveries for the ISTD varied between the different ISTDs. Recoveries are presented in Figure 10 as a median for all ISTDs in all samples in the different types, and as a Table in Appendix E.

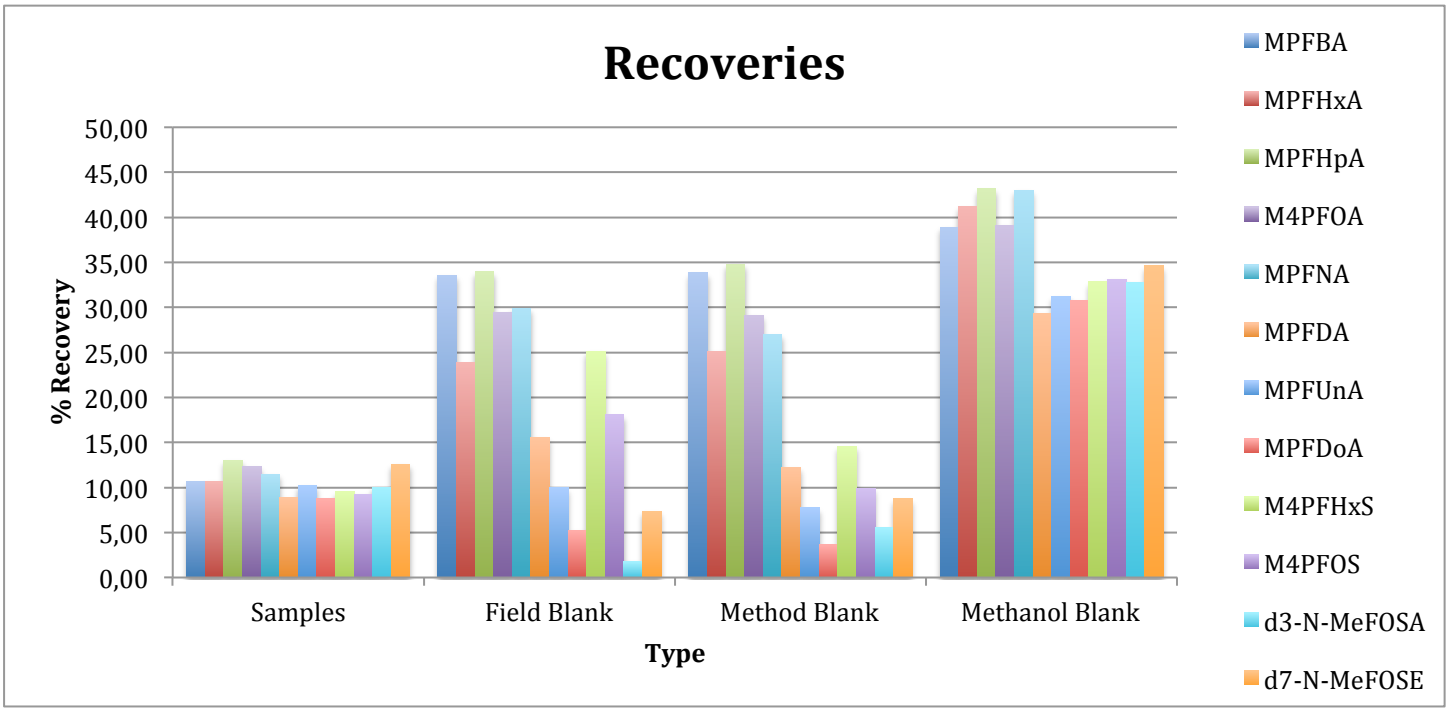

Figure. 11 % of ISTDs in samples(n=34), field blank (n=11), method blank (n=3) and methanol blank (n=3). The values presented are a median of all samples in the category.

Recoveries between 40% and 120% is considered as good, while recoveries between 20% to 40% is taken into account, with elevated overall method uncertainty. Figure 11 presents the median recoveries of the ISTDs in the samples, field blank, method blank and methanol blank. The recoveries are in general under 40%. The samples had low ISTD recoveries ranging from 8% to 12%. The field blank and the method blank had comparable results, and higher than in the samples, ranging from 2% to 34% and 3% to 35%, respectively. In common for the field blank and the method blank were the shorter acids, MPFHxS and MPFOS the highest ranging from 23% to 33%, while the longer acids, d3-N-MeFOSA, and d7-N-MeFOSE where significantly lower, ranging from 2% to 15%. The ISTD recoveries in the methanol blank were as expected the highest ranging from 31% to 43 %. In the samples and methanol blank, all components had less variation than in field blank and method blank.

4.3 Blanks and Limits

For most compounds there where no detectable contamination in the blank samples. For PFBA, PFOA and PFDoA there was detected in high enough concentrations to be considered when setting the MDL and MQL. For these equation X where used to calculate the MDL and MQL. For the rest of the component the lowest detectable linear standard where used to set the limit. All limits can be found in appendix G.

4.4 Quantification

Table 4: Concentrations of acid Compounds that where above the method Quantification Limit. The concentrations are displayed in [ng/g] DW. n.d = not detected, Detected = between MDL and MQL

Location	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFTrDA	PFUnA	PFTeDA	PFDoA
S10	1,47	n.d	0,54	0,32	n.d	2,41	0,1	n.d	0,63	n.d	n.d
S03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S05	2,05	n.d	0,15	0,27	n.d	0,43	n.d	n.d	0,14	n.d	0,14
S06	2,12	n.d	n.d	n.d	n.d	0,15	n.d	n.d	n.d	n.d	0,13
S04	Detected	n.d	n.d	0,11	n.d	0,19	n,d	n.d	n.d	n.d	n.d
S07	1,86	n.d	n.d	0,14	n.d	0,15	n.d	n.d	n.d	n.d	0,12
S02	n.d	n.d	n.d	n.d	n.d	0,23	n.d	n.d	n.d	n.d	n.d
S08	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S09	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

Table 4 shows the acid compounds. The airport where the one location where the most compound and the highest concentrations where found. PFPeA, PFOA, PFTrDA and PFTeDA where not detected in any samples. No analytes where detected in the sea sediment samples (S01, S02, S03, S08, S09, S10) with the exception of a small amount of PFNA in S02.

Table 5: Concentrations of the compounds that where above the detection limit displayed in [ng/g] Dw . N.D = Not detected

Location	PFBS	PFHxS	6:2 FTS	PFOS	PFOSA	N-MeFOSA	N-MeFOSE	N-EtFOSA	N-EtFOSE
S11	0,16	2,17	0,86	5,40	n.d	n.d	n.d	n.d	n.d
S03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S05	n.d	n.d	n.d	0,11	n.d	n.d	n.d	n.d	n.d
S06	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S04	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S07	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S02	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S09	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S10	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

The compounds in Table 5 where detected mostly in the airport sample. PFOSA, M-MeFOSA, M-MeFOSE, M-EtFOSA, and M-EtFOSE where not detected at all. PFOS where detected in one sample from Linnévatnet (S05) and at the airport (S11). PFBS, PFHxS, and 6:2 FTS where only detected in the airport sample.

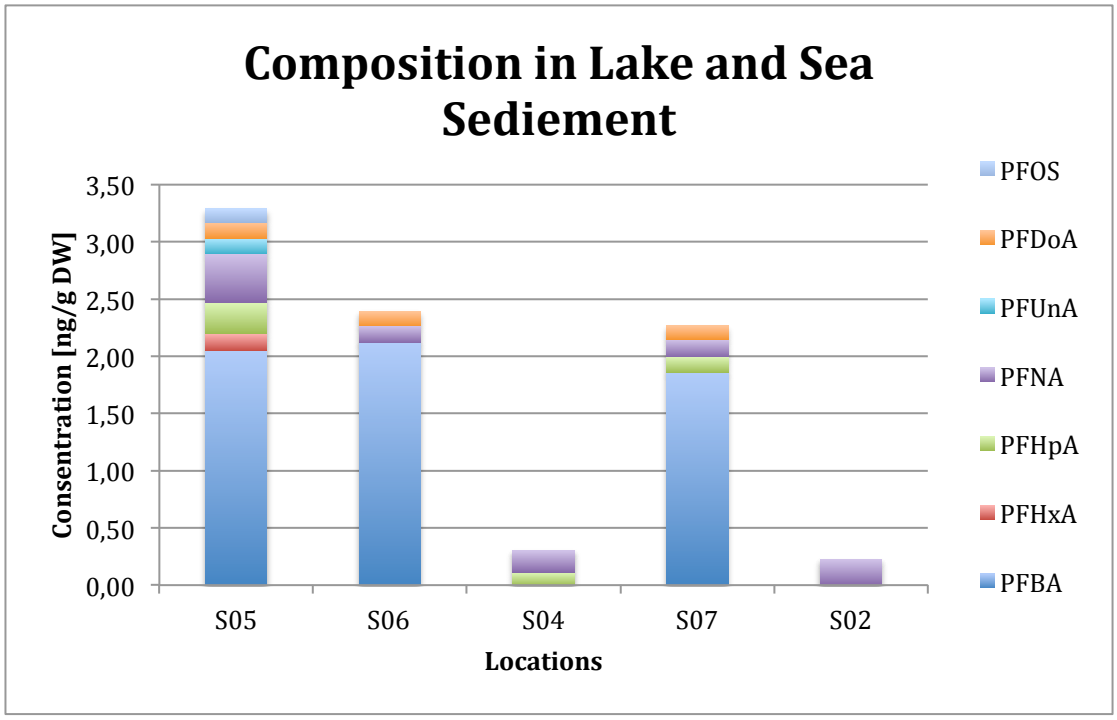

Figure 12: Compositions in lake and sea sediment samples

Figure 12 is a graphic presentation of Table 4 and Table 5. PFBA where detected in all samples from Linnévatnet, but where below the quantification limit in S04. The concentrations of PFBA in

Linnévatnet where in comparable levels between the different sampling locations. PFBA where also the highest concentrations of any analyte in these samples. PFHpA and PFDoA where both found in 3 out of 4 samples from Linnévatnet, in comparable concentrations. PFNA where detected inn all samples form Linnévatnet, in comparable levels in S04, S06, S07. In location S05, PFNA where found to be about 2 times the concentration of the others.

