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Doctoral thesis

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Håkon Austad Langberg

Trondheim, December 2020

SUMMARY

Per- and polyfluorinated alkyl substances (PFAS) are anthropogenic organic pollutants, defined as aliphatic substances that contain at least one perfluoroalkyl moiety, i.e. "-C_nF_{2n}-". Thousands of PFAS exists, and they are often referred to as "*forever chemicals"* due to their persistence in the environment. PFAS have unique properties and have thus been used in a variety of industrial processes and products. However, a wide range of adverse health impacts have been identified as potential effects of elevated PFAS exposure. These include kidney and testicular cancer, liver damage, dyslipidemia, decreased fertility, thyroid problems, immunotoxicity, and adverse developmental effects. The widespread use of PFAS, including in a range of consumer products, leads to continual diffuse human and environmental exposure. PFAS emitted to the environment from point sources add to the total environmental burden. In addition, point sources (and resulting hot spot areas) may act as an additional source to local wildlife (including fish and invertebrates) and humans, and increased levels of PFAS have been detected in populations affected by a local PFAS source.

The term PFAS mixture refers to the total number of substances that qualify as PFAS (according to the definition above). Many polyfluorinated PFAS can be transformed to other PFAS in the environment. The ultimate result of such transformation is the terminal PFAS. The PFAS undergoing transformation are termed precursors. Transformation of precursors can over time change the PFAS mixture in the environment. The overall objective of this work was to investigate how differences in PFAS mixtures released from different point sources (and hence products) can affect fate and transport in the aquatic environment, including uptake in biota. A thorough understanding of the fate and transport of the pollutants at a contaminated site is vital when carrying out risk assessments and selecting site remediation strategies. A subsequent objective was therefore to identify optimal ways in which PFAS contaminated site investigations can be carried out.

In order to explore different PFAS sources and environmental conditions, three different case study sites in Norway were selected, each representing a (or several) specific PFAS

source(s): 1) Lake Tyrifjorden, a freshwater lake polluted by PFAS, where a shutdown factory that produced paper products and a fire station were the two suspected PFAS sources; 2) Bodø airport where the local marine environment has been exposed to PFAS primarily from extensive use of aqueous film forming foam (AFFF) for firefighting; and 3) Svalbard airport where the local arctic marine environment was exposed to PFAS pollution from the use of AFFF, from runoff from local diffuse sources, and via long-range transport. Fieldwork and subsequent chemical analyses were conducted at the three case study sites. In order to investigate the spatial distribution of PFAS contamination, biota and abiotic media were sampled at different distances from the point source(s). PFAS profiles (i.e., the relative distribution of the different PFAS in a sample) and concentrations in samples from the recipients (the local marine environment or freshwater lake) were compared to concentrations and profiles in samples representing emissions from the sources. Concentrations of PFAS in animals at different trophic levels in the aquatic food chain were determined in order to investigate uptake and accumulation in the local biota. Investigations included zooplankton, benthic invertebrates, decapods, fish, and birds.

In addition to the investigated case study sites, differences in PFAS profiles in fish depending on PFAS source were explored using available data from Norwegian freshwater systems as examples. Fish data from lakes subject to three different sources of PFAS were explored: 1) production of paper products, 2) the use AFFF, and 3) long-range atmospheric transport. A total of eight sites were included in the data analysis: four airports, three large lakes without major PFAS point sources, and lake Tyrifjorden. Data for the different sources were provided by Norwegian stakeholders (Avinor and the Norwegian Defence Estates Agency (Forsvarsbygg in Norwegian)) who own land that is contaminated by PFAS (the airports), monitoring data compiled through monitoring programs commissioned by the Norwegian Environment Agency (the three large lakes without major PFAS point sources), and data from the lake Tyrifjorden case study site.

Both the abiotic and biotic compartments at all the case study sites (lake Tyrifjorden, Bodø airport, and Svalbard airport) showed elevated concentrations of PFAS in the environment close to the point sources compared to areas expected to receive PFAS

mainly via long-range transport. Similarly, the comparison of fish data from Norwegian freshwater systems subject to different sources of PFAS showed higher concentrations in fish from lakes receiving PFAS directly from point sources compared to lakes considered to mainly receive PFAS via long-range atmospheric transport. Clear differences in environmental PFAS profiles were found, both in abiotic compartments and in biota, depending on the type of PFAS source. PFAS pollution arising from the production of paper products was dominated by precursor compounds to perfluorinated alkyl acids (PFAA) in sediments, and by long chained perfluoroalkyl carboxylic acids (PFCA) and perfluorooctanesulfonic acid (PFOS) in biota. The precursors to PFAA in sediments which were detected in the highest concentrations, i.e. the di-substituted phosphate ester of N-ethyl Perfluorooctane sulfonamido ethanol (SAmPAP diester) and the long chained fluorotelomer sulfonates (FTS; 10:2 FTS, 12:2 FTS, and 14:2 FTS) are not routinely targeted by chemical analyses. Significant concentrations of long chained FTS were also detected in biota. Environmental samples from areas receiving PFAS from AFFF point sources were dominated by perfluoroalkane sulfonic acids (PFSA), in addition to 6:2 FTS at areas where newer AFFF formulations have been used. PFAS profiles in fish receiving PFAS mainly via long-range atmospheric transport were dominated by PFCA. Ratios for specific PFCA pairs indicative of long-range atmospheric transport were identified. It was concluded that the different PFAS profiles can be used to identify the sources of pollution (i.e., by comparing PFAS profiles in samples in order to explore the origin of the pollution, termed fingerprinting). Variations in partitioning and environmental fractionation behaviour between different PFAS and isomers should be taken into consideration when comparing PFAS profiles and concentrations in different samples.

Source tracking was conducted for lake Tyrifjorden using fingerprinting. PFAS profiles in samples representing the suspected sources and PFAS profiles in samples from the lake were compared. A sediment core was used to explore historic emissions of PFAS to the lake. It was concluded that the shutdown factory which produced paper products was the main source of the PFAS pollution in the lake. Further, it was concluded that emission volumes were high, and thus that production of paper products is likely a major, largely overlooked, global source of emissions of PFAS.

(Bio)transformation of precursors was found to have a significant effect on the observed fate and transport. (Bio)transformation was found to change the physiochemical properties of a compound and thus its partitioning and thereby its transport and biota exposure route (i.e., via ambient water or diet). In lake Tyrifjorden, the relationships between PFAA concentrations in fish and concentrations in ambient water (i.e. bioaccumulation factors, BAF) were very high compared to relationships reported elsewhere. It was concluded that the reason for this is that hydrophobic precursors to PFAA in sediments are taken up into biota and are biotransformed into PFAA as they are transferred through the food chain. The main exposure route of PFAA to fish in lake Tyrifjorden was determined to be via diet. Therefore, it was concluded that PFAS burdens in biota cannot necessarily be estimated with sufficient accuracy based solely on water or sediment concentrations. Depending on the specific PFAS, species-specific accumulation was reported. Significant accumulation of 6:2 FTS was reported in invertebrates at Bodø airport and Svalbard airport. However, very low concentrations were reported for vertebrates (fish and birds). It was hypothesised that (some) invertebrates have a lower capacity for biotransformation of 6:2 FTS compared to vertebrates. It was further concluded that several species as well as abiotic media should be investigated to assess the environmental PFAS mixture, especially when the environmental behaviour of the relevant PFAS, or the PFAS mixture used at the source is unknown.

The percentage of precursors (as a percentage of the total sum PFAS) decreased with distance from the PFAS sources. This was interpreted as an indication that precursor compounds in the environment are increasingly transformed to intermediate and terminal fluorinated degradation products with time, and hence distance. In lake Tyrifjorden, a strategy for characterising the total PFAS mixture was explored where a combination of targeted analyses and a method for estimating the total PFAS mixture were used for samples representing different degrees of (bio)transformation completeness. It was concluded that including a spatial dimension in a sampling campaign should be considered to evaluate the fate of the emitted PFAS mixture. Further, the combined approach of including a spatial dimension and applying both targeted analyses as well as approaches to quantify the total PFAS mixture, was considered to be a promising approach to more accurately understand PFAS environmental fate and transport.

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ABBREVIATIONS

3M Company	3M
Aqueous film forming foam	AFFF
Attention deficit/hyperactivity disorder	ADHD
Bioaccumulation factors	BAF
Branched	Br (e.g. branched PFOS (Br-PFOS))
Carbon atom	C
Department of Food Safety and Infectious Biology	MatInf
Electrochemical fluorination	ECF
European Chemicals Agency	ECHA
European Environment Agency	EEA
European Food Safety Authority	EFSA
Extractable organic fluorine	EOF
Firefighting training station	FFTS
Fluorine atom	F
Fraction of organic carbon	fOC
High performance liquid chromatography and mass spectrometric detection	HPLC/MS-MS
High resolution mass spectrometry	HRMS
Hydrogen atom	H
Hydrogen fluoride	HF
International Union of Pure and Applied Chemistry	IUPAC
Limit of quantification	LOQ
Linear	L (e.g. linear PFOS (L-PFOS))
Liquid chromatography quadrupole time-of-flight mass spectrometry	LC-qTOF-MS
Norwegian Institute for Water Research	NIVA
Norwegian University of Life Sciences	NMBU
Poly(tetrafluoroethylene)	PFTE (also known as Teflon)
Principal Component Analysis	PCA
Solid-phase extraction	SPE
Standard error of the mean	SEM
Total oxidizable precursor assay	TOP assay
Trophic magnification factors	TMF
United Nations Environment Programme	UNEP
University Centre in Svalbard	UNIS
Wastewater treatment plants	WWTP

ABBREVIATIONS FOR GROUPS AND SUBSTANCES WITHIN PER AND POLYFLUOROALKYL SUBSTANCES (PFAS)

Per- and polyfluorinated alkyl substances	PFAS
Perfluorinated alkyl acids	PFAA
Perfluorooctane sulfonyl fluoride	PFOSF
Perfluoroalkane sulfonic acids	PFSA
Perfluoroalkyl carboxylic acids	PFCA
Fluorotelomer alcohols	FTOH
Fluorotelomer sulfonates	FTS
Fluorotelomer mercaptoalkyl phosphate esters	FTMAP
Fluorotelomer sulfonamidoalkyl betaine	FTAB
PFOS precursor substances with eight perfluorinated carbons	preFOS
Mono-, di- and tri-substituted phosphate esters of N-ethyl Perfluorooctane sulfonamido ethanol	SAmPAP
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPA, PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnDA
Perfluorododecanoic acid	PFDoDA
Perfluorotridecanoic acid	PFTrDA
Perfluorotetradecanoic acid	PFTeDA
Perfluoropentadecanoic acid	PFPeDA
Perfluorobutanesulfonate	PFBS
Perfluorohexanesulfonate	PFHxS
Perfluoroheptanesulfonate	PFHpS
Perfluorooctanesulfonic acid	PFOS
Branched Perfluorooctanesulfonic acid isomers	Br-PFOS
Perfluorodecanesulfonate	PFDS
Perfluorododecansulfonate	PFDoDS
Perfluorooctanesulfonamide	FOSA
N-methyl Perfluorooctanesulfonamide	MeFOSA
N-ethyl Perfluorooctanesulfonamide	EtFOSA
N-ethyl Perfluorooctanesulfonamidoethanol	EtFOSE
Perfluoro-1-octansulfonamidoacetic acid	FOSAA
N-methylPerfluorooctansulfonamido acetic acid	MeFOSAA

N-ethylPerfluorooctansulfonamido acetic acid	EtFOSAA
6:2 Fluorotelomer sulfonate	6:2 FTS
8:2 Fluorotelomer sulfonate	8:2 FTS
10:2 Fluorotelomer sulfonate	10:2 FTS
12:2 Fluorotelomer sulfonate	12:2 FTS
14:2 Fluorotelomer sulfonate	14:2 FTS
Perfluoro-3,7-Dimethyloctanoic acid	PF-3,7-DMOA
5:3 Fluorotelomer carboxylic acid	5:3 FTCA
7:3 Fluorotelomer carboxylic acid	7:3 FTCA

KEY TERMS AND PHRASES

PFAS

Per- and polyfluorinated alkyl substances (PFAS) are defined as aliphatic substances that contain at least one perfluoroalkyl moiety (i.e. at least one carbon atom (C) on which all the hydrogen atoms (H), present in the nonfluorinated analogue substance they are derived from, have been replaced by fluorine atoms (F)), i.e. "-C_nF_{2n}-" (OECD, 2018). The most well-investigated group of PFAS is the perfluorinated alkyl acids (PFAA). PFAA are further divided into several groups, including perfluoroalkane sulfonic acids (PFSA) and perfluoroalkyl carboxylic acids (PFCA).

PFAS mixture

According to the International Union of Pure and Applied Chemistry (IUPAC), the definition of the term *mixture* is "Portion of matter consisting of two or more chemical substances called constituents" (International Union of Pure and Applied Chemistry, 2019). Therefore, the term *PFAS mixture* is defined herein to refer to the total number of substances that qualify as PFAS (according to the definition above) present in the matter or compartment in question (e.g. in the environment as a whole, in sediments or water or air or biota at a specific site, in commercial products such as AFFF, etc.). Thus, the terms *environmental PFAS mixture* and *the PFAS mixture in sediments* are used to describe the total number of substances in the environment (globally or within a specific area) that fit the definition of PFAS, and the total number of substances that fit the definition of PFAS within the sediments in question, respectively. Similar phrases are used for other compartments.

PFAS profiles

The composition of the different PFAS in a sample (i.e., their relative distribution) is termed the PFAS profile.

Precursors

PFAS that can be transformed to other PFAS are termed precursors in this thesis. Many polyfluorinated PFAS are ultimately transformed into PFAA in the environment and are thus termed precursors to PFAA.

Hot spots and point sources

In this thesis, *hot spots* are defined as areas where environmental PFAS concentrations, due to a local source, are significantly higher than concentrations observed at sites dominated by long-range transport and diffuse sources. Such local PFAS sources are termed *point sources*.

Environmental fractionation

Depending on physiochemical properties, environmental partitioning, and hence transport, differ between different substances. This results in that substances (with different physiochemical properties) in the environment over time will be separated. This effect is termed *environmental fractionation*.

Source tracking and fingerprinting

Investigations with the aim of identifying the source(s) of the pollution is termed *source tracking*. One approach for source tracking is to compare the identified substances and the relationships between them in a specific sample (i.e. the chemical "fingerprint") to other samples in order to explore the origin of the pollution (e.g. sources and exposure pathways). Such approaches are termed *fingerprinting*.