Location S05 where the location where the most analytes where detected. This where the only location where PFHxA, and PFUnA where found in the sea and lake sediment.

In the sea sediment, only location S02 had detectable levels of one of the PFASs analyzed in this study. PFNA where found here in levels similar to levels found in the Linnévannet samples.

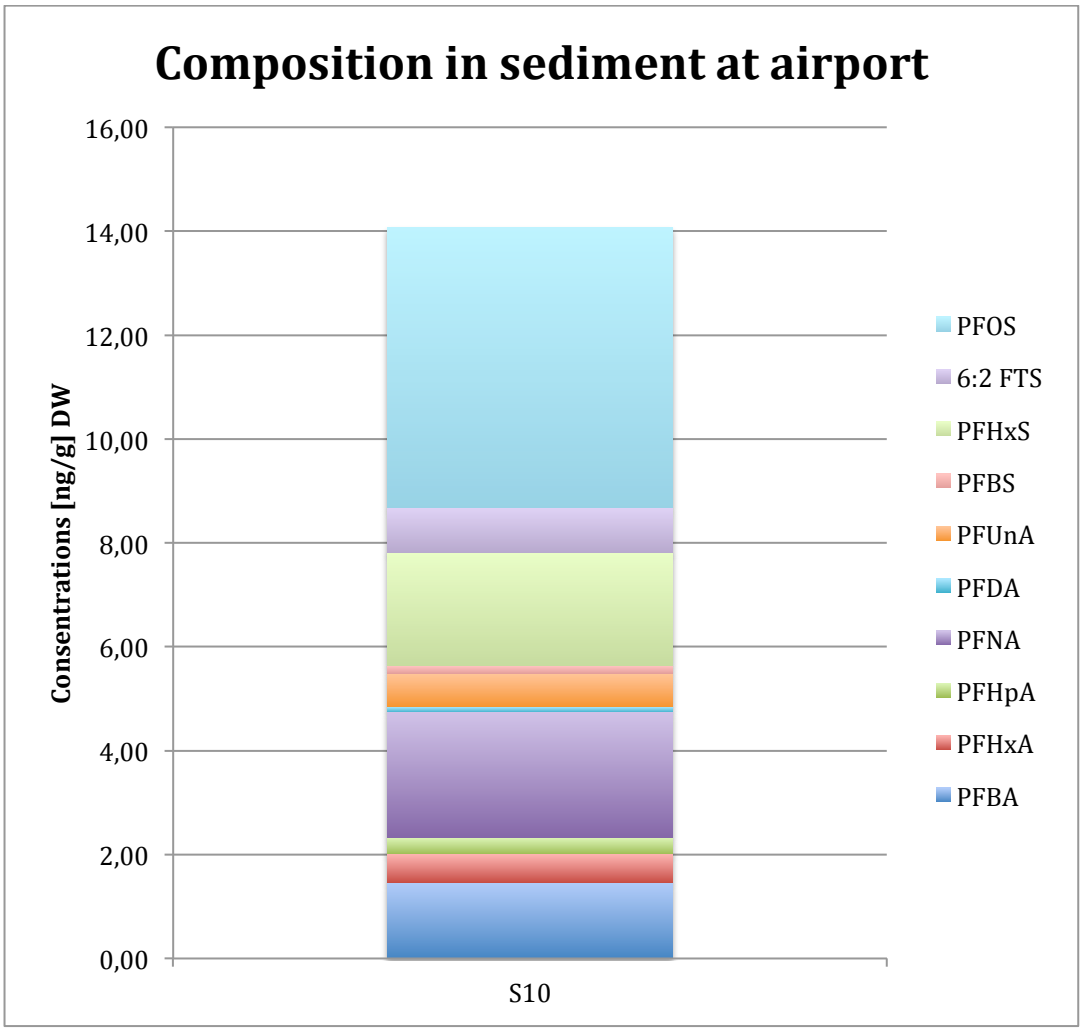

Figure 13: Concentration in sediment samples taken at location S10

In the Airport sample (S10), the highest amount, and number of analytes where found. This where the only location where PFBS, PFHxS and 6:2 FTS where found. The highest contributors were PFOS (38,4%), PFNA (17,1%) ,PFHxS (15,4%) and PFBA (10,4%).

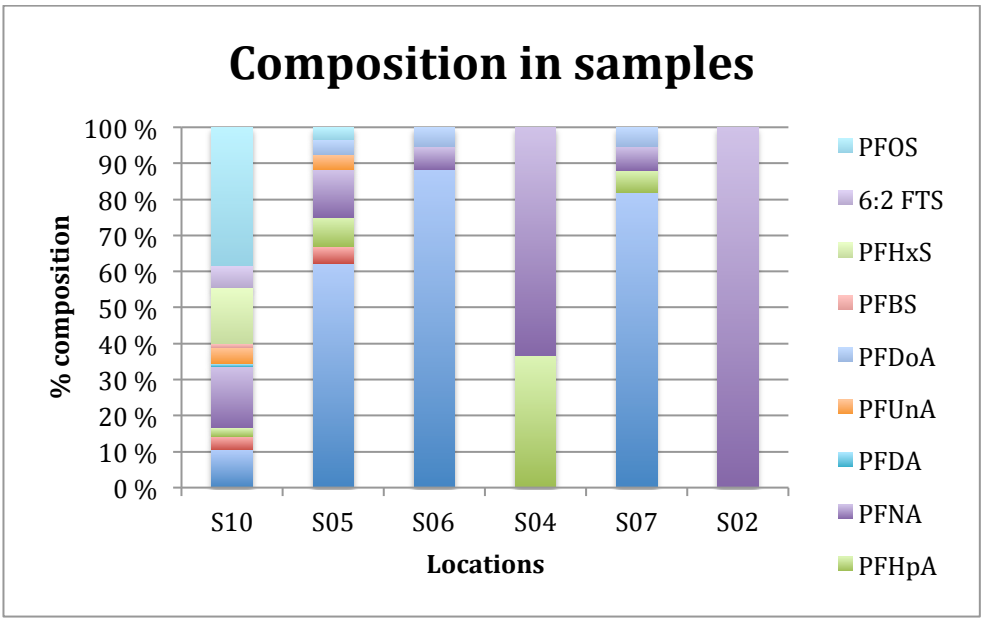

Figure 14 : Relative contribution (5) of the different compounds in the different samples

The relative contribution (%), based on the concentrations of PFAS substances within each sample were PFAS where detected, is presented in Figure 14.

The lake samples (S04, S05, S06, S07) look similar in regards to the components that are found in multiple locations.

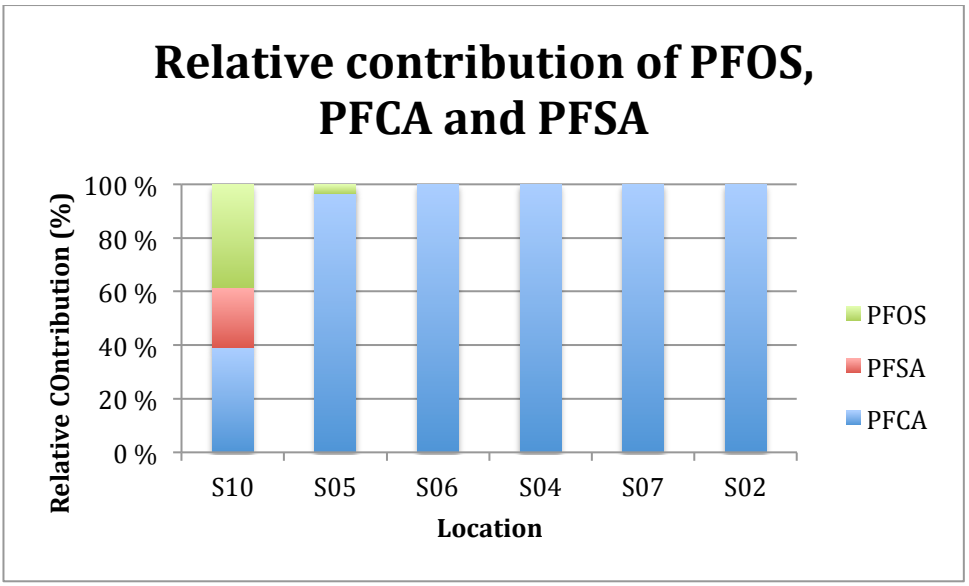

Figure 15: Mean proportions of the two PFAS classes and PFOS measured in each sample location. Proportions were calculated as a percent of total sum of PFASs within a sample. Note: PFSA = all PFSAs except PFOS.

Figure 15 shows the relative contribution of the PFCA, PFSA and PFOS. In the sea and lake sediment samples everything found were PFCAs except for a small amount of PFOS in sample S05. In the airport sample (S10) the largest contributor were also the PFCAs (39%), but PFOS (38%) were the largest single compound contributor. The airport sample were also the only location where the PFSAs where found.

5. Discussion

5.1 Method

The methanol blank had low recoveries of most ISTD, slightly below 40% limit are considered as satisfying results (above the 20% lower limit). This may indicate that the instrument setup was not sufficiently optimized, giving the here described relatively low recoveries.

As expected, the method blank and field blank had low ISTD recoveries when compared to the methanol blank. The ISTD acids with a carbon chain length longer than ten carbons had noticeable lower recoveries in the method and field blank, compared to the same components in the methanol blank. This implies that during sample extraction or preparation the PFCAs are qualitatively excluded or irreversibly absorbed, longer carbon chains have stronger binding to particles, organic material, or surfaces. This could make the extraction of these less effective with the here applied method.

The d3-N-MeFOSA and d7-N-MeFOSE where also lower in the field blank compared to the methanol blank. These components are more volatile and where expected to have a noticeable loss due to the up concentration process and sample handling.

The recovery of ISTD in the samples is lower than in the other blank samples for most of the ISTDs. This suggests that there is a stronger association to matrix making the extraction of the components less effective in the samples compared to the blanks. It might also be a

result of matrix effects cased by components in the sediment that interfered or reacted in a way that the blanks did not mimic.

Matrix effects are the combined effects of all the components other than the analytes in the sample. Ion suppression is one form for matrix effect that LC-MS/MS techniques suffer from. These effects negatively affect the detection capability, precision, and accuracy (Matuszewski et al. 2003). There are many possible sources of ion suppression ranging from compounds in the sample matrix, to contaminants that entered during sample preparation. Some compounds with high mass, and similar retention time as the analytes or alkaline properties are prone to cause such effects. Even if these interfering compounds are not recorded, they can affect the response of the analyte (Smith 2003).

There are techniques to investigate these effects, like blank spike. This could have been done to investigate the problem. There are also some methods that may be used to minimize the effects. The ionization method plays an important role. In this study ESI jet stream where used. To reduce the effect of matrices effects, APCI could have tested. APCI is considered as an ionization method giving less ion suppression. It is hard to minimize these effects, and it usually consists of either improving the sample preparation, or change the chromatographic system (Jessome & Volmer 2006).

After analysis there was discovered salts in the MS. This could count for some of the loss of analyte, due to formation of PFAS salts. The person that used the instrument before the PFAS analysis used a

method with alkaline mobile phases. Before the PFAS method was started, a 4 hour cleaning program and conditioning with new mobile phases where used. This might not have been sufficient, and the change in pH due to residue of the alkaline mobile phase might also have influenced the generation of salts.

5.2 Concentrations

Compared to other resent studies it looks like the method used in this project gives significantly poorer results with regards to recoveries. A study by Lescord et al. has found recoveries at 90 ± 12%.

This study is quite similar to the Lescord et al. (2015) study since they has an airport in close proximity of some of the lakes, but also some atmospherically fed lakes. Their method consisted of freeze-drying, grounding, and extracted using a liquid extraction and WAX clean up. Freeze drying where not used in this study due to fear for loosing the more volatile analytes. Approximately 500 mL of water and 0.250–0.500 g of dry sediments were analyzed using an elemental analyzer interfaced with a Finnegan Delta Plus Mass Spectrometer (Lescord et al. 2015).

The highest concentrations detected in sediment samples by Lescord et al. (2015) were PFOS, FTSs, PFOA, and PFNA. PFNA was detected in most samples in this study as well, but PFOS and 6:2 FTS where only detected at the airport (S10) in comparable levels. The compositions are also similar with mostly PFCA in the atmospherically fed lakes, and more PFSA in the airport contaminated lakes.

The concentrations found and the number of components found at the airport (S10) is higher than Linnévatnet (S04-S07). This is similar to what Lescord et al. (2015) found. Lescord et al. (2015) results showed that the airport where a local point source. The same conclusion seems to be true for Longyearbyen as well. Two of the components found at the airport, PFOS and 6:2 FTS, may be a result of contamination from AFFF. Since sampling location S10 is located downstream from the fire fighting training area at Longyearbyen airport, it might be the source of these components. PFNA where found at the wastewater outlet from the airport (S02). This where the only sea sediment sample where any PFAS where found.

Concentrations found in the remote lakes by Lescord et al. (2015) where in the range of range from 2.7 ± 0.18 to 0.19 ± 0.03 ng/g, dry wt. this is comparable to concentrations found in this study which ranged from 3.17 to 0,30 ng/g dw. In Linnévatnet only PFCAs where detected. In the Lescord et al. (2015) study PFCAs counted for close to 70% of the total PFAS in the atmospherically fed lakes. High percentages of PFCA have also been reported by others (Myers et al. 2012; Stock, Naomi L. et al. 2007; Yeung et al. 2013).

PFBA where detected in all samples from Linnévatnet, but only quantifiable in 3 out of 4 samples. PFBA where not analyzed by Lescord et al (2015), but was reported in high concentrations in Arctic char by Garsjø (2013). Due to these high concentrations the shot chained components where the biggest contributor to the total PFAS in Linnévatnet. Garsjø (2013) found elevated levels of PFNA, PFUnA, PFHxA, PFPeA, PFBA and 6:2FTS. This has similarities to the

results found in this study. PFBA and PFNA where some of the highest, and also PFHxA and PFUnA where found in the Linnévatnet samples (S04-S07). 6:2 FTS where not found at any locations at Linnévatnet.

Sample S08 and S09 where taken in Grønnfjorden close to Barentsburg. This was an expected local source, but in this sample set, there where not found any PFASs in detectable levels in the samples from these locations. These samples where taken in the sea, and in general it seams like sea sediments have low concentrations compared to lakes. To properly examine if Barentsburg is a local point source it would be interesting to look at sediments from the creeks running down from the town to the ocean. For investigating if Barentsburg is a local source for Linnévatnet, it would be interesting to look for airborne contaminants, since this it the most lightly rout for contaminants to Linnédalen.

Due to the position of the lake it is expected that contaminants found are atmospherically transported. Data from the new Adventdalen weather station (available from http:"//www.unis.no /resources/weather-stations-and-web-cameras/") suggests that the predominant wind direction runs along Linnédalen. This makes contamination from Barentsburg miss Linnédalen, but it is expected that some contamination still will reach Linnédalen.

There is some snowmobile traffic from Longyearbyen to Isfjord radio, but if this contributes to the PFAS concentrations in Linnévatnet is not known.

5.3 Comparison from a parallel sampling campaign (Swedish study)

During sampling a group from SLU sampled at the same locations as described in section 3.4. After sampling the samples underwent the exactly the same storage, transportation and sample pre treatment as described in section 3.6.1.

For extraction they used half of the material, 5g instead of 10g. Their extraction where done by adding 2 mL sodium hydroxide solution (100 mM, 80/20 methanol/Millipore water). This where left to soak for 30 min, then spiked with ISTD and 20mL Methanol. The solution where sonicated for 60 min and centrifuged (3000 rpm, 15 min). The supernatant where then decanted before 1 mL sodium hydroxide solution (100 mM, 80/20 methanol Millipore) where added. The sample where added 10mL Methanol and left to soak in 30 min, before the supernatant where decanted. The sample where then added 0.1 mL hydrochloric acid, shaken by hand, centrifuged (3000 rpm, 5 min) and then ¼ of the solution was transferred into another polypropylene tube.

This extraction is done in 3 stages, with less sediment, and more solvent. The soaking time combined with the alkaline and acidic extraction probably gave a better chance of complete extraction.

For up concentration they used a stream of N_2 while this study uses TurboVap. For the sample clean up the same method where used, with the exception that the Swedish method did not use SpinX centrifuge filters as a last clean up step.

The detection of peaks in chromatograms and determination of MDL and MQL where done in the same way as described in section 3.8.3.

Table 6: Comparison of ISTD recoveries between the Swedish method and the method used in this project.

ISTD for compound	Swedish		Norwegian	
	Average	SD	Average	SD
PFBA	42	9	14	7
PFHxA	48	10	14	8
PFOA	48	9	14	5
PFNA	49	11	16	10
PFDA	58	14	11	7
PFUnA	62	12	12	7
PFDoA	61	11	11	8
MeFOSA	72	25	10	2
MeFOSE	69	12	13	2
PFOS	93	18	11	4
PFHxS	87	12	11	5

Table 6 clearly shows better recoveries in the Swedish method. Since the clean up and up concentrations where similar, it lightly that the better recoveries are a result of more complete extraction.