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LIST OF FIGURES

LIST OF PAPERS

This thesis consists of five papers:

Paper I — Langberg, H. A.; Hale, S. E.; Breedveld, G. D.; Jenssen, B. M.; and Jartun, M. '**PFAS fingerprints in fish from Norwegian freshwater bodies subject to different source inputs**'. Submitted to Environmental Science & Technology.

Paper II — Langberg, H. A.; Arp, H. P.; Breedveld, G. D.; Slinde, G. A.; Grønning, H. M.; Høisæter, Å.; Jartun, M.; Rundberget, T.; Jenssen, B. M.; and Hale, S. E. (2020) '**Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: source and historic emission tracking**'. Environmental Pollution, 116259. https://doi.org/10.1016/j.envpol.2020.116259

Paper III — Langberg, H. A.; Breedveld, G. D.; Slinde, G. A.; Grønning, H. M.; Høisæter, Å.; Jartun, M.; Rundberget, T.; Jenssen, B. M. and Hale, S. E. (2020) '**Fluorinated Precursor Compounds in Sediments as a Source of Perfluorinated Alkyl Acids (PFAA) to Biota**', Environmental Science & Technology, 54(20), pp. 13077–13089. doi: 10.1021/acs.est.0c04587.

Paper IV — Langberg, H. A.; Breedveld, G. D.; Grønning, H. M.; Kvennås, M.; Jenssen, B. M. and Hale, S. E. (2019) '**Bioaccumulation of Fluorotelomer Sulfonates and Perfluoroalkyl Acids in Marine Organisms Living in Aqueous Film-Forming Foam Impacted Waters**', Environmental Science & Technology, 53(18), pp. 10951–10960. doi: 10.1021/acs.est.9b00927.

Paper V — Ali, A. M.; Langberg, H. A.; Hale, S. E.; Kallenborn, R.; Hartz, W. F.; Mortensen, Å.-K.; Ciesielski, T. M.; McDonough, C. A.; Hartz, W.; Jenssen, B. M. and Breedveld, G. D. '**The fate of poly- and perfluoroalkyl substances in a marine food web influenced by land-based sources in the Norwegian Arctic**'. Submitted to Environmental Science: Processes & Impacts.

Declaration of contribution:

Paper I: HAL, MJa, and GBr planned the work. HAL and MJa collected data, carried out the data analysis and made figures. HAL was the main author. The paper was written with contributions from the co-authors.

Paper II: The field campaign was planned by HAL, GSl, HMG, SaH, and MJa. Fieldwork was performed by HAL, GSl, HMG, SaH, and MJa. Laboratory work was performed by TRu and MJa. HPA carried out the modelling and made the associated figures. HAL carried out the other data analysis and made

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figures. HAL was the main author and wrote the paper with contributions from the co-authors.

Paper III: The field campaign was planned by HAL, GSl, HMG, SaH, and MJa. Fieldwork was performed by HAL, GSl, HMG, SaH, and MJa. Laboratory work was performed by TRu and MJa. HAL carried out the data analysis and made figures. HAL was the main author and wrote the paper with contributions from the co-authors.

Paper IV: The field campaign was planned by HAL in collaboration with MKv. HAL and HMG performed the field work. Laboratory work was performed by Eurofins Environment Testing Norway. HAL carried out the data analysis and made figures. HAL was the main author and wrote the paper with contributions from the co-authors.

Paper V: The field campaign was planned by HAL in collaboration with SaH, GBr, BMJ, and RKa. Fieldwork was performed by HAL, GBr, CAM, ÅKM, TMC, and WFH. Laboratory work was performed by AAM, HAL and WFH. AAM carried out the data analysis and made figures. The main writing and preparation of the manuscript was done by AAM and GBr with contributions from the co-authors.

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AIMS AND HYPOTHESES OF THE THESIS

Per- and polyfluorinated alkyl substances (PFAS) refer to a large class of anthropogenic organic pollutants. Due to their unique properties such as high chemical stability and being both water and fat repellent, PFAS have been used in a variety of industrial processes and consumer products. These include aqueous film-forming foams (AFFF) used for firefighting, additives when producing water and fat resistant disposable paper products and food contact materials, processing aids for non-stick cookware, in waterproof and stain repellent clothing and textiles, and in ski waxes. PFAS are relatively mobile in the aquatic environment, can undergo long-range transport and as such are ubiquitous worldwide. Although some PFAS can be (bio)transformed in the environment, their terminal end products are extremely persistent and do not degrade under normal environmental conditions. For this reason, PFAS have been given the popular name "*forever chemicals"* in wider society. Toxicokinetics vary depending on compound specific properties and differences between organisms, and large species and gender-dependent variations have been reported. Some long-chained perfluorinated alkyl acids (PFAA) have been shown to biomagnify in aquatic ecosystems, especially the eight carbon perfluorinated sulfonic acid, perfluorooctanesulfonic acid (PFOS). The reason for the higher biomagnification potential of PFOS compared to other PFAA has been suggested to be due to transformation of PFOS precursor compounds as these are transferred through the food chain, and similar mechanisms are suspected to be confounding factors for biomagnification of other PFAS.

Concerns related to toxic effects on the environment and human health have resulted in several legacy PFAS being regulated and phased out in some parts of the world. However, the phased-out PFAS are often replaced by new PFAS with unknown environmental behaviour and toxicity. The sum of PFAS quantified using targeted analyses is often small compared to the sum of PFAS estimated using methods for estimating total PFAS. This is likely due to the large number of environmentally relevant PFAS, including known and unknown PFAS used directly in industrial processes and consumer products, replacement compounds for phased-out PFAS, impurities, and degradation products. This combined makes it practically impossible to target each individual substance.

Certain contaminated areas have been identified as PFAS hot spots owing to PFAS production and/or use in industrial processes or products. In this work, these hot spots are defined as areas where environmental PFAS concentrations, due to a local source, are significantly higher than concentrations observed at comparable sites dominated by PFAS from diffuse sources and long-range transport.

The overall objective of this thesis was to investigate how differences in PFAS mixtures released from different point sources (and hence products) can affect fate and transport of PFAS in the aquatic environment. The difference in PFAS formulation depending on the year of production was also taken into consideration. In addition, a subsequent objective was to identify optimal ways in which PFAS contaminated site investigations can be carried out. A sound understanding of a polluted site is vital for carrying out risk assessments and selecting site remediation strategies.

Three different case study sites in Norway were selected, representing different PFAS sources and environments: 1) lake Tyrifjorden, a freshwater lake polluted by a factory producing disposable paper products coated with PFAS (**Paper II** and **Paper III**); 2) Bodø airport where the local marine environment was exposed to PFAS primarily from extensive use of AFFF (**Paper IV**); and 3) Svalbard airport where the local arctic marine environment was exposed to PFAS pollution from the use of AFFF, from runoff from local diffuse sources, and via long-range transport (**Paper V**). In addition, differences in PFAS profiles in fish subjected to different source inputs were explored in **Paper I**.

The objectives were divided into specific aims (1-3) and each aim was further divided into hypothesis (a-c). These were as follows:

Aim 1. Investigate whether PFAS profiles and concentrations of specific compounds and isomers can be used to identify the source of the pollution (**Paper I** and **Paper II**).

Hypotheses:

a. PFAS mixtures released at point sources differ depending on source type (i.e. application or product) and date released. This results in different environmental PFAS mixtures dependant on the main source(s).
b. Indicative individual PFAS and/or PFAS profiles, including the relationship between linear and branched isomers, can be used to identify PFAS sources.

Aim 2. To ascertain the importance of directly measuring concentrations of PFAS in biota, and including organisms representing different phylogenetic groups, and/or different habitats and diets, including trophic level (**Paper III**, **Paper IV**, and **Paper V**).

Hypotheses:

a. The physiochemical properties, and hence the environmental partitioning, of precursor PFAS might be altered by (bio)transformation, which may affect relationships between concentrations of degradation products in environmental compartments. Therefore, uptake of a specific compound by biota cannot solely be predicted by concentrations of that compound in abiotic compartments such as sediment or water.
b. Relationships between PFAS concentrations in sediments and/or water and PFAS concentrations in various biota can be better evaluated by accounting for: 1) differences in exposure routes for biota with different habitats and diets, including trophic level; and 2) differences in biotransformation and/or depuration between different species.

Aim 3. Investigate approaches that can be used to determine the fraction of environmental PFAS not accounted for using targeted analyses (**Paper III** and **Paper IV**).

Hypotheses:

a. PFAS mixtures detected at distances further from point source releases represent older releases composed of smaller fractions of precursors due to more complete transformation to terminal degradation products.
b. Targeted chemical analyses of a limited number of compounds in biota from different trophic levels and abiotic media with varying distance from the source can be used to evaluate potential transformation of unknown PFAS to targeted PFAS. The use of methods for estimating total PFAS in samples can complement the targeted analyses to give information about quantity and final degradation products of the unaccounted PFAS.

INTRODUCTION

Per- and polyfluorinated alkyl substances (PFAS) refer to a large class of anthropogenic organic pollutants that have been produced since the late 1940s (Wang *et al.*, 2017a). PFAS are often referred to as "*forever chemicals"* due to their persistence in the environment (Kwiatkowski *et al.*, 2020). Buck et al. (2011) defined PFAS as aliphatic substances that contain at least one perfluoroalkyl moiety (i.e. at least one carbon atom (C) on which all the hydrogen atoms (H), present in the nonfluorinated analogue substance they are derived from, have been replaced by fluorine atoms (F)) (Buck *et al.*, 2011). In recent years the definition of a perfluoroalkyl moiety has been expanded from "C_nF_{2n+1}-" in Buck et al. (2011) to "-C_nF_{2n}-" in order to include substances with both ends of the perfluoroalkyl moiety attached to functional groups and/or poly- or nonfluorinated moieties (OECD, 2018). Substances that either have a functional group which provides surfactant properties, or nonpolymer compounds that can be transformed into such substances have attracted the most attention within the PFAS research community (Buck *et al.*, 2011; Sha *et al.*, 2019; Kwiatkowski *et al.*, 2020). Other substances, such as fluoropolymers and perfluoroalkanes (e.g. octadecafluorooctane, shown in Figure 1, or the refrigerants tetrafluoromethane and hexafluoroethane) are by definition PFAS (because they contain perfluoroalkyl moieties) but have generally not been the focus of PFAS research (Buck *et al.*, 2011; Sha *et al.*, 2019; Kwiatkowski *et al.*, 2020).

Fluorocarbon Chemistry

Fluorine belongs to group 17 in the periodic table, the halogens. The valence electrons belonging to the elements in this group experience high effective nuclear charges due to a relatively low screening effect by the core (non-valence) electrons compared to the nuclear charges of halogens. As a consequence, the valence electrons in this group are generally attracted more strongly to the nucleus which results in smaller atomic radii compared to other elements in the same period (i.e. elements with valence electrons in the same electron shell/valence electrons with the same principal quantum number). As fluorine belongs to period 2 in the periodic table, its valence electrons are in the second shell and are therefore closer to the nucleus and experience stronger forces compared to

the other halogens. Thus, fluorine is the smallest halogen, one of the smallest elements, and the most electronegative element (Tro, 2008).

Together, these properties are the underlying cause of many of the unique characteristics of fluorocarbons (Lemal, 2004; Krafft and Riess, 2015b) including the following. First, the difference in electronegativity between carbon and fluorine means that C-F bonds are highly polar. This makes them among the strongest bonds in organic chemistry, as well as them being relatively short. Second, the ability of fluorine to bind strongly to carbon combined with its small size makes it possible for fluorine to replace hydrogen in most organic molecules. Third, the C-C bonds in fluorocarbons are strengthened by the electron withdrawing fluorine which, in combination with the strong C-F bonds, results in the extreme persistence of these substances. Fourth, perfluoroalkanes are nonpolar and have a higher surface area and lower intermolecular forces than alkyl chains of comparable length. This means they are much more hydrophobic than alkyl chains (of the same length) and are practically immiscible with water. Fifth, due to low polarizability (due to the proximity of the valence electrons to the nucleus) of the fluorine atom, dispersion forces are weak, and the surface energies of fluorocarbons are low. Due to fluorine's weak dispersion forces, the interaction energy of hydrocarbon molecules with themselves is greater than with fluorocarbon molecules, and as a result their mutual solubility is low. Due to the low surface energies, cohesive forces between fluorocarbon molecules are low, resulting in low surface tension, and materials with low surface energy have weaker interactions with other molecules.

Fluorocarbons have been used in a tremendous number of different processes and products due to their useful properties. The characteristics listed above make up many of the desired properties of fluorocarbons, such as being water and fat repellent, resistant to chemical and terminal degradation, and possessing non-stick properties (Lemal, 2004; Krafft and Riess, 2015b).

To obtain the desired properties for use in processes and products, hydrophobic perfluoroalkyl chains are combined with highly hydrophilic moieties such as acidic groups (e.g. carboxyl group (-COOH), sulfonate group (-SO_3H), or phosphate groups (-

$OP(O)(OH)_2$)), resulting in amphiphilic molecules (Krafft and Riess, 2015b). As an example, one of the most investigated PFAS, perfluorooctanesulfonic acid (PFOS) has a perfluorinated alkyl chain of eight C and a sulfonate group, shown in Figure 1. This results in high surface activity. In aqueous mixtures, PFOS will preferentially accumulate at the air-water interface and lower the surface tension of the mixture, providing the ability to foam and to easily form films above hydrocarbon liquids. For this reason, and in combination with its remarkable persistence, PFOS and other fluorinated surfactants have been widely used in aqueous film forming foams (AFFF) used to extinguish fires (Kärrman *et al.*, 2011; Place and Field, 2012).

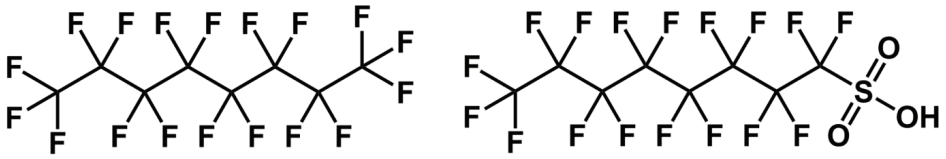

Figure 1. The hydrophobic eight carbon perfluoroalkane, octadecafluorooctane, with all the hydrogen atoms in octane replaced by fluorine atoms (to the left) and the amphiphilic PFOS with a hydrophobic perfluoroalkyl chain and a hydrophilic functional group (to the right).