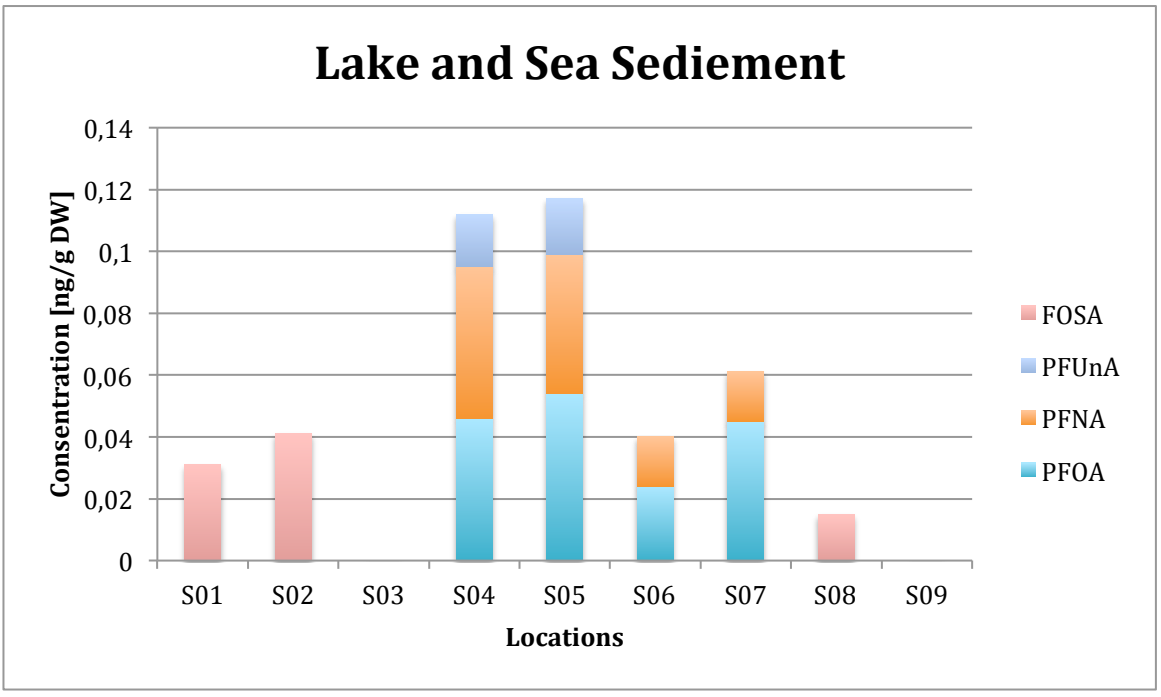

Figure 16: The results from the Swedish method.

Figure 16 shows the results from the Swedish analysis. It is only PFUnDA that are found in bout studies at the same location. PFUnDA where found to be one order of magnitude higher in the Swedish study compared to this study. The samples from Linnévatnet (S04-S07) consist of only PFCA, this was also seen in this study.

6. Conclusion and further perspectives

Sampling on ice surface provided a good access to the sampling site. For grab sediment sampling the ice cover needs to be penetrated. Extensive labor and equipment was needed in order to drill suitable holes and extend them (by sawing) to provide sufficient large openings for reliable sampling. By using a core sampler as described in Strand (2014) a smaller hole would be required, making sampling less time and energy consuming (Strand 2014). Also a core sampler makes it easier to get the upper most layer of the sediment, giving a more accurate picture of recent contaminations.

The recoveriy of ISTD in the samples where in general to low (less than 20%) giving the results to high insecurity to be definite. The results have similarities to other studies and might be an indication of actual concentrations. Also the result indicates that the airport is a local source.

The method was developed for biota, and used by Garsjø (2013) giving recoveries between 40-50% (Garsjø 2013). The recoveries found in this study indicate that the method might not be transferable to sediment. A spike blank could be used to investigate further and may improve the method by making recoveries better. A better wash between the alkaline and acidic method should be tried to eliminate possible effects cased by changing pH, and possible salt formation. The extraction has room for improvements, and a similar extraction to the Swedish method described in 5.3 is recommended for further studies.

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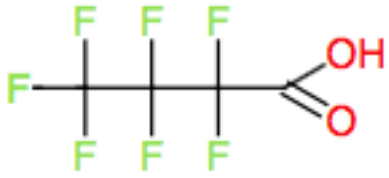
Appendix A: Standard Solutions

The name, producer, lot #, and purity of the standards. n.a = not available

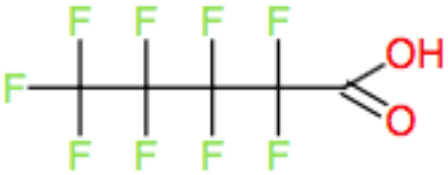
Standard name	Producer		Lot #	Purity
PFAC-MXA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	PFAXMXA0514	n.a
M5PFHxA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	M5PFHxA0810	>98%
M4PFHpA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	M4PFHpA1213	>98%
MFHET	Wellington Laboratories Inc.	Guelph, Ontario, Canada	MFHET0513	>98%
dNMeFOSA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	dNMeFOSA0114M	>98%
d7NMeFOSE	Wellington Laboratories Inc.	Guelph, Ontario, Canada	d7NMeFOSE1213M	>98%
NMeFOSA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	NMeFOSA0114M	>98%
NEtFOSA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	NEtFOSA0714M	>98%
NMeFOSE	Wellington Laboratories Inc.	Guelph, Ontario, Canada	NMeFOSE0314M	>98%
NEtFOSE	Wellington Laboratories Inc.	Guelph, Ontario, Canada	NEtFOSE0114M	>98%
FBET	Wellington Laboratories Inc.	Guelph, Ontario, Canada	FBET0807	>98%
FHET	Wellington Laboratories Inc.	Guelph, Ontario, Canada	FHET0313	>98%
FOET	Wellington Laboratories Inc.	Guelph, Ontario, Canada	FOET1112	>98%
FOSA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	FOSA113	>98%
62FTS	Wellington Laboratories Inc.	Guelph, Ontario, Canada	62FTS1014	>98%
MPFAC-MXA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	MPFACMXA0214	n.a
M8PFOA	Wellington Laboratories Inc.	Guelph, Ontario, Canada	N8PFOA0514	>97,9

Appendix B: Structures

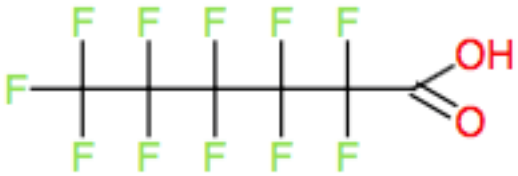
All structures are drawn in the program ChemDoodle Web Components, produced by iChemLabs. This program is available from https://web.chemdoodle.com/about/



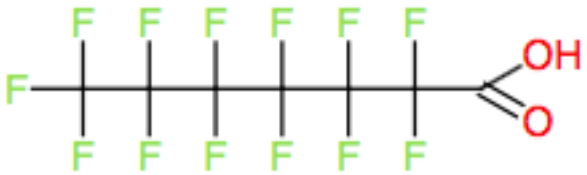
Perfluorobutanoic acid (PFBA)



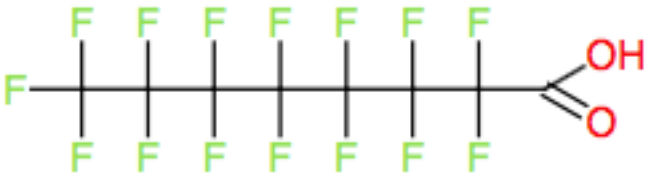
Perfluoropentanoic acid (PFPeA)



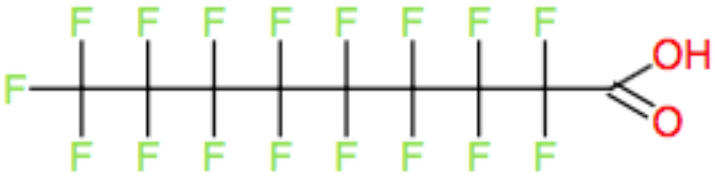
Perfluorohexanoate (PFHxA)



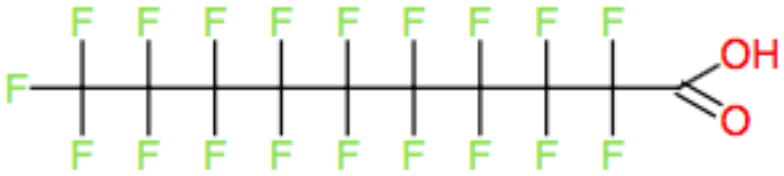
Perfluoroheptanoic acid (PFHpA)



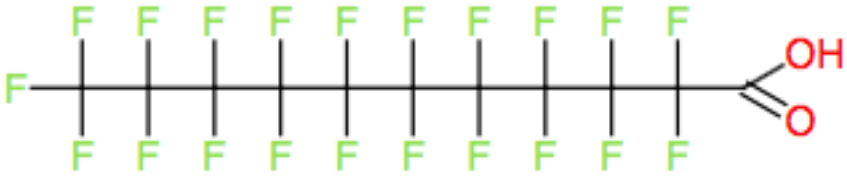
Perfluorooctanoic acid (PFOA)



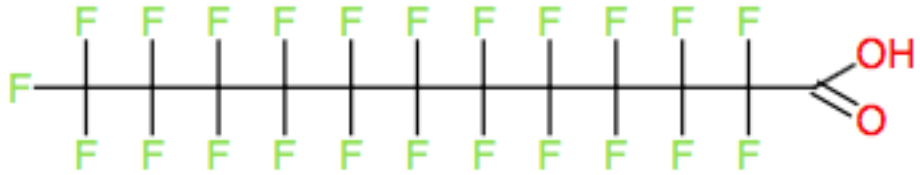
Perfluorononanoic acid (PFNA)



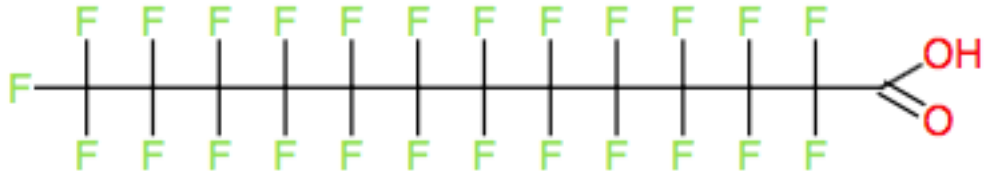
Perfluorodecanoic acid (PFDA)



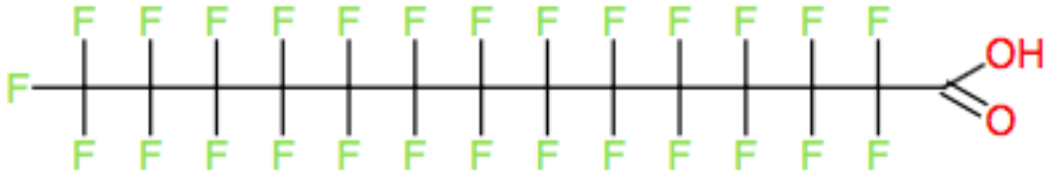
Perfluoroundecanoic acid (PFUnA)



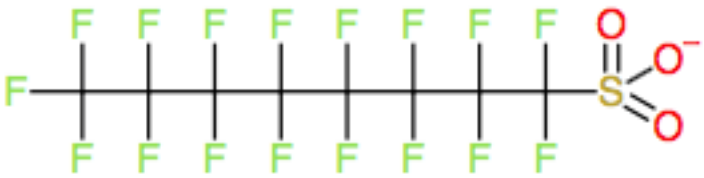
Perfluorododecanoic acid (PFDoA)



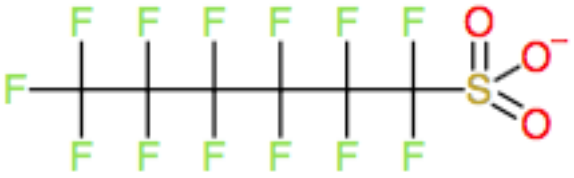
Perfluorotetradecanoic acid (PFTeA)



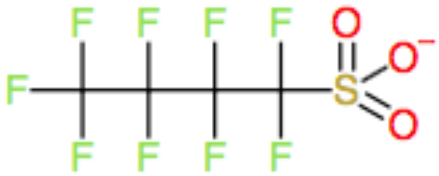
Perfluorotridecanoic acid (PFTrA)



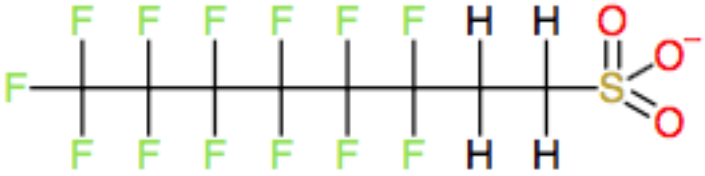
Perfluorooctan sulfonate (PFOS)



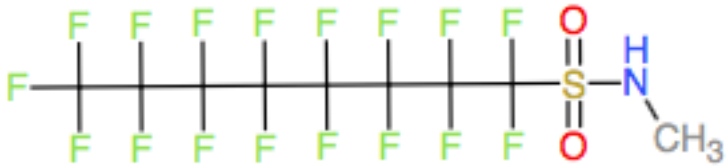
Perfluorohexane sulfonate (PFHxS)



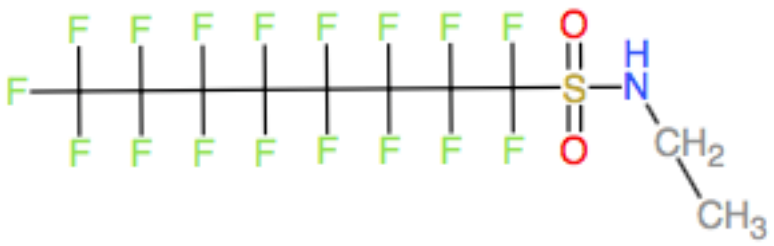
Perfluorobutane sulfonate (PFBS)



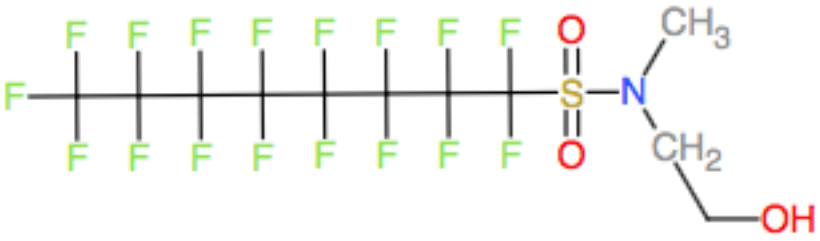
6:2 Fluorotelomer sulfonate (6:2 FTS)



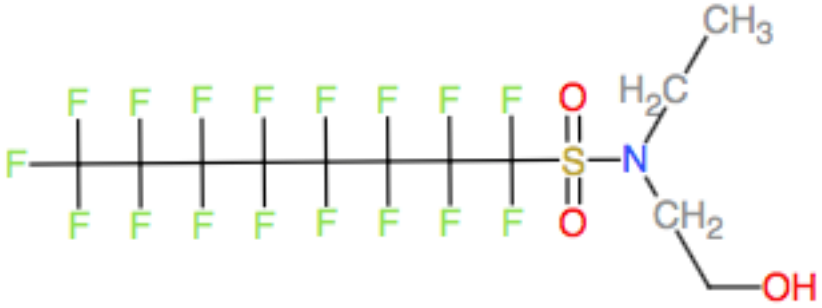
N-Methylperfluoro-1-octanesulfonamide (N-MeFOSA)



N-ethylPerfluoro-1-octaneSulfonamide (N-EtFOSA)

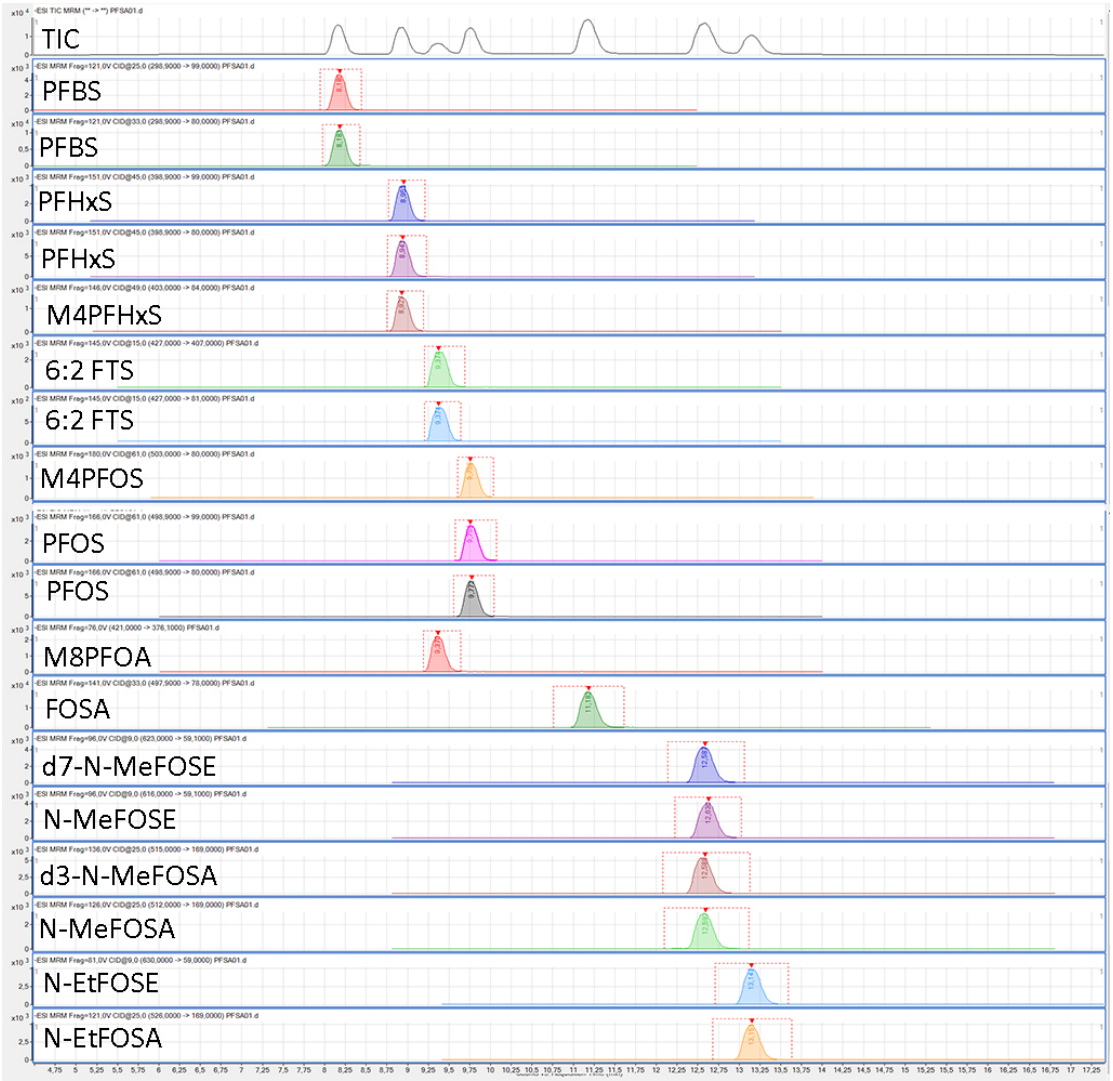


2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)