PFAS history and regulation

Discovery and production

The early history of PFAS has been summarised by Krafft and Riess (2015b) and Lemal (2004). The first PFAS to be synthesized was perfluoroacetic acid (also termed trifluoroacetic acid) in 1920, and some key points from the hundred years of PFAS history are summarised in Table 1. After the serendipitous discovery of poly(tetrafluoroethylene) (PFTE, (e.g. Teflon)) in 1938, it was used for the separation of uranium isotopes by the Manhattan project in the 1940s. Following this, commercial exploitation of PFAS increased with little regulation, and thousands of PFAS have been synthesised and sold on the market (Lemal, 2004; Krafft and Riess, 2015b). However, the majority of research and regulatory focus has been on only a few PFAS (Wang *et al.*, 2017a).

Buck *et al*. (2011) reviewed the methods for PFAS production. Two main techniques have been used for large scale PFAS production, electrochemical fluorination (ECF) and

telomerization. ECF is a technique where electrolysis in anhydrous hydrogen fluoride (HF) is used to replace all H atoms on a raw material such as octane sulfonyl fluoride ($C_8H_{17}SO_2F$) or octanoyl fluoride ($C_7H_{15}COF$), shown in Figure 2. ECF of octanoyl fluoride results in perfluorooctanoyl fluoride which is used to make perfluorooctanoic acid (PFOA) and its salts, while ECF of octane sulfonyl fluoride results in perfluorooctane sulfonyl fluoride (PFOSF), used to make PFOS and related compounds (termed POSF based products) such as the *N*-alkylated perfluorooctanesulfonamides (Buck *et al.*, 2011). Due to the free-radical nature of the ECF process, which results in C chain rearrangement and breakage, it produces a mixture of linear and branched isomers in addition to impurities of other fluorinated compounds (Prevedouros *et al.*, 2006; Buck *et al.*, 2011; Jiang *et al.*, 2015).

Prevedouros *et al*. (2006) have summarised the production history of PFAS for commercial purposes. The 3M Company (3M) began large scale production of perfluoroalkyl carboxylic acids (PFCA) with eight or more carbon atoms (C≥8, i.e. PFOA and longer) in 1947 using ECF (Prevedouros *et al.*, 2006). 3M started producing PFOSF using ECF for production of PFOS and related substances (POSF based products), in 1949 (Paul *et al.*, 2009).

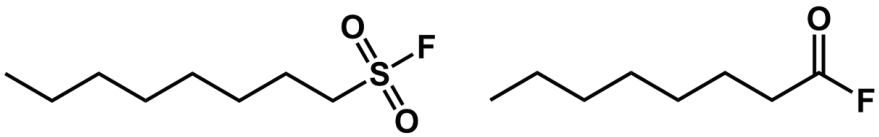

Figure 2. Examples of raw materials used for ECF. To the left: octane sulfonyl fluoride used to make perfluorooctane sulfonyl fluoride (PFOSF) which is further used to make PFOS and related products (POSF based products). To the right: octanoyl fluoride used to make perfluorooctanoyl fluoride, which is further used to make PFOA and PFOA salts.

Telomerization has been used for PFAS production since the 1970s, producing many of the same PFAS as by ECF (Prevedouros *et al.*, 2006). In telomerization, a perfluoroalkyl iodide ($C_nF_{2n+1}I$) such as perfluoroethyl iodide ($F(CF_2)_2I$) reacts with tetrafluoroethylene ($CF_2=CF_2$) resulting in mixtures of perfluoroalkyl iodides with longer perfluorinated chains than the raw material (e.g. perfluorooctyl iodide, $F(CF_2)_8I$). These can be used to make PFCA such as PFOA, or ethylene can be inserted in a second telomerization step

resulting in fluorotelomer iodides (i.e. X:Y Iodide, where X is the number of perfluorinated C atoms, and Y is the number of nonfluorinated C atoms in the C chain) (Buck *et al.*, 2011). Fluorotelomer iodides are used to make other telomer products such as fluorotelomer alcohols (FTOH) and fluorotelomer sulfonates (FTS). When the starting material (the perfluoroalkyl iodide) is linear, the resulting products will also be linear. Linear starting materials have dominated commercial PFAS production by telomerization, and it is not known whether branched starting materials have been used for commercial production (Buck *et al.*, 2011). ECF (producing linear and branched isomers) and telomerization (producing linear PFAS) are summarised in Figure 3.

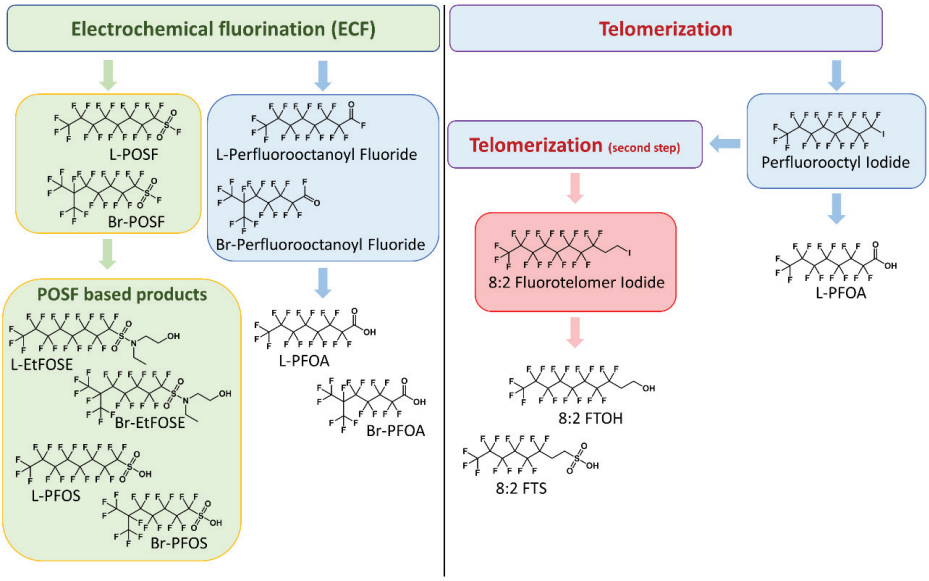

Figure 3. Simplified overview of the two main production techniques for large scale PFAS production, electrochemical fluorination (ECF) and telomerization. ECF results in a mixture of linear (L) and branched (Br) products, while telomerization results in linear products (provided that linear raw materials are used). Note that the intermediate and end products shown in the figure are examples and that many more are possible. An example of a *N*-alkylated perfluorooctanesulfonamide, perfluorooctanesulfonamidoethanol (EtFOSE) is shown to illustrate a POSF based product in addition to PFOS.

Detection and subsequent phase-out

Through the 1960s, 1970s and 1980s, organic fluorine of unknown origin was found in human plasma from the general population around the world (Taves, 1968; Guy *et al.*,

1976; Belisle, 1981; Yamamoto *et al.*, 1989). Elevated levels of organic fluorine in the blood, and PFOA in the urine, of workers at a perfluorochemical production factory were reported in 1980 (Ubel *et al.*, 1980). Following the development of a sensitive method for analysing individual PFAS, Hansen et al. (2001) identified PFOS, PFOA, perfluorohexanesulfonic acid (PFHxS), and perfluorooctanesulfonamide (FOSA) in human sera (Hansen *et al.*, 2001), and global distribution of PFOS in wildlife was reported in 2001 (Giesy and Kannan, 2001). Due to concerns about toxicological and environmental impacts, 3M voluntarily phased-out PFOA, and PFOS and other POSF related products between the years 2000 and 2001 (Dorrance *et al.*, 2017). The phase-out of legacy PFAS resulted in the need for alternatives, and different PFAS including short chained perfluorinated alkyl acids (PFAA), fluorotelomer based surfactants, and perfluoroalkyl ethers have been used (Moe *et al.*, 2012; Place and Field, 2012; Hoke *et al.*, 2015; The Swedish Chemicals Agency (KEMI), 2015; Wang *et al.*, 2015, 2019). However, some of these fluorinated alternatives for legacy PFAS have been reported to be equally or more toxic compared to the PFAS they replaced (Gomis *et al.*, 2018).

Use of PFAS in industrial processes and consumer and industrial products

Due to the unique properties discussed above, PFAS have been used in a variety of industrial processes and products. Since the first Teflon frying pan, "The Happy Pan" (taking advantage of perfluorocarbons non-stick properties and persistence) came on the market in the 1960s (The New York Times, 1986), PFAS have been used in a vast amount of applications and consumer products including: water and fat resistant paper products and food contact materials, waterproof and stain repellent clothing and textiles, cosmetics, household products, medical devices, oil production, pesticides, aqueous film forming foams (AFFF), ski waxes, and many others (Lindstrom *et al.*, 2011; Wang *et al.*, 2017a; Fang *et al.*, 2020; Glüge *et al.*, 2020). Different PFAS have been used in different products and as PFAS production methods have changed over the years, the PFAS used in a product have changed as well (Herzke *et al.*, 2012). To illustrate this, the history of PFAS for two different examples: AFFF and PFAS coated paper products, is summarised in Table 1. AFFF produced until the 1970s were based on PFCA, however AFFF formulations based on POSF dominated from the 1970s (Prevedouros *et al.*, 2006). In

addition, fluorotelomer based AFFF were also produced from the late 1970s, and have been used in large quantities owing to the phase out of PFOS in the 2000s (Prevedouros *et al.*, 2006; Dorrance *et al.*, 2017). This change in PFAS mixture over time is seen in Norway. In 2007, Norway phased out the use of PFOS based AFFF (as an early adoption to EU regulations) (Norwegian Government, 2006). Fluorotelomer based AFFF were therefore used at Norwegian airports from 2007 until all PFAS based AFFF were phased out at Norwegian airports between 2012 and 2015 (the Norwegian Defence Estates Agency, personal communication, C.E. Amundsen, June 2016).

Table 1. A brief summary of key events (discovery and development, production, market use, and regulation) from a hundred years of PFAS history

Time Period	Event	References
1920	The first PFAS, perfluoroacetic acid, was synthesized	Krafft and Riess (2015b) and references therein
1926	The first perfluoroalkane, carbon tetrafluoride, was isolated	Krafft and Riess (2015b) and references therein
1938	The serendipitous discovery of poly(tetrafluoroethylene) (PFTE, (e.g. Teflon))	Krafft and Riess (2015b); Lemal (2004) and references therein
1940s	The first applications of fluorocarbon chemistry: The Manhattan Project required extremely inert materials for the separation of uranium isotopes	Lemal (2004) and references therein
1947	Large scale PFCA production began using electrochemical fluorination (ECF).	Prevedouros *et al.* (2006); Dorrance *et al.* (2017) and references therein
1949-2000	Large scale manufacture of PFOSF based products (including PFOS) using ECF.	Paul *et al.* (2009); Dorrance *et al.* (2017) and references therein
1960s-1970s	PFCA based AFFF were produced	Prevedouros *et al.* (2006)
1960s	The first teflon frying pan, "The Happy Pan" reached the market	The New York Times (1986)
1970s-2002	AFFF based on POSF were produced and largely replaced PFCA based AFFF	Prevedouros *et al.* (2006); Dorrance *et al.* (2017) and references therein
1970s	High concentrations of organic fluorine were detected in the blood of workers at a perfluorochemical production factory	Krafft and Riess (2015b) and references therein
1970s	Large scale PFAS production using telomerization	Prevedouros *et al.* (2006) and references therein
Late 1970s-present	Fluorotelomer based AFFF were produced. They were used to a large extent after the PFOS phase-out in the early 2000s.	Prevedouros *et al.* (2006); Dorrance *et al.* (2017) and references therein
1974	POSF based PFAS introduced in paper products	Olsen et al. (2005)
1995	Fluorotelomer based PFAS commercialized for use in paper products	Lee and Mabury (2011)
2000-2002	3M voluntarily phase-out PFOA and PFOS and other POSF related products due to concerns about toxicological and environmental impacts.	Dorrance *et al.* (2017) and references therein
2002	PFOS is no longer produced in the United States.	Dorrance *et al.* (2017) and references therein

Time Period	Event	References
2002	DuPont took over large scale PFOA production. As DuPont used telomerization, this became the dominate production technique for PFOA production.	Dorrance *et al.* (2017) and references therein
2000s	Asian PFAS production increases, leading to a shift in global emission pathways	Krafft and Riess (2015a) and references therein
2006-2015	Eight global companies, including DuPont, stopped the production of PFOA and related PFAS and their precursors. Many PFAS based products were reformulated to contain PFAS with alternative chemistries	Dorrance *et al.* (2017) and references therein
2007	PFOS based AFFF is phased-out in Norway. Replaced by fluorotelomer based AFFF	Norwegian Government (2006)
2009	PFOS including its salts and POSF are included in the Stockholm convention	UNEP - The Stockholm Convention (2019)
2012-2015	All PFAS based firefighting foams are phased out in Norway	The Norwegian Defence Estates Agency, personal communication, C.E. Amundsen, June 2016
2013	PFOS and its derivatives are included as a priority hazardous substance under the EU Water Framework Directive. Annual average value Environmental Quality Standard (AA-EQS) values of 0.65 ng L^{-1} and 0.13 ng L^{-1} were set for PFOS in inland surface waters and in seawater, respectively. An EQS of 9.1 µg kg^{-1} was set for PFOS in biota	Directive 2013/39/EU (2013)
2019	PFOA including its salts and precursors are included in the Stockholm convention	United Nations Environment Programme - The Stockholm Convention (2019)
2019	HFPO-DA (tradename GenX) its salts and its acyl halides, are identified as substances of very high concern by the European Union under the regulation *Registration, Evaluation, Authorisation and Restriction of Chemicals* (REACH) Perfluorobutane sulfonic acid (PFBS) and its salts are identified as substances of very high concern under REACH	(European Chemicals Agency, 2019a, 2019b)
2020	The European Food Safety Authority (EFSA) set a safety threshold for tolerable weekly intake (TWI) of PFOA, PFOS, perfluorononanoic acid (PFNA), and perfluorohexanesulfonic acid (PFHxS) of 4.4 nanograms per kilogram of body weight per week	European Food Safety Authority (2020); Schrenk *et al.* (2020)

PFAS in the environment: sources, fate and transport

Sources of PFAS to the environment

PFAS are ubiquitous in the environment and are even found at remote pristine locations such as in the Arctic and Antarctic (Ellis *et al.*, 2004; Tomy *et al.*, 2004; Houde *et al.*, 2011; Liu and Mejia Avendaño, 2013; Lescord *et al.*, 2015; Gao *et al.*, 2019), reflecting the widespread use and large emission volumes. The total sum of global emission volumes of PFOS, preFOS and POSF between 1958 and 2015 have been estimated to be in the ranges of 1228-4930, 1230-8738, and 670 tons respectively (Wang *et al.*, 2017b). However, as this study focused mostly on emissions to air, volumes could be higher (Wang *et al.*, 2017b).