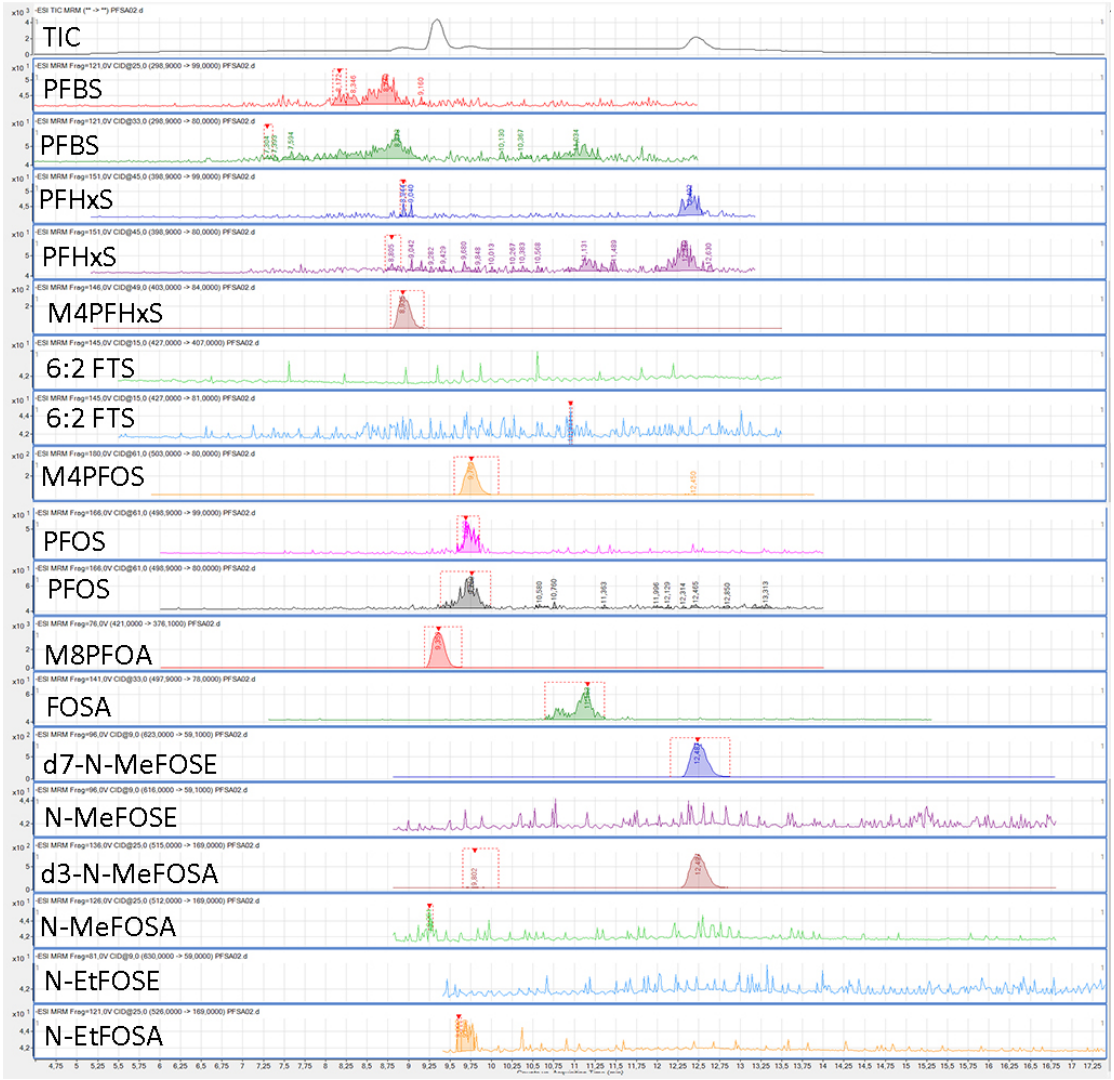


2(N -ethyl perfluorooctane sulfonamido)ethanol (N-EtFOSE)