The highest environmental PFAS concentrations have been reported for sites contaminated by local PFAS production and/or use in industrial processes or products (Moody and Field, 2000; Rahman *et al.*, 2014; Filipovic *et al.*, 2015; Anderson *et al.*, 2016; Hu *et al.*, 2016; Dauchy *et al.*, 2017; Gebbink *et al.*, 2017; Knutsen *et al.*, 2019). The use of AFFF for firefighting training at specific sites such as airports (see Figure 4), is one of the most investigated PFAS point sources. The use of AFFF has resulted in PFAS hot spot pollution in soil, sediment, water, and biota (Moody and Field, 2000; Rahman *et al.*, 2014; Ahrens *et al.*, 2015; Filipovic *et al.*, 2015; Anderson *et al.*, 2016; Hu *et al.*, 2016). As an example, mean concentrations of ∑PFAS 7 in perch (*Perca fluviatilis*) muscle from pristine Swedish lakes were reported between 0.31 and 3.4 μg kg^{-1} (Åkerblom *et al.*, 2017), while the mean concentration of ∑PFAS 11 (mostly PFOS) was 330 μg kg^{-1} in the muscle of perch sampled near Stockholm Arlanda Airport (AFFF PFAS point source) (Ahrens *et al.*, 2015).

Figure 4. The fire training area at Svalbard airport, including the airplane body used for training on extinguishing burning airplanes. Photo: Håkon Austad Langberg.

Despite the use of AFFF being one of the most well-investigated point sources of PFAS, it has been reported that only about 5% of the total volume of POSF (and POSF based products expressed as PFOS equivalents) produced was used for AFFF (Paul *et al.*, 2009). Therefore, 95% of the total volume of produced POSF based products has been used for applications other than AFFF. Estimates of the total volume of fluorochemicals used in the United Kingdom and Canada showed that 14-48% was used for carpets, 43-48% was used for apparel, 15-28% was used for paper and packaging, 6-16% was used for AFFF, while 8-20% was used for other performance chemicals (Paul *et al.*, 2009 and references therein). It is however the amounts emitted to the local environment, not the amounts used at a facility, in combination with fate and transport of the emitted PFAS that decide if the facility is a point source that generates a PFAS hot spot. Therefore, depending on factors such as production methods (including emission pathways to the environment) and PFAS volume used for the application, releases from industrial processes which use PFAS represent examples of potential PFAS point sources in addition to AFFF.

Physiochemical properties

The partitioning of substances between air, water, soil/sediment and biota provides information related to their environmental fate. Differences in PFAS physiochemical properties arise from differences in structure, including molecule size and functional hydrophilic group, and result in different partitioning between environmental media. PFAS exist as anions, cations, zwitterions, or neutral compounds in the environment (Xiao, 2017). Ions are generally more hydrophilic compared to comparably sized neutral homologues, and larger PFAS are generally more hydrophobic and have higher affinities for soil/sediment compared to smaller PFAS (Higgins and Luthy, 2006; Milinovic *et al.*, 2015; Barzen-Hanson *et al.*, 2017; Lee and Mabury, 2017; Brendel *et al.*, 2018; Zou *et al.*, 2018).

Due to fluorine's high electronegativity, PFAA tend to be strong acids (small pK_a values) and are present as anions at environmentally relevant pH (Interstate Technology & Regulatory Council, 2017). Due to the relatively high solubility of many PFAA, they are relatively mobile in the aquatic environment and water-living organisms are important environmental compartments for PFAA partitioning (Conder *et al.*, 2008). Effects of the physiochemical properties of PFAS on accumulation in biota is elaborated below in the chapter *Toxicokinetics and transport in the food chain*.

Precursors to PFAA

Many polyfluorinated PFAS are precursors to PFAA, especially to (perfluoroalkane sulfonic acids) PFSA and PFCA (Land *et al.*, 2018). As an example, large amounts of POSF have been used as the starting material for the production of PFOS and N-alkyl substituted perfluorooctane sulfonamides with eight perfluorinated C (Paul *et al.*, 2009), shown in Figure 5. These N-alkyl substituted perfluorooctane sulfonamides have been shown to be ultimately transformed to PFOS in the environment (Benskin *et al.*, 2013; Peng *et al.*, 2014; Gaillard *et al.*, 2017; Zhang *et al.*, 2018), and these PFOS precursors are therefore termed preFOS throughout this work. Similarly, many fluorotelomer based products including fluorotelomer alcohols (FTOH) are precursors to PFCA (Prevedouros *et al.*, 2006). Long-range atmospheric transport and subsequent degradation of such

neutral precursor compounds is suggested to be one important mechanism for the global distribution of PFSA and PFCA (Ellis *et al.*, 2004; Houde *et al.*, 2011; Liu and Mejia Avendaño, 2013). Some precursors to PFAA are neutral at environmentally relevant pH, which combined with their larger size, makes them less water soluble and thus more prone to reside in environmental compartments other than water, compared to their anionic degradation products (Hekster and De Voogt, 2002; Ding and Peijnenburg, 2013).

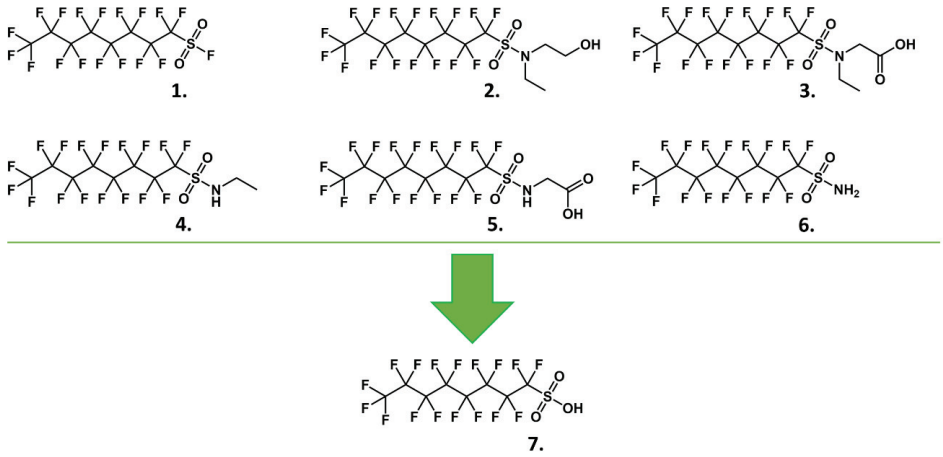

Figure 5. Structures of POSF, some POSF based PFOS precursors (preFOS) and their final degradation product, PFOS: 1) Perfluorooctanesulfonyl fluoride (POSF); 2) N-Ethyl Perfluorooctanesulfonamido Ethanol (EtFOSE); 3) N-Ethyl Perfluorooctansulfonamido Acetic Acid (EtFOSAA); 4) N-Ethyl Perfluorooctanesulfonamide (EtFOSA); 5) Perfluorooctansulfonamido Acetic Acid (FOSAA); 6) Perfluorooctanesulfonamide (FOSA); 7) Perfluorooctanesulfonic Acid (PFOS)

Toxicokinetics and transport in the food chain

Toxicokinetics for PFAS vary between organisms, and large species and gender-dependent variations, as well as differences depending on compound specific properties have been reported (Krafft and Riess, 2015a). For example, long chained PFAA (C ≥ eight for PFCA, and C ≥ six for PFSA) have higher bioaccumulation potentials than their shorter chain homologues (Buck et al., 2011; Ng and Hungerbühler, 2014) and PFSA have been reported to have longer half-lives compared to the same chain length PFCA (Martin et al., 2003a, 2003b; Conder et al., 2008). The serum half-life of PFOS has been

reported to be several years in humans (Krafft and Riess, 2015a), months in rodents (Krafft and Riess, 2015a), and days in fish (Martin et al., 2003a).

Unlike many other organic contaminants which mainly accumulate in lipid rich compartments in animals, the long chained PFAA (as well as many other PFAS) accumulate in tissues such as the blood, kidneys, and liver. The reason for this is likely that these PFAS bind to transport proteins such as albumins and therefore mainly accumulate in tissues which are rich in these proteins (Ng and Hungerbühler, 2013; Falk *et al.*, 2015). Long chained PFAA have been shown to biomagnify in aquatic ecosystems (Martin *et al.*, 2004b; Fang *et al.*, 2014; Xu *et al.*, 2014). PFOS has been reported to have higher trophic magnification factors (TMF) compared to other PFAS (Martin *et al.*, 2004b; Kelly *et al.*, 2009; Fang *et al.*, 2014) and biotransformation of the large amount of POSF based precursors (Jackson and Mabury, 2013) to PFOS has been suggested as the explanation behind this (Fang *et al.*, 2014).

Exposure from point sources to humans and the ecosystem

The widespread use of PFAS, including in a range of consumer products leads to a constant diffuse human exposure (Herzke *et al.*, 2012). PFAS emitted to the environment via point sources add to the total environmental burden. In addition, hot spot areas may act as a source to local wildlife and humans (in addition to the diffuse exposure). This is illustrated in Figure 6, which shows examples of the diffuse PFAS exposure from consumer products, food, and water that the general population is subjected to and how a PFAS point source might add to the exposure via a hot spot area. A wide range of adverse health impacts have been identified as potential effects of elevated PFAS exposure (Kwiatkowski *et al.*, 2020). Highly elevated blood levels of PFAA in humans have been associated with kidney and testicular cancer, damage to the liver, dyslipidemia, decreased fertility, thyroid problems, immunotoxicity, and adverse developmental effects (Kwiatkowski *et al.*, 2020). Of these, the most well-established health impacts of PFAS exposure are immunotoxicity (including suppressed immune response) and dyslipidemia (including disturbed cholesterol profiles) (Knutsen *et al.*, 2018; Sunderland *et al.*, 2019).

Studies on the impact of point sources arising from the use of PFAS containing products on human PFAS exposure are relatively limited. Hansen et al. (2016) investigated the impact of the consumption of fish from water bodies impacted by AFFF contamination from Evenes airport in the northern Norway on blood serum levels of consumers. The participants in the study were classified into three groups based on consumption: high consumption (more than two meals per month), moderate consumption (from one to two meals per month), low consumption (less than one meal per month), and nonconsumers. Higher serum concentrations of ∑PFAS 15 were reported for the high consumption group (geometric mean, 28 ng mL^{-1}) compared to the low consumption group and nonconsumers (11 and 10 ng mL^{-1}, respectively) (Hansen *et al.*, 2016). Associations between increased PFAS concentrations in the blood and several adverse human health effects have been reported for levels comparable to, or lower than, levels reported by Hansen et al. (2016). These included decreased amounts of normal spermatozoa (sperm cells) in ejaculate (Joensen *et al.*, 2009), disruption of thyroid function (Melzer *et al.*, 2010; Kim *et al.*, 2011; Ji *et al.*, 2012), increased prevalence of attention deficit/hyperactivity disorder (ADHD) in children with elevated PFAS serum levels (Hoffman *et al.*, 2010), and immune toxicity (reduced concentrations of antibodies against vaccines) (Grandjean *et al.*, 2017) (as mentioned above, immune toxicity is one of the most well-established health impacts of PFAS exposure (Knutsen *et al.*, 2018; Sunderland *et al.*, 2019)). Based on this, it is clear that there is a cause for concern associated with the PFAS concentrations that are observed at Norwegian PFAS point sources.

In addition to being an exposure pathway for humans, wildlife, including fish and invertebrates, might be adversely affected by PFAS point sources themselves (illustrated in Figure 6). Many studies report concentrations of PFAA in wildlife exposed to PFAS from point sources, however research on potential adverse effects in wildlife is relatively scarce. One example is a study by Guillette et al. (2020) who reported that elevated levels of PFAS in Cape Fear River Striped Bass (*Morone saxatilis*) were associated with biomarkers of altered immune and liver function (Guillette *et al.*, 2020). Potential air-breathing animals that feed mainly on organisms exposed to PFAS from point sources (e.g. birds) might be at even higher risk, given the low rate of respiratory elimination in

air-breathing animals compared to water-breathing animals (Kelly *et al.*, 2009). PFOS has been reported to be positively associated with plasma levels of the free form of the thyroid hormone, triiodothyronine, in glaucous gull (*Larus hyperboreus*) (Melnes *et al.*, 2017). PFOS and several PFCA have been reported to be higher in snow bunting (*Plectrophenax nivealis*) eggs collected in the vicinity of Longyearbyen (and the airport) on Svalbard compared to eggs collected in proximity to an abandoned coal mining town (Warner *et al.*, 2019), thus providing an example of increased exposure near a point source.

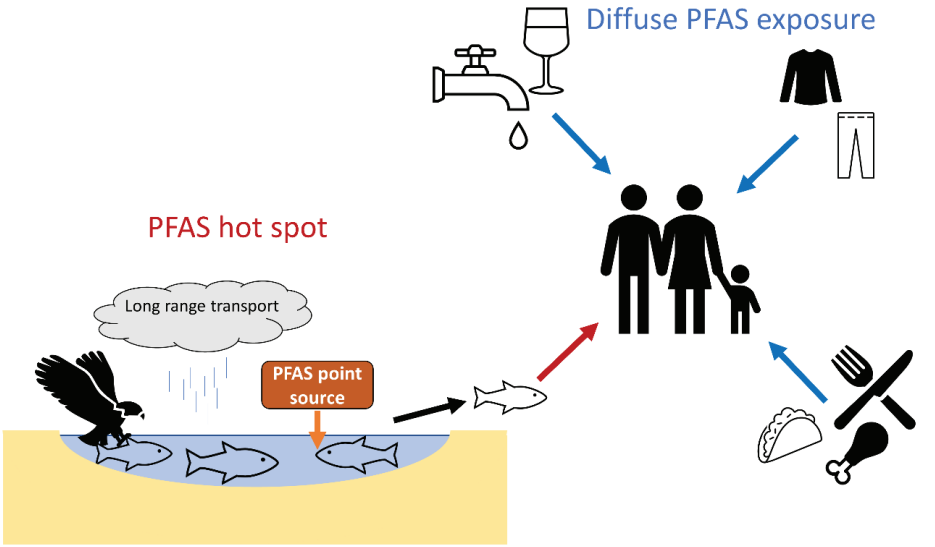

Figure 6. The environmental burden at a PFAS hot spot is subjected to both diffuse exposure (e.g. from long-range transport) and exposure from a point source. Thus, PFAS point sources may act as an additional PFAS source to local wildlife and humans. For humans, examples of diffuse PFAS exposure (which apply for the general population) are indicated with blue arrows, while an example of additional exposure from a PFAS point source (applying for exposed groups) is indicated using a red arrow. The idea for this figure is inspired by figure 2 at the European Environment Agency's PFAS information page (European Environment Agency, 2019).

It is practically impossible to remediate the diffuse global PFAS pollution. However, specific strategies have been/are being developed for PFAS hot spots (Ross *et al.*, 2018). A site-specific understanding of the nature (e.g. fate and transport properties) and extent of the contamination is required for developing successful remediation approaches (Dorrance *et al.*, 2017; Ross *et al.*, 2018). In addition, considering the risk posed by highly

contaminated PFAS hot spots, investigations are needed in order to identify sources, quantify contamination levels, and perform risk assessments (Dorrance *et al.*, 2017).

Strategies to characterize point sources

A variety of strategies and sample types have been used to characterize sources and to estimate emission volumes of PFAS pollution (Dorrance *et al.*, 2017). Targeted analyses are used to investigate concentrations of individual substances and to explore chemical profiles (where PFAS compositions in different samples are compared), which in combination with interpretations of spatial distribution (e.g. how concentrations and profiles change with distance from sources) and PFAS history (e.g. knowledge of when certain substances where introduced or phased out, what products or processes they have been used for, etc.) are valuable for source characterization (Trier *et al.*, 2011; Shi *et al.*, 2015; Zhang *et al.*, 2016; Dorrance *et al.*, 2017; Hu *et al.*, 2018). However, the great number of PFAS (more than 4000 are distributed on the global market) including known and unknown PFAS used directly in industrial processes and consumer products, replacement compounds for phased-out PFAS, impurities, and degradation products, makes it practically impossible to target each individual substance in the environmental PFAS mixture (Wang *et al.*, 2017a; Nakayama *et al.*, 2019).

Suspect screening using high resolution mass spectrometry (HRMS) can be used to identify non-target compounds but this method is time consuming and therefore expensive on a routine basis (Benotti *et al.*, 2020). To overcome this challenge, non-specific inclusive approaches have been developed to estimate the total mass of PFAS in samples. Two approaches that have been increasingly used the recent years are the total oxidizable precursor (TOP) assay, and the measurement of extractable organic fluorine (EOF) (McDonough *et al.*, 2019; Nakayama *et al.*, 2019). The principle of the TOP assay is that a sample is oxidized by an excess of hydroxyl radicals in order to transform precursor compounds into degradation products, and the concentrations of specific PFAS before and after oxidation are compared. One disadvantage of the TOP assay is that it will only detect the substances that are targeted in the analyses, as well as substances that, as a result of the oxidation treatment, are transformed into those target substances. Thus, the method will not detect untargeted substances that are persistent to the treatment, or

degraded into untargeted compounds. Another drawback is that substances might transform into other end products in the TOP assay than what can occur under environmental conditions. For example, substances that are known to be transformed into PFOS in the environment are transformed into PFOA in the TOP assay (Houtz and Sedlak, 2012). For EOF measurements, the total extractable organic fluorine in a sample is measured and compared to the sum fluorine from compounds detected using targeted analyses. One drawback of this approach is that potential organic fluorine from substances other than PFAS will also be included (McDonough *et al.*, 2019; Nakayama *et al.*, 2019). A simplified comparison of the different methods is shown in Figure 7.

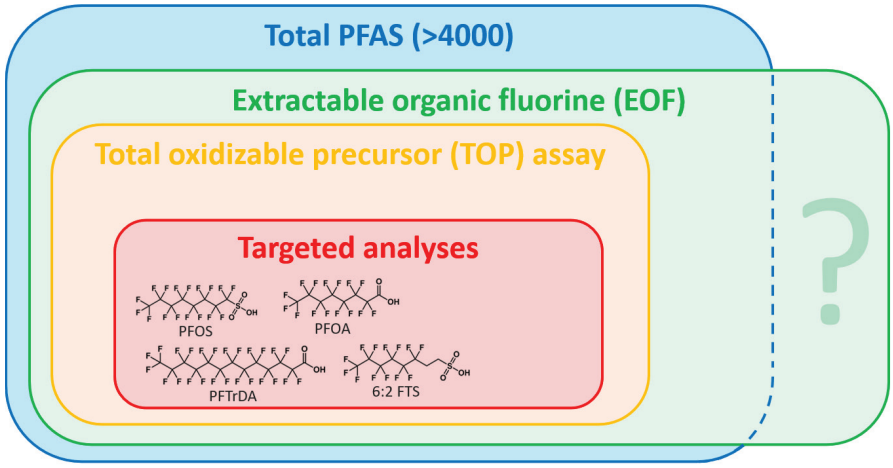

Figure 7. A simplified comparison of how the methods extractable organic fluorine (EOF) and the total oxidizable precursor (TOP) assay perform compared to the total environmental PFAS mixture, and targeted PFAS analyses (a few PFAS are shown as examples of typically targeted PFAS). The idea for the figure is inspired by figure 2 in the study by McDonough *et al.* (2019).

METHODS

In order to investigate differences in emitted PFAS mixtures and their environmental fate and transport between different point sources and environments, three different case sites in Norway were selected (Figure 8) for the investigations reported in papers II-V: 1) lake Tyrifjorden, a freshwater lake suspected to be polluted by a factory producing PFAS coated paper products and/or a fire station (**Paper II** and **Paper III**); 2) Bodø Air Station (Bodø airport) where the local marine environment was primarily exposed to PFAS from extensive use of AFFF (**Paper IV**); and 3) Svalbard airport, Longyearbyen where the local arctic marine environment was exposed to point source PFAS pollution from the use of AFFF, runoff from local diffuse sources, and via long-range transport **(Paper V**). In addition, in order to thoroughly investigate differences in environmental PFAS profiles depending on type of source, data for different point sources provided by Norwegian stakeholders and a monitoring program, as well as data from the lake Tyrifjorden case study site (Paper II and Paper III), were explored in **Paper I**.

A similar sampling approach was applied at each of the three case study sites (lake Tyrifjorden, Bodø airport, and Svalbard airport). Sampling was performed at different distances from the point source(s) in order to investigate the spatial distribution of PFAS contamination, including how the composition of the PFAS mixture changes with distance. Profiles and concentrations in samples representing emissions from sources were compared to concentrations and profiles in samples from the recipients (the local marine or lacustrine environment). To investigate uptake and accumulation in local biota, concentrations of PFAS in animals at different levels in the aquatic food chain were determined.

Clean equipment was used for all sampling activities, and laboratory blank samples were used to control potential contamination at all case study sites. Concentrations in biota are reported using wet weight (w.w.), while dry weight (d.w.) is used for sediment concentrations. Arithmetic means and percentages of the total detected PFAS, with the standard error of the mean (SEM) are reported where appropriate. Statistical analyses were carried out using R version 3.4.2 (R Core Team, 2017). The different case study

sites and the sampled matrices are briefly described below. Details about sampling procedures, sampled matrices, chemical analyses, limits of quantifications (LOQ), quality assurance procedures, and data treatment and statistics are described in papers I-V.

Figure 8. Overview map showing the three case study sites: 1) lake Tyrifjorden; 2) Bodø airport; and 3) Svalbard airport (green dots indicate airports, while the orange dot indicates the PFAS impacted lake).

Lake Tyrifjorden (Paper II and Paper III)

Lake Tyrifjorden (60.03° N, 10.17° E) is a freshwater lake in the southern part of Norway. In 2015, high levels of PFOS were reported in perch livers (*Perca fluviatilis*) sampled in the middle of the lake (mean 183 µg kg^{-1}) (Fjeld *et al.*, 2016). A shutdown factory that

produced paper products from 1964 to 2013 and a fire station were later identified as the two suspected PFAS sources (Slinde and Høisæter, 2017). In the present work, samples (water, sediments, and a paper plate) representing PFAS emissions from the two sources were analysed. Sampling areas in the river and lake were selected in order to capture the spatial distribution of PFAS pollution and are shown in Figure 9.

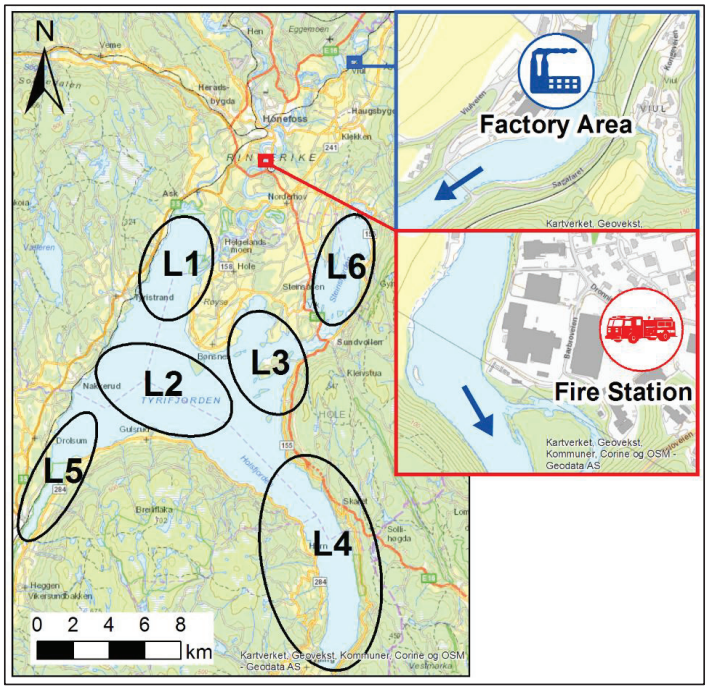

Figure 9. The two (suspected) PFAS sources to lake Tyrifjorden (paper product factory and fire station), and sampling areas in the lake (circles). L1 is the area closest to the inflowing river while L4 to L6 are the furthest away. L5 is connected to the outflow of the lake.

Water was sampled from five areas in the lake (L1, L3, L4, L5, and L6) and from the river downstream the factory. Sediments were sampled in the river from two locations upstream and nine locations downstream the factory, and downstream the fire station. Lake sediments were sampled at 94 locations, and a sediment core from the lake (taken in area L1) was dated in order to explore historic PFAS emissions. Fish (perch (*Perca fluviatilis*), pike (*Esox Lucius*), whitefish (*Coregonus lavaretus*), roach (*Rutilus rutilus*), trout (*Salmo trutta*), bream (*Abramis brama*), arctic char (*Salvelinus alpinus*)) and

crayfish (*Astacus astacus*) were sampled from the river and lake. The number of individuals and species varied between areas. Details are given in Paper II and Paper III.

Extraction and analyses were performed at the Norwegian Institute for Water Research (NIVA). Individual samples of liver and/or muscle were analysed for fish, while individual muscle samples were analysed for crayfish. Water samples were extracted using solid-phase extraction (SPE). Sediment and biota samples were extracted using acetonitrile (no clean-up was performed as extraction using acetonitrile was considered to result in relatively clean extracts). PFAS were analysed using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS). 44 PFAS were targeted using authentic and internal standards. An additional 19 PFAS were screened for using exact mass and retention time from authentic standards and 28 PFAS were screened for using exact mass and estimated retention time. In addition, SAmPAP diester was analysed for in a few samples. Concentrations of extractable organic fluorine (EOF) were analysed in selected samples, and the ratios between the stable, carbon ^{13}C and ^{12}C ($\delta^{13}C$) and nitrogen ^{15}N and ^{14}N ($\delta^{15}N$), isotopes in muscle tissue were determined for the assessment of carbon sources and trophic level. Stepwise regression was used to evaluate relationships between K_D values, fraction of organic carbon (f_{OC}), and particle size distribution. Spearman rank correlation coefficient (Spearmans ρ) was used to evaluate relationships between relative trophic level or trophic level adjusted $\delta^{13}C$, and PFAS concentrations in biota. Differences in trophic level adjusted $\delta^{13}C$ or relative trophic level between pike and perch were tested using unpaired Wilcoxon Test (Mann-Whitney test). Kruskal-Wallis and Bonferroni correction were used to test differences in PFAS concentrations and profiles for fish livers, sediments, and pore water at the different areas. Principal component analysis (PCA) was used to compare PFAS profiles in the paper product, sediments from the lake, and sediments representing the two sources (factory and fire station). Details are given in Paper II and Paper III.

Bodø Air Station (Paper IV)

Bodø Air Station (67.26° N, 14.36° E) is a military airbase which shares facilities with the civil airport in Bodø (Bodø Airport). Sampling stations were selected in order to

capture the main PFAS release points (from the use of AFFF) in storm water and run-off leaching from the soil from the airport (Figure 10). Stations B, E, and F were located in areas considered to be directly impacted by runoff from firefighting training activities. Station B was close to the release point of PFAS contaminated storm water from a fire station. Station E was at a release point of storm water assumed to have high concentrations of AFFF related PFAS. Station F was in an area where AFFF contaminated water leached from the soil at the firefighting training area. Stations A, C, D, G, and H were located at discharge points for storm water that were not associated with any particular PFAS source. A reference station was selected, located on the other side of the fjord, approximately 5 kilometres from the Air Station.