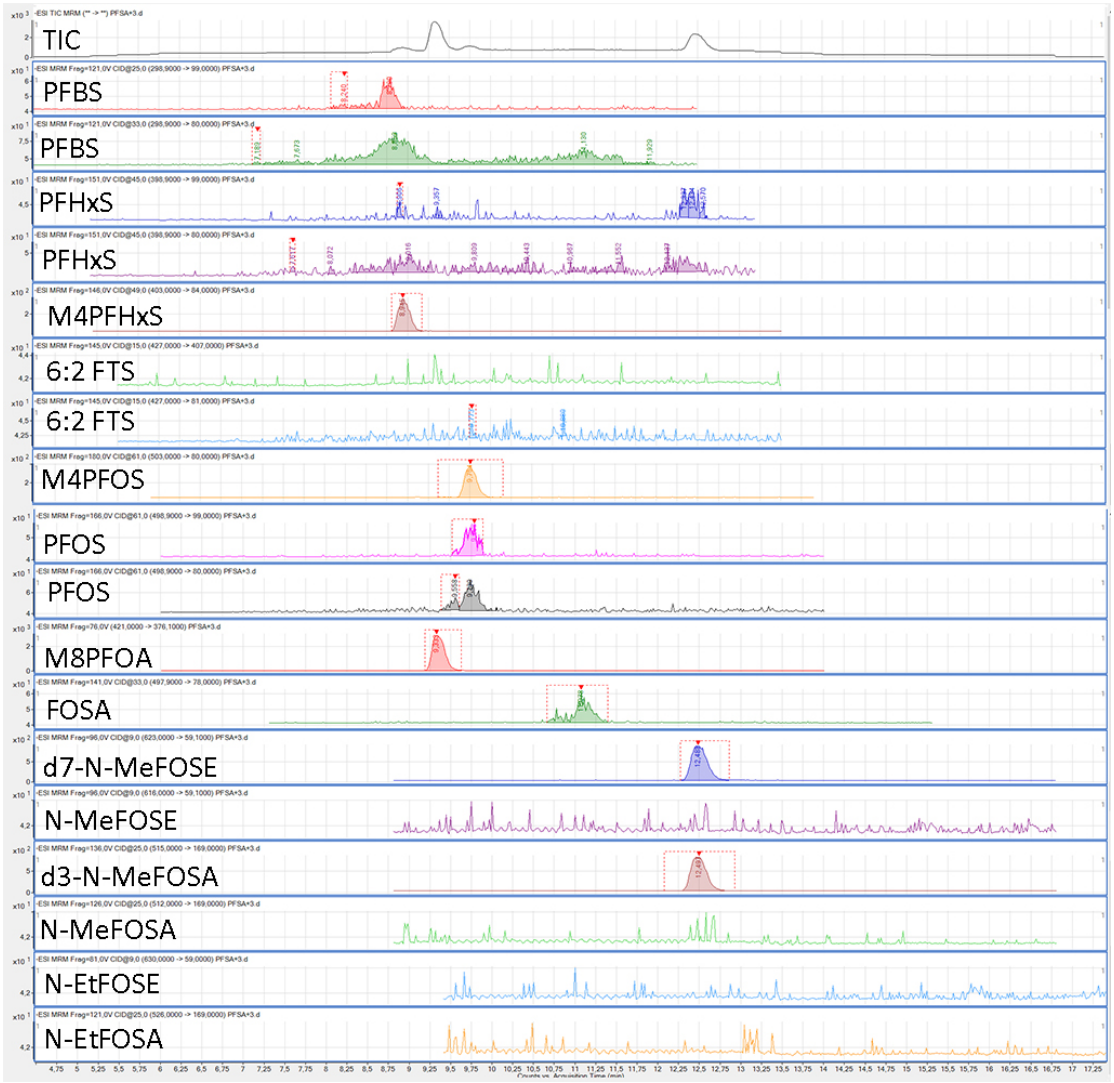
Appendix C: Chromatograms



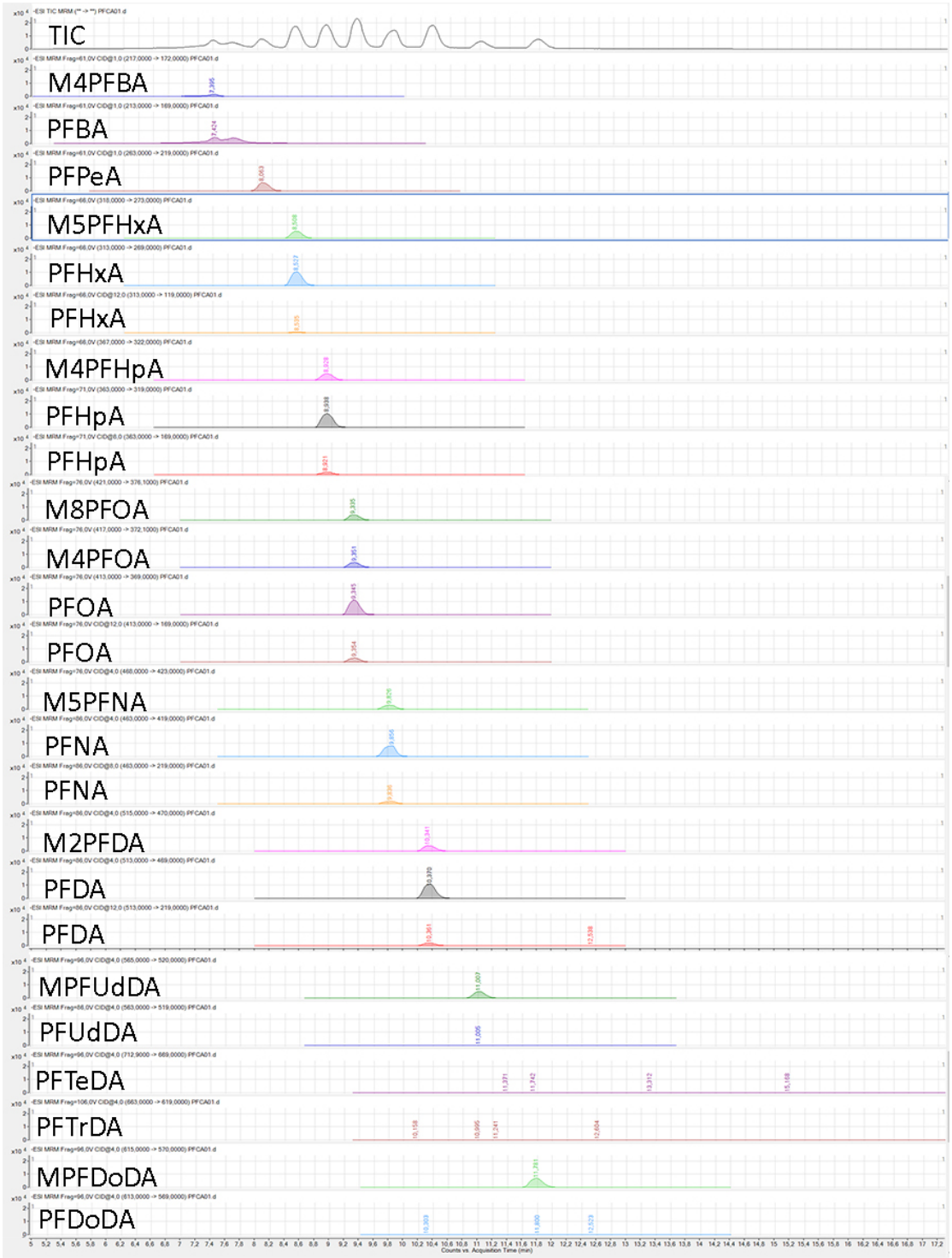
Chromatograms for linearity standard for PFSA. This is a modified screenshot from Masshunter Workstation Software: Qualitative analysis for QQQ version B.06.00 / Build 6.0.633.10



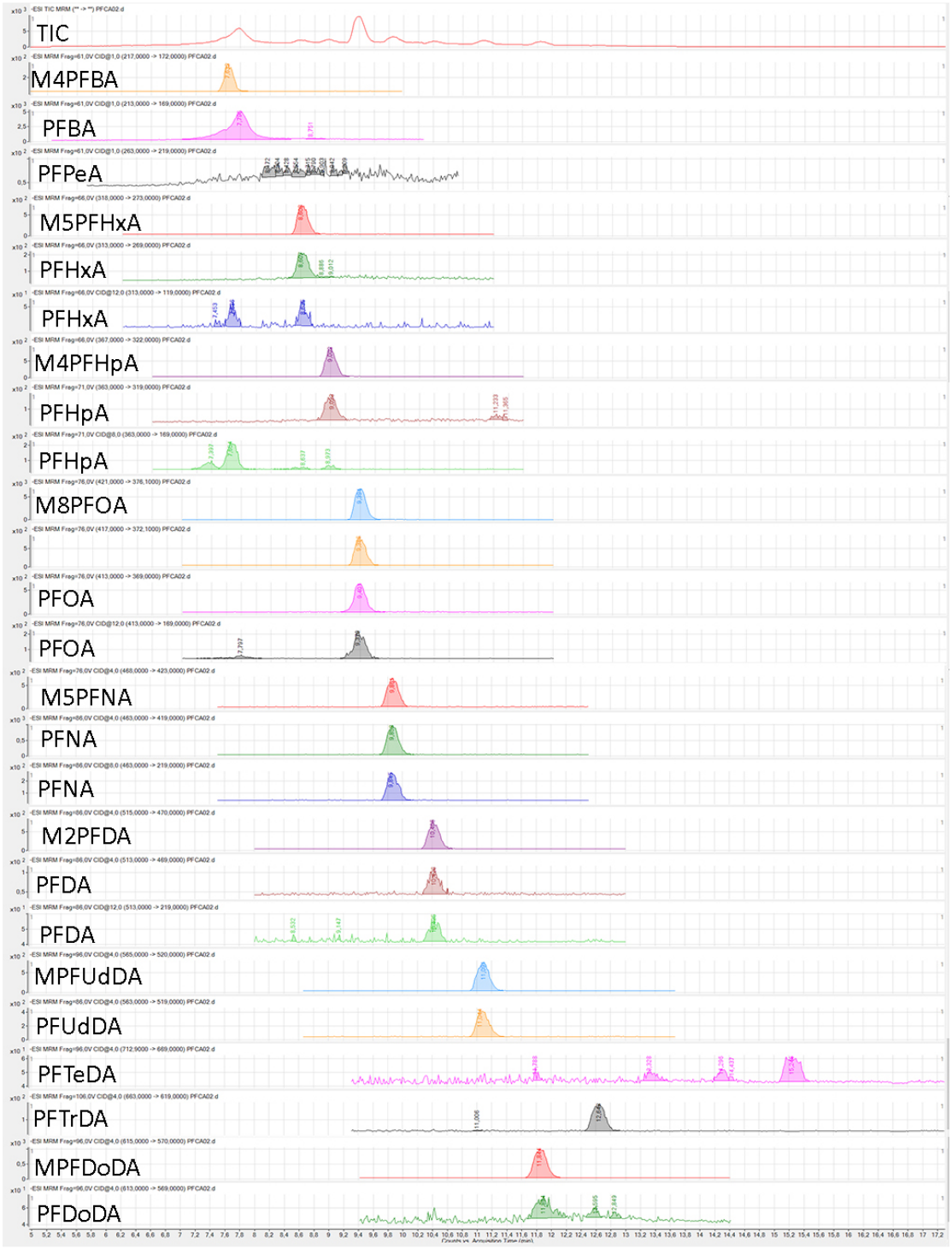
Chromatograms for PFSA at location S4. This is a modified screenshot from Masshunter Workstation Software: Qualitative analysis for QQQ version B.06.00 / Build 6.0.633.10



Chromatograms for PFSA at S10. This is a modified screenshot from Masshunter Workstation Software: Qualitative analysis for QQQ version B.06.00 / Build 6.0.633.10



Chromatograms for PFCA in Linearity standard. This is a modified screenshot from Masshunter Workstation Software: Qualitative analysis for QQQ version B.06.00 / Build 6.0.633.10



Chromatograms for PFCA at S4. This is a modified screenshot from Masshunter Workstation Software: Qualitative analysis for QQQ version B.06.00 / Build 6.0.633.10

APPENDIX D: Instrumental settings

Setup for instrumental analysis

HPLC		
	HiP Sampler	Agilent 1367
	Binary Pump	Agilent 1312
	Colom Pump	Agilent1316
	Colom	Agilent Eclipse plus C18 separation column (2,1 X 150mm 3,5µm)
	Guard Colom	Supelco supelguard discovery 18 (2cm x 2,1mm 55µm)
	mobile phase A	2 mM NH_4OAc in 90:10 methanol/water
	Mobile Phace B	2 mM NH_4OAc in methanol
	Injector volume	10µL
	Needle wash	YES
	Flow	0,2 mL/min
	Colom temp	21
MS/MS		
	QQQ	Agilent 6460 triple quadrupole mass spectrometer
	Gas	N2
	Gas Temp.	300
	Gas flow	5
	Capillary (V)	5000
	Ion Source	Agilent jet stream ESI

Ion Source settings for PFCA method

Gas Flow [L/min]	5
Gas Temp [C]	300
Nebulizer [psi]	25
Sheat Gas Flow [mL/min]	8
Sheath Gas Heater [C]	400
Capillary [V]	5000/-2500
Vcharging [V]	2000 / -500

Ion Source settings for PFSA method

Gas Flow [L/min]	9
Gas Temp [C]	350
Nebulizer [psi]	30
Sheat Gas Flow [mL/min]	8
Sheath Gas Heater [C]	400
Capillary [V]	5000 / -4000
Vcharging [V]	2000 / 0

Values for PFSA method

Compound name	Precursor ion	Product ion	Fragmentor (V)	CV (V)	Retention time (min)
6:2 FTS	427	407	145	15	10,44
6:2 FTS	427	81	145	15	10,44
d3-N-MeFOSA	515	169	136	25	14,91
d7-n-MeFOSE	623	59,1	96	9	14,94
FOSA	497.9	78	141	33	13,04
M4PFHxS	403	84	146	49	9,7
M4PFOS	503	80	180	61	10,88
M8PFOA	421	376,1	76	0	10,36
N-EtFOSA	526	169	121	25	15,55
N-EtFOSE	630	59	81	9	15,52
N-MeFOSA	512	169	126	25	14,91
N-MeFOSE	616	59,1	96	9	14,94
PFBS	298.9	99	121	25	8,49
PFBS	298.9	80	121	33	8,49
PFHxS	398.9	99	151	45	9,7
PFHxS	398.9	80	151	45	9,7
PFOS	498.9	99	166	61	10,88
PFOS	498.9	80	166	61	10,88