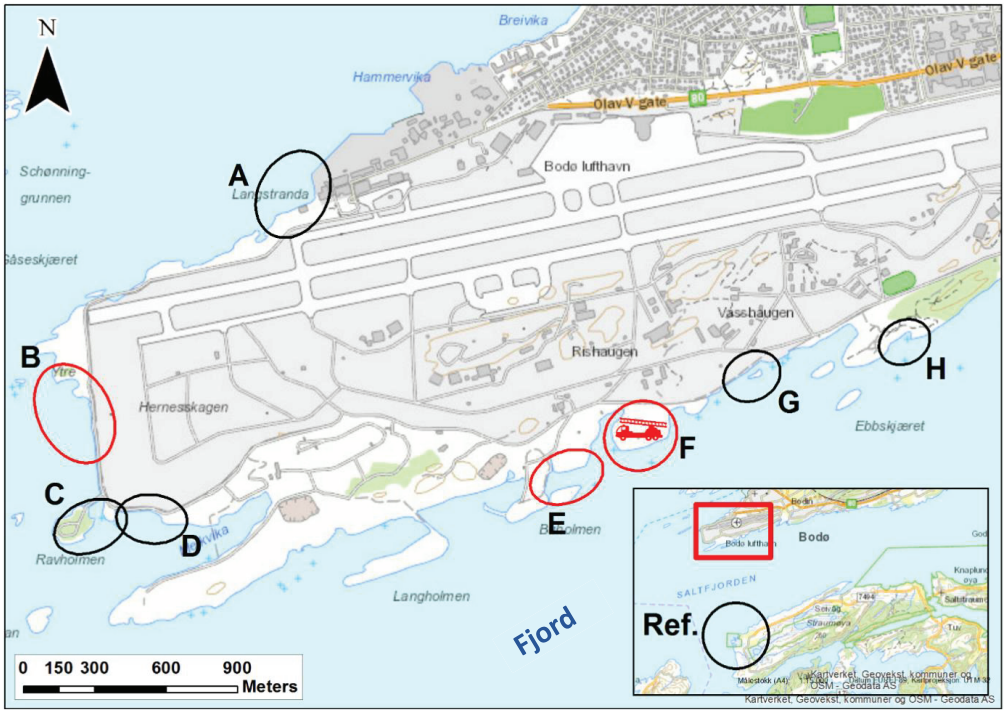

Figure 10. Sampling stations (circles) located at the Air Station (A-H) and the Reference Station (Ref.) on the other side of the fjord. Stations B, E, and F (red circles) are considered to be directly impacted by AFFF from firefighting training (station F is a designated fire training area).

Storm water or soil leachate water entering the fjord was sampled at each station. Marine sediments were sampled at each station (except for station G where the sea floor consisted of rocks). Marine invertebrates: snails (*Patellidae*); two species of small crabs: green shore crab (*Carcinus maenas*) and great spider crab (*Hyas araneus*); and the larger edible crab (*Cancer pagurus*), and fish (Atlantic cod (*Gadus morhua*); and two species of flatfish: European place (*Pleuronectes platessa*) and Lemon sole (*Microstomus kitt*)) were sampled. The number of individuals and species varied between areas.

Pooled samples of snails and small crabs (green shore crab and great spider crab) (whole organisms), and individual samples of edible crab (hepatopancreas) and fish (liver and remaining whole organisms) were analysed. Extraction, clean-up, and analyses were performed by a commercial laboratory (Eurofins Environment Testing Norway AS). Water was extracted using SPE. Biota and sediments were extracted using methanol. Extracts were analysed using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS). A total of 30 PFAS were analysed, however the number of analysed compounds varied between the different sampled media. The difference between PFOS concentrations in cod caught near the Air Station and cod caught at the Reference Station was tested using the unpaired Wilcoxon Test. Differences in the proportional levels of 6:2 FTS in different biota were tested using Kruskal-Wallis test and Bonferroni correction. Relationships between length, weight, Fulton's condition factor, or liver somatic index and ΣPFAS 22 were evaluated using Spearman's rank correlation coefficient (Spearman's ρ). Differences between PFAS profiles in different organisms and tissues were explored using PCA. Details are given in Paper IV.

Svalbard airport, Longyearbyen (Paper V)

Svalbard Airport (N 78°14', E 15°30') lies approximately five kilometres northwest of the town, Longyearbyen. The sampling campaign was designed to capture PFAS profiles in the local marine environment arising from the suspected sources of PFAS pollution, which are shown in Figure 11. Sampling was performed at four sampling stations in the marine environment. Stations 1 and 2 were located where residues of AFFF, used during firefighting training at two firefighting training stations (FFTS) associated with the

airport, were assumed to be transported to the sea, via a small creek and leachate water, respectively. Station 3 was selected in order to investigate PFAS from local diffuse pollution from human activities (consumer products, etc.). Leachate water from a landfill used for waste disposal between the period 1991-2007, and river water downstream Longyearbyen settlement were selected as representatives of local diffuse pollution from human activities, both entering the sea at station 3. A creek draining into the sea at station 4 was considered to originate from meltwater, and therefore representative of PFAS from atmospheric transport. In addition, snow samples were taken from the glacier, Foxfonna to further investigate contribution from atmospheric deposition.

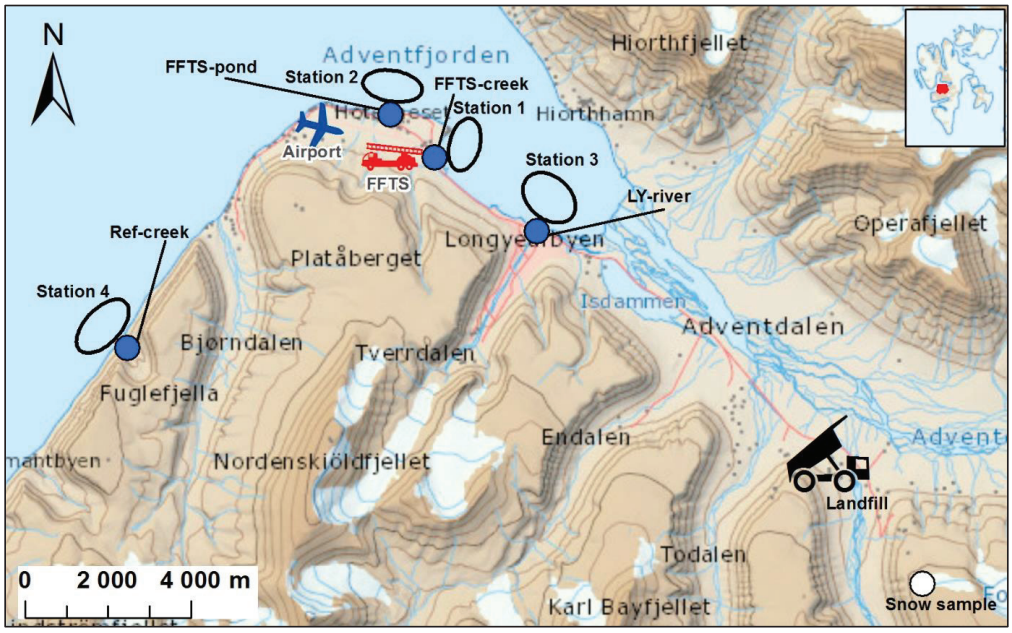

Figure 11. Marine sampling stations (circles), sampling points for freshwater samples (blue dots) and snow samples (white dot), in addition to the landfill in the vicinity of Longyearbyen.

At each station, runoff water entering the sea (creeks, river, leachate water), representative of the different sources, was sampled. In addition, at the four marine stations, sea water, surface sediments, benthic organisms (polychaetes), pelagic zooplankton (copepods, mainly *calanus* spp.), crabs (*Hyas Araneus)*, and fish (Sculpin (*Myoxocephalus scorpius*), and wolfish (*Anarhichas lupus*)) were sampled. The number

of individuals and species varied between areas. In addition, twenty glaucous gulls (*Larus hyperboreus*) were sampled in the proximity of Svalbard airport at Adventpynten (between station 1 and 2). Details are given in Paper V.

Pooled samples of whole organisms for plankton and benthic organisms, and individual samples of crabs (whole organisms), fish (liver and muscle), and glaucous gulls (liver) were analysed. Extraction and clean-up were performed at the University Centre in Svalbard (UNIS). Analyses were performed at the Algae toxin laboratory at the Department of Food Safety and Infectious Biology (MatInf) at the Norwegian University of Life Sciences (NMBU). Water samples were extracted using SPE. Sediment and biota were extracted with methanol and cleaned up using ENVICARB. Quantitative determination of PFAS was done using high-performance liquid chromatography with tandem mass spectrometry (HPLC/MS-MS). 19 PFAS were targeted, however N-Methyl Perfluorooctanesulfonamido Ethanol (MeFOSE), N-Methyl Perfluorooctanesulfonamide (MeFOSA), EtFOSE, and EtFOSA showed unacceptable low recoveries for several matrices, and consequently were excluded from the dataset. Perfluorobutanoic acid (PFBA) was also excluded from quantification as it has only one multiple reaction monitoring (MRM) transition in the applied analytical method. Thus, 14 PFAS were quantified. PCA was used to investigate variations in PFAS profiles within the dataset. Differences in PFAS concentrations between areas were tested using unpaired Wilcoxon Test (Mann-Whitney test). Correlations between PFAS concentrations and biological parameters were tested using Spearman's correlation test. Details are given in Paper V.

PFAS fingerprints in fish from Norwegian freshwater bodies subject to different source inputs (Paper I)

Paper I focused on differences in PFAS profiles in fish between different PFAS sources using Norwegian freshwater systems as examples. PFAS profiles at the different sites were investigated with respect to the different sources, in order to identify PFAS profiles and individual PFAS indicative of specific source types.

Data for the different sources were provided by Norwegian stakeholders who own land that is contaminated by PFAS, as well as monitoring data compiled under monitoring

programs commissioned by the Norwegian Environment Agency in the period from 2008 to 2019. The stakeholders who provided data were Avinor who owns most of the civil airports in Norway, and the Norwegian Defence Estates Agency (in Norwegian: Forsvarsbygg), who owns the military airports in Norway. The monitoring programs are performed in order to monitor PFAS concentrations (as well as other contaminants) in freshwater food chains in large Norwegian lakes. In addition, data from Lake Tyrifjorden reported in Paper II and Paper III were included in the dataset that comprised a total of eight sites, shown in Figure 12.

Figure 12. Overview map showing the point sources included in Paper I: 1) Oslo Airport, AFFF source; 2) Evenes Airport, AFFF source; 3) Fagernes Airport, AFFF source; 4) Rygge Airport, AFFF source; 5) Lake Tyrifjorden, impacted by production of paper products; 6) lake Mjøsa, urban runoff, and mixed sources including long-range atmospheric transport; 7) lake Femunden, long-range atmospheric transport; and 8) lake Randsfjorden, long-range atmospheric transport. (green dots indicate airports, the orange dot indicates the PFAS impacted lake Tyrifjorden, purple dots indicate long-range atmospheric transport, and the black dot indicates mixed sources,
i.e., long-range atmospheric transport and urban runoff).

Data for a total of 11 species were explored: Arctic Char (*Salvelinus alpinus*), Bream (*Abramis brama*), Brown Trout (*Salmo trutta*), European smelt (*Osmerus eperlanus*), Perch (*Perca fluviatilis*), Pike (*Esox lucius*), Roach (*Rutilus rutilus*), European chub (*Squalius cephalus*), Vendace (*Coregonus albula*), Whitefish (*Coregonus lavaretus*), and Zander (*Sander lucioperca*). The sites investigated were: 1) Oslo Airport (AFFF PFAS source), 2) Evenes Airport (AFFF PFAS source), 3) Fagernes Airport (AFFF PFAS source), 4) Rygge Airport (AFFF PFAS source), 5) Lake Tyrifjorden (paper industry

PFAS source), 6) lake Mjøsa (diffuse PFAS sources including industry, wastewater treatment plants (WWTP), and urban runoff); 7) lake Femunden (PFAS via long-range atmospheric transport), and 8) lake Randsfjorden (PFAS via long-range atmospheric transport). A total of 581 muscle samples and 454 liver samples were included in the study. Differences in PFAS concentrations, percentages, and ratios, as well as differences in PC 1 scores from PCA were tested using Kruskal-Wallis test and Bonferroni correction. Differences in fish PFAS profiles were explored using PCA.

MAIN RESULTS AND DISCUSSION

The use of PFAS profiles and concentrations of specific compounds and isomers to identifying sources

The use of chemical fingerprints has been suggested as a way to identify and explore PFAS contamination sources (Dorrance *et al.*, 2017). This includes the use of knowledge about compound-specific fate and transport properties, and the use history of PFAS, including differences in PFAS mixtures used for different products and purposes (Dorrance *et al.*, 2017). Such source identification is often termed environmental forensics and includes identification of sources, the date of the release to the environment, and the amount released from different sources (Dorrance *et al.*, 2017).

The hypothesis investigated in this chapter is that PFAS mixtures released from different sources and/or at different times vary from each other (due to differences in desired properties or substitution as certain PFAS have been phased-out), and that these differences can be detected in environmental samples. Based on the results from this work, distinct differences between different PFAS sources could be identified. An environmental forensics approach using PFAS profiles and knowledge of environmental fate and transport of individual PFAS, is discussed using lake Tyrifjorden as an example (Paper II). In lake Tyrifjorden, PFAS profiles, including isomer patterns, and sediment core dating were used for source tracking. These techniques are concluded to be valuable for source identification and characterization of environmental PFAS pollution in future studies.

PFAS mixtures released at point sources differ depending on source type and date of release

Paper I reported PFAS profiles (fingerprints) in fish from different Norwegian freshwater systems, receiving PFAS pollution from different sources. A total of 581 muscle samples and 454 liver samples were included in the study, shown in Table 2 and Table 3, respectively.

Table 2. Number of muscle samples from the different fish species at the different sites.

	PFAS source	AFFF				Paper industry	Diffuse	Long-range atmospheric transport	
	Site	Oslo Airport	Evenes Airport	Fagernes Airport	Rygge Airport	Lake Tyrifjorden	Lake Mjøsa	Lake Femunden	Lake Randsfjorden
Species	Arctic char		15			1			1
	Brown Trout		34	46 (3)		6	125		24
	European smelt						120 (1)		21 (7)
	Perch			34	16	42			
	Pike	2			14	14			
	European chub	1							
	Whitefish			30 (2)				24 (23)	
	Zander				11				

Numbers inside brackets () indicate the number of samples for which PFAS were not detected

Table 3. Number of liver samples from the different fish species at the different sites.

	PFAS Source	AFFF	Paper industry	Diffuse	Long-range atmospheric transport	
	Site	Rygge Airport	Lake Tyrifjorden	Lake Mjøsa	Lake Femunden	Lake Randsfjorden
Species	Arctic char		1			7
	Bream		2			
	Brown Trout		6	84	66	34
	European smelt			61		28
	Perch	15	42			
	Pike		14			
	Roach		8			
	Vendace			37		
	Whitefish		13		36	

Differences in muscle PFAS burdens were observed between different source types. Higher concentrations were reported for sites affected by PFAS point source releases compared to sites mainly affected by long-range atmospheric transport. Further, muscle samples from sites affected by AFFF point sources showed higher concentrations and relative percentages of PFSA (as a percentage of ΣPFAS) compared to sites affected by other sources. Compared to muscle samples, higher numbers of PFAS above the LOQ, and more distinct differences with respect to profiles and concentrations between sites were reported for liver samples. The reason for this is likely that many PFAS, including the long chained PFAA, bind to transport proteins such as albumins and therefore mainly accumulate in tissues which are rich in these proteins, such as blood, liver and kidney (Ng and Hungerbühler, 2013; Falk *et al.*, 2015). Therefore, such tissues (including the liver) were concluded to be better for source tracking purposes. However, for three AFFF impacted sites (Oslo Airport, Evenes Airport, and Fagernes Airport) only muscle samples

were available. Differences in accumulation of PFAS between species have previously been reported (Becker *et al.*, 2010; Fang *et al.*, 2014; Xu *et al.*, 2014; Munoz *et al.*, 2017; Simonnet-Laprade *et al.*, 2019). Thus, species-specific comparisons were performed.

Perch livers were sampled at both lake Tyrifjorden (paper product production point source) and in the lake receiving runoff from Rygge Airport, lake Vansjø (AFFF point source). ΣPFAS concentrations were relatively similar between the two sites, however PFAS profiles differed. Profiles were compared using Principal Component Analysis (PCA), shown in Figure 13. Samples from lake Vansjø grouped to the right based on their high percentage of PFSA relative to samples from lake Tyrifjorden which have higher percentages of preFOS (i.e., PFOS precursors, see Figure 5 page 17) and PFCA. The separation along PC 1 was significant ($p<0.01$). The higher percentages of PFSA in perch liver samples exposed to PFAS from Rygge airport (lake Vansjø) were echoed in muscle samples.

PFSA dominated in AFFF before the phase-out of firefighting foams containing PFOS in Norway in 2007, as shown in Table 1 (Norwegian Government, 2006; Herzke *et al.*, 2012). These older AFFF mixtures have been reported to contain mostly PFOS and some other PFSA (Herzke *et al.*, 2012). The high percentages of PFSA in fish sampled at AFFF impacted sites (both for muscle and liver samples) reflected the high historic emissions of PFSA at these sites. PFHxS and perfluoroheptanesulfonate (PFHpS), which have shorter chain lengths than PFOS, have previously been reported to have lower bioaccumulation potentials and shorter half-lives in fish than PFOS (Labadie and Chevreuil, 2011; Falk *et al.*, 2015; Lescord *et al.*, 2015; Zhong *et al.*, 2019). However, accumulation of PFHxS in fish was reported in Paper IV (Bodø), and has been observed for other AFFF polluted sites (Kärrman *et al.*, 2011; Filipovic *et al.*, 2015; Lanza *et al.*, 2017), reflecting its presence in AFFF. Overall, these results show that high percentages of PFOS and the presence of other PFSA are indicative of a potential AFFF PFAS source (where an older AFFF formulation has been used).

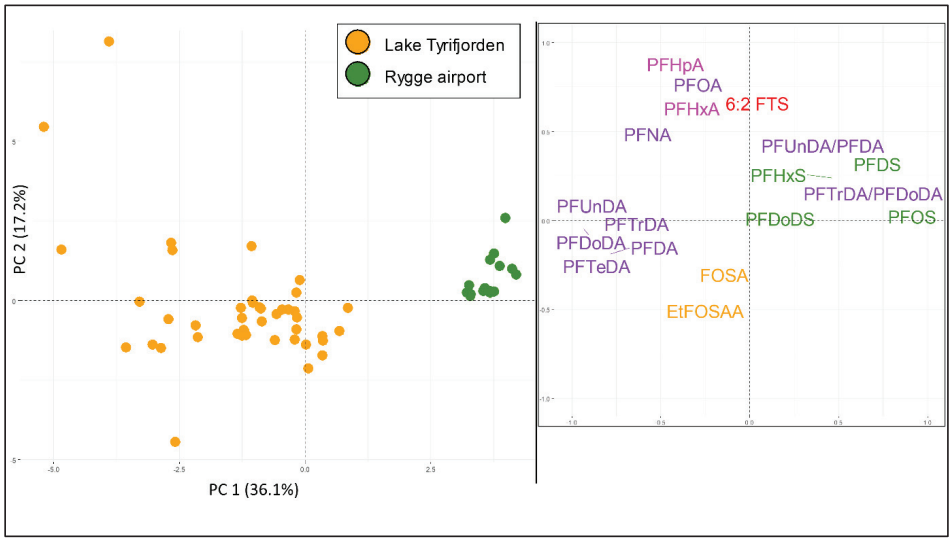

Figure 13. Principal Component Analysis (PCA) for PFAS profiles in perch livers from two Norwegian lakes, lake Tyrifjorden and lake Vansjø (Rygge airport). The score plot is shown to the left and the loading plot is shown to the right. Only individual PFAS targeted at both sites and detected above the LOQ in at least one perch liver sample were included. Concentrations below the LOQ were treated as 0. From Paper I.

In **Paper I** (PFAS fingerprints in fish), PFAS concentrations were reported for Brown trout livers sampled at four large lakes: lake Femunden and lake Randsfjorden which are both considered to mainly receive PFAS via long-range atmospheric transport; lake Mjøsa which, in addition to atmospheric long-range transport, is polluted by diffuse sources including industry, WWTP, and urban runoff; and lake Tyrifjorden which is polluted by the production of PFAS coated paper products (point source). ΣPFAS concentrations were higher in lake Tyrifjorden compared to the other sites. Comparison of PFAS profiles were performed using PCA, as shown in Figure 14. Samples from the two lakes considered to be mainly affected by long-range atmospheric transport plotted to the left and close to the centre (PC 1 scores of -1.7 ±0.2 and -1.5 ±0.3 for lake Femunden and lake Randsfjorden, respectively). Samples from lake Mjøsa plotted close to the centre and to the right (PC 1 scores of 1.6 ±0.1), while samples from lake Tyrifjorden plotted to the right (PC 1 scores of 4.2 ±0.5). PC 1 scores for samples from lake Tyrifjorden differed significantly to the lakes mainly receiving PFAS via long-range atmospheric transport and lake Mjøsa ($p<0.01$). For PFAS (the loading plot, right panel in Figure 14), the C13 PFCA, perfluorotridecanoic acid (PFTrDA), plotted to the left,

which indicates lower percentages of this substance in fish from lake Tyrifjorden compared to fish from the other lakes. The C6, perfluorohexanoic acid (PFHxA); C7, perfluoroheptanoic acid (PFHpA); C10, perfluorodecanoic acid (PFDA); C11, perfluoroundecanoic acid (PFUnDA); and C12, perfluorododecanoic acid (PFDoDA) PFCA were plotted to the right along with PFOS, FOSA, and EtFOSAA, reflecting that the percentages of these were higher in lake Tyrifjorden compared to the other lakes.

Previously, the concentration of a given odd chain length PFCA was reported to be higher than the concentration of the shorter adjacent even chain length homologue in biota samples not directly affected by a specific PFAS point source (Martin *et al.*, 2004a; Shaw *et al.*, 2009; Bossi *et al.*, 2015; Spaan *et al.*, 2020). The mechanism behind this is suggested to be the degradation of FTOH in the atmosphere which results in even and odd chained PFCA (i.e. 8:2 FTOH is degraded to PFOA and PFNA, 10:2 FTOH is degraded to PFDA and PFUnDA, and 12:2 FTOH is degraded to PFDoDA and PFTrDA). Subsequently, the longer PFCA is more bioaccumulative than its shorter homologue (for these PFCA pairs) (Ellis *et al.*, 2004; Shaw *et al.*, 2009). This pattern is seen in samples from lake Femunden and lake Randsfjorden where PFNA concentrations are higher than PFOA concentrations, PFUnDA concentrations are higher than PFDA concentrations, and concentrations of PFTrDA are higher than concentrations of PFDoA. However, concentrations in samples from lake Tyrifjorden do not follow this pattern. For example, PFDoA (C12) concentrations in trout livers from lake Tyrifjorden are on average 200% of PFTrDA (C13) concentrations. This difference is shown in Figure 14. In conclusion, even though both fish affected by a paper industry point source and fish mainly affected only by long-range atmospheric transport show high percentages of PFCA, the relationship between the percentages of the different PFCA differ, which thus implies that they are impacted by different PFAS sources. In addition, samples affected by the paper industry point source show higher percentages of PFOS and preFOS.

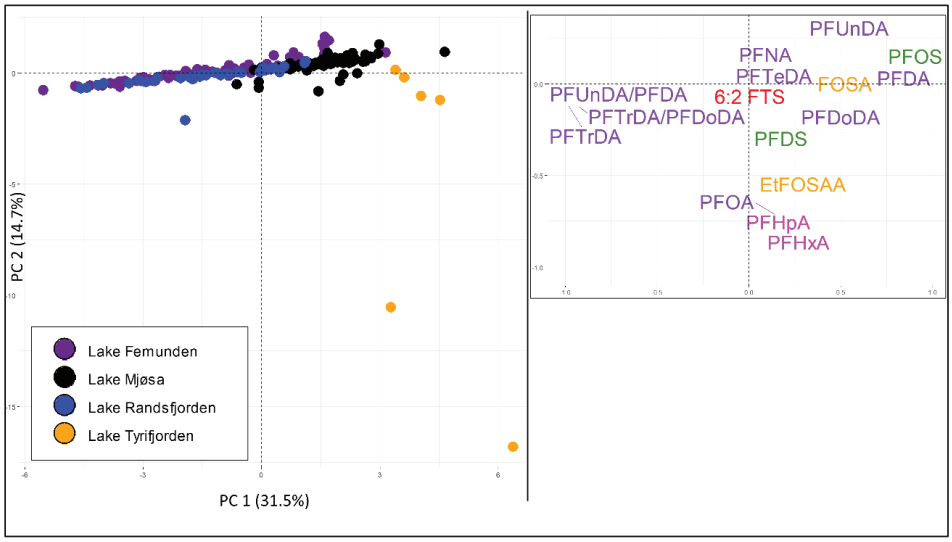

Figure 14. Principal Component Analysis (PCA) for PFAS profiles in Brown Trout livers from four large Norwegian lakes: lake Femunden, lake Mjøsa, lake Randsfjorden, and lake Tyrifjorden. The score plot is shown to the left and the loading plot is shown to the right. Only individual PFAS targeted at all sites and detected above the LOQ in at least one sample were included. Concentrations below the LOQ were treated as 0. From Paper I.

Conclusion to hypothesis 1a

The results from the comparison of PFAS concentrations and profiles in fish from different Norwegian freshwater bodies reported in Paper I support hypothesis 1a: PFAS mixtures released at point sources differ depending on source type (i.e. application or product) and date released. This results in different environmental PFAS mixtures depending on the main source(s).

PFAS concentrations and profiles in environmental samples differed depending on pollution source. For biota samples, species-specific differences as well as differences between tissues should be taken into consideration.

Individual PFAS and/or PFAS profiles, including the relationship between linear and branched isomers, can be used to identify major PFAS sources

Paper II reported the use of PFAS concentrations and profiles for source tracking in lake Tyrifjorden. Based on previous site investigations (Slinde and Høisæter, 2017), a factory producing disposable paper products and a fire station were investigated as possible sources. As access to the factory was not possible, samples of water and sediments from a creek downstream a landfill that received factory waste were used to represent emissions from the factory. In addition, a paper plate produced by the factory in 2007 was analysed to explore the PFAS mixture used at the time. Emissions from the fire station were represented by water and sediments sampled when the storm water system was cleaned. Locations of the factory, the fire station and the landfill are shown in Figure 15.

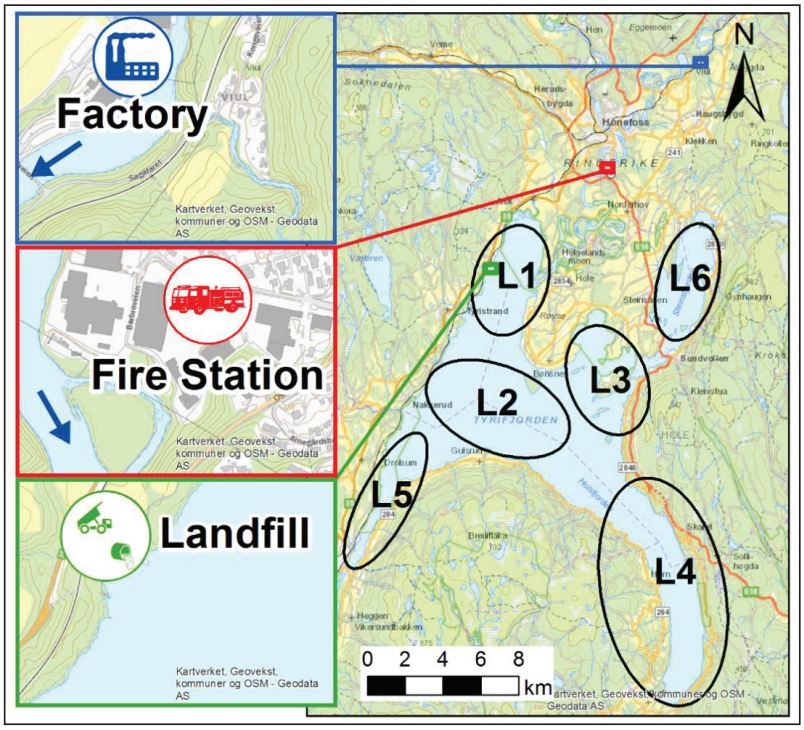

Figure 15. Geographical location of source areas and lake sampling areas (L1-L6) in lake Tyrifjorden. Arrows are indicating directional river flow. The main outlet from the lake is southwest of area L5. From Paper II.

PFAS concentrations and profiles in the samples used to represent the two suspected sources in lake Tyrifjorden were compared to profiles in river and lake sediments using PCA, shown in Figure 16. Samples of sediments from the river downstream the factory, the creek downstream the landfill (with waste from the factory), and the lake grouped together (approximately PC 1 scores of 0), while samples from the fire station storm water system grouped separately (to the left) based on their percentages of PFSA and 6:2 FTS. The paper plate did not group with any other sample. However, the PC 1 score for the paper plate was comparable to PC 1 scores for lake-, river-, and landfill sediments.