Values for PFCA method

Compound name	Precursor ion	Product ion	Fragmentor (V)	CV (V)	Retention time (min)
M2PFDA	515	470	86	4	12,78
M4PFBA	217	172	61	1	8,85
M4PFHpA	367	322	66	0	10,68
M4PFOA	417	372,1	76	0	11,33
M5PFHxA	318	273	66	0	10,13
M5PFNA	468	423	76	4	12,04
M8PFOA	421	376,1	76	0	11,33
MPFDoA	615	570	96	4	14,26
MPFUnA	565	520	96	4	13,53
PFBA	213	169	61	1	8,85
PFDA	513	469	86	4	12,78
PFDA	513	219	86	12	12,78
PFDoA	613	569	96	4	14,26
PFHpA	363	319	71	0	10,68
PFHpA	363	169	71	8	10,68
PFHxA	313	269	66	0	10,13
PFHxA	313	119	66	12	10,13
PFNA	463	419	86	4	12,04
PFNA	463	219	86	8	12,04
PFOA	413	369	76	0	11,33
PFOA	413	169	76	12	11,33
PFPeA	263	219	61	1	9,58
PFTeDA	712,9	669	96	4	16
PFTrDA	663	619	106	4	15
PFUnA	563	519	86	4	13,53

Appendix E: Recovery

Recoveries for all compounds, in all samples. Red= below 20% recovery, Yellow = 20-40% recovery and green = above 40% recovery

Location	MPFBA	MPFHxA	MPFHpA	PFOA	PFNA	PFDA	MPFUnA	MPFDoA	M4PFHxS	M4PFOS	d3-N-MeFOSA	d7-N-MeFOSE
Airport Blank	40,9	28,8	36,3	29,0	27,4	11,8	6,8	2,5	25,5	17,0	1,4	3,0
Field Blank	31,1	23,9	33,1	29,2	30,6	17,0	14,2	10,1	23,7	18,2	4,3	9,0
S01	16,5	17,1	20,9	15,2	17,7	12,8	13,0	11,6	11,2	11,3	9,8	12,6
S02	16,3	15,2	16,1	14,4	13,1	10,7	12,4	12,4	13,5	14,4	11,5	13,9
S03	15,0	16,6	20,3	16,2	18,3	13,0	13,7	12,6	11,1	11,8	9,7	12,1
S04	10,0	9,4	11,9	12,3	12,1	7,5	8,8	8,0	8,8	8,7	9,5	13,5
S05	6,8	6,5	8,2	8,9	8,3	5,2	6,2	5,9	6,2	6,2	9,1	11,0
S06	5,9	5,5	6,9	8,0	7,0	4,5	5,5	5,2	5,3	5,6	7,4	9,7
S07	7,6	7,3	9,2	9,8	9,3	5,9	6,5	5,7	8,4	8,6	9,0	12,5
S08	29,2	33,2	39,0	18,6	39,9	28,7	28,8	32,1	17,0	17,9	14,8	17,4
S09	8,5	9,5	11,5	12,2	10,9	7,8	9,2	7,9	10,2	10,4	9,4	13,1
S10	19,6	18,9	23,4	24,9	23,8	15,2	14,5	10,1	19,5	17,5	10,8	11,2
Method blank	33,6	25,4	34,7	28,5	26,2	12,0	7,6	3,9	21,9	18,1	15,0	17,5
Methanol blank	38,7	39,1	42,2	38,6	42,8	28,9	30,8	30,0	30,3	29,8	26,6	29,4

Appendix F: Sampling Locations

This table additional information about the sampling sites, like % water loss, % organic material

Sample ID	% Water loss	% Organic Matter	Latitude	Longitude	Sampling Date	Notes
S01	33,35	1,78	78°14'35. 2	15°39'50	12-06-2015	Waste water outlet (sea) 59 m
S02	24,27	0,93	78°15.08,9	15°29'48	12-06-2015	Airport outlet 20.5m
S03	33,18	1,47	78°06.51,3	14°56'49.5	12-06-2015	Coalsbukta 30 m
S04	29,17	1,44	78°02'03.1	13°51'16.3	15-06-2015	Depth 13 m, first hole close to inlet at Linnévatnet
S05	36,11	1,81	78°02'23.0	13°49'37.5	15-06-2015	Depth 33 m, second hole at Linnévatnet
S06	36,90	4,82	78.04803	13.80148	16-06-2015	Depth 36 m, third hole at Linnévatnet
S07	32,93	2,98	78.06000	13.77238	16-06-2015	Depth 28 m, fourth hole close to outlet at Linnévatnet
S08	28,38	2,02	77°58'49.7	14°16'03.8	17-06-2015	Depth 85 m, Barentsburg first stop
S09	38,50	1,80	78°00'25.0	14°16'40.8	17-06-2015	Depth 50 m, Barentsburg second stop
S10	20,20	0,49	78°04'01.6	13°37'54.8	18-06-2015	Depth 13 m, Isfjord Radio first stop
S11	NA	NA	78°14'25	15°32'13		Creek from Airport Fire Training Site

Appendix G: Limits (MDL &MDQ)

Limits for sample S10 (in ng/g dw)

	MPFBA	Mph	MPFHpA	PFOA	PFNA	PFDA	MPFUnA	MPFDOA	M4PFHxS	M4PFOS	d3-N-MeFOSA	d7-N-MeFOSE
Detection	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3
MDL	1,04	0,1	0,1	2,70	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
MQL	1,18	0,1	0,1	3,49	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1

Limits for samples S01-S09 (in ng/g dw)

	MPFBA	MPHxA	MPFHpA	PFOA	PFNA	PFDA	MPFUnA	MPFDOA	M4PFHxS	M4PFOS	d3-N-MeFOSA	d7-N-MeFOSE
detection	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3	S/N=3
MDL	1,32	0,1	0,1	1,68	0,1	0,1	0,1	0,13	0,1	0,1	0,1	0,1
MQL	1,55	0,1	0,1	2,08	0,1	0,1	0,1	0,19	0,1	0,1	0,1	0,1

Appendix H: Concentrations

Concentrations in analyzed samples (in ng/g dw)

Location	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFTrDA	PFUnA	PFTeDA	PFDoA
S10	1,47	n.d	0,54	0,32	n.d	2,41	0,1	n.d	0,63	n.d	n.d
S03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S05	2,05	n.d	0,15	0,27	n.d	0,43	n.d	n.d	0,14	n.d	0,14
S06	2,12	n.d	n.d	n.d	n.d	0,15	n.d	n.d	n.d	n.d	0,13
S04	Detected	n.d	n.d	0,11	n.d	0,19	n.d	n.d	n.d	n.d	n.d
S07	1,86	n.d	n.d	0,14	n.d	0,15	n.d	n.d	n.d	n.d	0,12
S02	n.d	n.d	n.d	n.d	n.d	0,23	n.d	n.d	n.d	n.d	n.d
S08	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S09	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

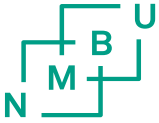
concentrations in analyzed samples (in ng/g dw)

Location	PFBS	PFHxS	6:2 FTS	PFOS	PFOSA	N-MeFOSA	N-MeFOSE	N-EtFOSA	N-EtFOSE
S10	0,16	2,17	0,86	5,40	n.d	n.d	n.d	n.d	n.d
S03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S05	n.d	n.d	n.d	0,11	n.d	n.d	n.d	n.d	n.d
S06	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S04	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S07	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S02	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S08	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
S09	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

Appendix I: Apparatus, consumables, sampling equipment and Instrumental setup

Apparatus		Producer
	Mettler Toledo Excellence Plus Fine Scale	Mettler Toledo, Oslo, Norway
	Heraeus Function Line oven	Thermo electron corporation, Langenselbolg, Germany
	BIOHIT Proline 20-100 µL pipette	Biohit (Now: Sartorius Herlev, Denmark)
	BIOHIT Proline 1-10 mL Pipette	Biohit (Now: Sartorius Herlev, Denmark)
	Vortex	VWR International AS, Oslo, Norway
	Ultrasonic bath	VWR International AS, Oslo, Norway
	50ml centrifuge	VWR International AS, Oslo, Norway
	Eppendorf centrifuge	Eppendorf Norge A/S, Oslo, Norway
	Biotage TurboVap II	Biotage, Uppsala, Sweeden
Consumables		
	50 ml PP-centrifuge tube	VWR International AS, Oslo, Norway
	1.5 ml Eppendorf centrifuge tube	Eppendorf Norge A/S, Oslo, Norway
	Pasteur pipettes	VWR International AS, Oslo, Norway
	Corning® Costar® Spin-X® centrifuge tube filters(pore size 0.22 µm)	Corning Incorporated, New York, USA
	gloves	VWR International AS, Oslo, Norway

Sampling equipment	Aluminum boxes	Not Known
	motorized drill (with a 200 mm cut)	STIHL PTY. LTD, Stihl Inc. Headquarters, Virginia Beach, Virginia, US
	Aluminum foil	Not Known
	Rope	Not Known
	Ice Saw	Not Known
	Grab Sampler	Not Known
	Plastic bags	Not Known
LC-QqQ	Agilent 6460 QqQ	Agilent Technologies, Santa Clara, California, USA
	Agilent 1260- degasser	Agilent Technologies, Santa Clara, California, USA
	Agilent 1200- Auto sampler	Agilent Technologies, Santa Clara, California, USA
	Agilent vin pump SL	Agilent Technologies, Santa Clara, California, USA
	Agilent Eclipse plus C18 (2,1 X 150mm 3,5µm) colon	Agilent Technologies, Santa Clara, California, USA
	Supelco supelguard discovery 18 (2cm x 2,1mm 55µm)	Agilent Technologies, Santa Clara, California, USA



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