Based on the similar PFAS profiles in sediments in the river downstream the factory, in the creek downstream the landfill, and in the lake, and based on the fact that the dominant compounds, i.e. preFOS and FTS (and related compounds), have been reported to be used in paper production (Trier *et al.*, 2011, 2017), emissions originating from the factory were concluded to be the main PFAS source to the sediments in lake Tyrifjorden.

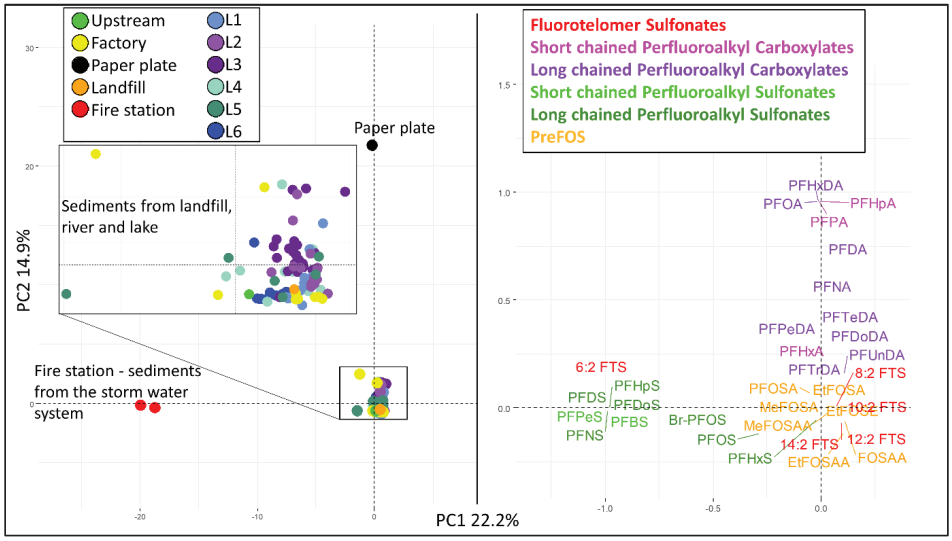

Figure 16. Principal Component Analysis (PCA) for sediment samples and the paper plate from the factory. The score plot is shown to the left and the loading plot is shown to the right. Concentrations below the LOQ were treated as 0. From Paper II.

Paper II reported the use of a dated sediment core (dated using unsupported ^{210}Pb) from lake Tyrifjorden to explore historical PFAS emission volumes and mixture(s). Based on

the dating, the core presents PFAS concentrations in sediments that settled between 1934 and 2017 (Figure 17). Concentrations of different PFAS in the core varied with depth; PFCA and FTS showed peaks during the second half of the 1990s, preFOS and SAmPAP diester peaked around 1984, with a smaller peak around 1960, while the peak for PFOS was at approximately 1960. The low concentrations in top (recent) sediments compared to deeper (older) sediments likely reflect lower concentrations in sediments that settled after the shutdown of the factory in 2013.

Modelling based on the assumption that the core is representative of concentrations in most of the lake bed indicated that, depending on the organic carbon-water partitioning coefficients used in the model, between 44 and 205 tons of PFAS have been emitted to the lake since the emissions began, which is assumed to be in the 1970s. These amounts are high compared to previous estimated global emissions for POSF, preFOS and PFOS which are in ranges of 670 tons, 1230-8738 tons, and 1228-4930 tons, respectively (Wang *et al.*, 2017b).

10:2 FTS and 12:2 FTS dominate in sediments dated to have settled after the year 2000, and concentrations peaked in 2006. Fluorotelomer mercaptoalkyl phosphate esters (FTMAP) are, based on their structure which contains the (suspected) FTS precursor moiety (Trier *et al.*, 2011), likely precursors to FTS, and have been reported to have been used in food packaging since 1995 (Lee and Mabury, 2011). The detected PFAS (SAmPAP and preFOS) in sediments dated to have settled before 1995 corresponds to a 3M product called Scotchban which was used for paper products (Martin *et al.*, 2010; Trier *et al.*, 2017). Therefore, the sediment core profile can be used to shed light on the historic use of PFAS in paper products and provides further evidence that the majority of the PFAS pollution in lake Tyrifjorden originates from the factory. Further, in combination with the results from the modelling, this indicates that the production of paper products could be a significant, largely overlooked, source of PFAS to the environment.

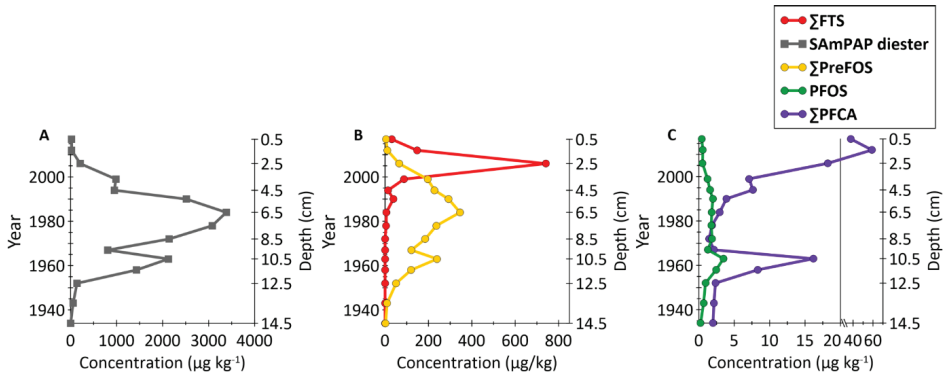

Figure 17. PFAS concentrations in sediments from the dated core sample from area L1. Panel A: concentrations of SAmPAP diester. Panel B: Concentrations of ΣFTS and ΣpreFOS. Panel C: Concentrations of PFOS, and ΣPFCA (PFOS was the only PFSA above the LOQ). The black vertical line in C shows that the x-axis is split at the interval 20-35 µg kg^{-1}. From Paper II.

PFOS produced by 3M using electrochemical fluorination (ECF) have been reported to consist of approximately 30% branched and 70% linear isomers (Vyas *et al.*, 2007; Benskin *et al.*, 2010; Jiang *et al.*, 2015). In **Paper II** (lake Tyrifjorden), the percentages of L-PFOS were reported to be 74.3-89.3% in pore water, 92.0-99.3% in perch liver, and 97.0-99.6% in pike liver. The percentages were reported to increase with distance from the factory, as shown in Figure 18.

Most Br-PFOS isomers have a higher water solubility and faster elimination in organisms compared to L-PFOS (Benskin *et al.*, 2009a; Zhang *et al.*, 2013; Chen *et al.*, 2015a, 2015b). In **Paper II**, it was hypothesised that these processes result in environmental fractionation whereby Br-PFOS is removed with water exchange, while L-PFOS is retained in biota and sediments. Thus, for this type of transport scenario, the amount of L-PFOS relative to Br-PFOS is expected to increase over time and with increasing distance from a point source. This is the likely mechanism behind the increasing percentages of L-PFOS observed with distance from the factory. It is also likely that the faster biotransformation of branched isomers results in more Br-PFOS precursors being transformed closer to the source compared to L-PFOS precursors (Benskin *et al.*, 2009b; Ross *et al.*, 2012; Peng *et al.*, 2014; Chen *et al.*, 2015a). Therefore, the isomer profiles in pore water, perch livers, and pike livers provide further evidence that the factory is the

main point source of PFOS to lake Tyrifjorden and illustrate that isomer profiles can be used for source tracking. However, as there are few other studies exploring this, further studies are needed to confirm this for similar case study sites elsewhere.

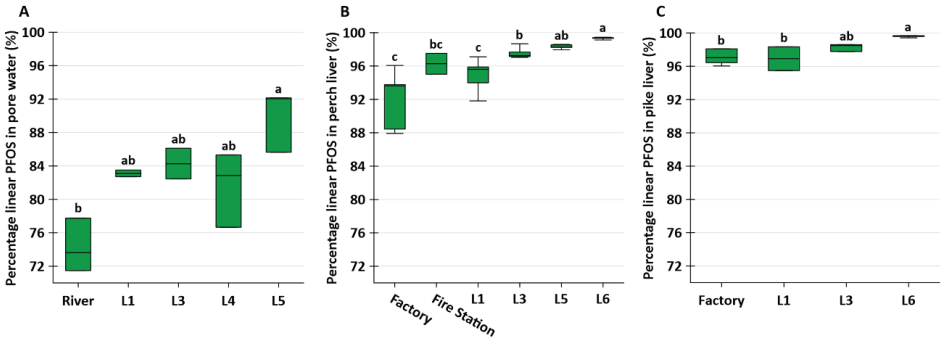

Figure 18. Linear PFOS in pore water (A), perch liver (B), and pike liver (C) at the different sampling areas expressed as a percent of total PFOS (sum of branched and linear isomers). Whiskers show maximum and minimum values, boxes show lower and upper quartile, and the mid black line shows the median. Different letters denote significant differences, $p<0.05$ (Kruskal-Wallis and Bonferroni correction. Pore water: n=2-3, perch livers: n=2- 5, pike livers=2-5). Y-axis starts at 70%. From Paper II.

Conclusion to hypothesis 1b

Results from the source tracking carried out in lake Tyrifjorden support hypothesis 1b: Indicative individual PFAS and/or PFAS profiles, including the relationship between linear and branched isomers, can be used to identify major PFAS sources.

Similar PFAS profiles between samples representing the factory and samples taken from lake Tyrifjorden indicated that the factory was the major source. This was strengthened by the correspondence between PFAS profiles observed at different sediment depths in the dated sediment core and the known historical use of PFAS in paper products. PFOS isomer profiles showed increasing percentages of L-PFOS with distance from the factory, in agreement with expected environmental fractionation due to different physiochemical properties between different isomers. Overall, the approaches for source tracking demonstrated in Paper II, as well as similar approaches using indicative PFAS (including different isomers) and/or PFAS profiles are valuable tools for future studies that aim to identify PFAS point sources.

Importance of directly measuring concentrations of PFAS in biota, and to include organisms representing different phylogenetic groups, and/or different habitats, diets, and trophic levels

Differences in structures of individual PFAS, including functional hydrophilic groups and molecular size directly influence environmental fate, transport and partitioning, and hence resultant concentrations in different environmental compartments. In the following, the effect of biotransformation of precursor PFAS on environmental partitioning will be discussed. Results showed that the observed relationships between PFAS concentrations in abiotic compartments and concentrations in biota can be greatly affected by precursor biotransformation, which makes it difficult to predict biota concentrations based on concentrations in sediment or water. In addition, differences between organisms in relation to environmental partitioning, exposure routes, and precursor biotransformation and depuration are discussed. Results showed that the combination of precursor biotransformation and differences in exposure routes and biotransformation/depuration potential complicate assessments of PFAS bioaccumulation and should be accounted for when investigating PFAS contaminated sites.

Precursor biotransformation affect environmental distribution

Paper III address the fate and transport of PFAS, including the contribution from transformation of precursor compounds in lake Tyrifjorden polluted by a shutdown factory which produced PFAS coated paper products. Targeted chemical analyses of PFAS in lake and river water, sediments and biota were performed, and determination of extractable organic fluorine (EOF) in sediments and biota was applied. Stable carbon and nitrogen isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) were used to assess carbon sources and trophic level for the investigated biota. Sediment-water partitioning coefficients (K_D), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), and trophic magnification factors (TMF) were calculated for PFCA, PFSA, preFOS, and FTS.

High PFAA concentrations were reported for biota (for example the mean PFOS concentration in perch livers was 149 $\mu g\ kg^{-1}$) compared to surrounding water (where the maximum PFOS concentration was 0.18 $ng\ L^{-1}$) in lake Tyrifjorden. The relationship between PFOS concentrations in biota and surrounding water, BAF, were therefore very

high compared to values reported elsewhere. For PFOS, the calculated BAF for perch livers were between 804 900 and 3 811 416 for lake Tyrifjorden. For comparison, PFOS BAF in perch livers sampled near a fire training facility at Stockholm Arlanda Airport in Sweden was 39 000 (Ahrens *et al.*, 2015). These BAF were calculated for the same substance in the same species and it is therefore unlikely that differences in depuration capacities between perch at the different sites are the reason for the observed large difference. BAF observed in lake Tyrifjorden were also very high compared to other studies investigating different species and/or tissues, summarized in Table 4 for PFOS in perch and pike sampled at the areas where water concentrations were measured directly: factory area and area L6. The high BAF in lake Tyrifjorden indicate other exposure pathways than direct uptake from surrounding water.

Table 4. Bioaccumulation factors (BAF, water:biota tissue) for PFOS in Tyrifjorden (Paper III) compared to literature values. Only literature studies reporting specific species and tissue (liver, muscle or whole organism) were included.

Species		Marine or freshwater	BAF (L kg^{-1})	Water concentration (ng L^{-1})	PFAS source	Study type	Reference
Common Name	**Scientific Name**						
Liver							
Perch	*Perca fluviatilis*	Freshwater	804 900 - >3 714 600	<0.10-0.18	Paper industry	Field	Paper III
Pike	*Esox Lucius*	Freshwater	386 000 - >484 900	<0.10-0.18	Paper industry	Field	Paper III
Perch	*Perca fluviatilis*	Freshwater	39 000	98	AFFF	Field	(Ahrens *et al.*, 2015)
Common shiner	*Notropus cornutus*	Freshwater	6 250 - 124 700	320	AFFF	Field	(Moody *et al.*, 2002)
Mullet	*Mugilidae*	Marine	12 400	13	Industry/WWTP	Field	(Yoo *et al.*, 2009)
Bluegil	*Lepomismacrochirus*	Freshwater	41 600 [a]	7	Industry/WWTP	Field	(Taniyasu *et al.*, 2003)
Silver Perch	*Bidyanus bidyanus*	Freshwater	26 000	10	Reclaimed water	Field	(Terechovs *et al.*, 2019)
Crucian carp	*Carassius carassius*	Freshwater	1 500 [b]	13-18	Industry/WWTP	Field	(Shi *et al.*, 2018)
Chub	*Leuciscus cephalus*	Freshwater	4 600	27	WWTP	Field	(Becker *et al.*, 2010)
Muscle							
Perch	*Perca fluviatilis*	Freshwater	59 200 - >251 900	<0.10-0.18	Paper industry	Field	Paper III
Pike	*Esox Lucius*	Freshwater	18 700 - >57 200	<0.10-0.18	Paper industry	Field	Paper III
Perch	*Perca fluviatilis*	Freshwater	3 400	98	AFFF	Field	(Ahrens *et al.*, 2015)
	Cyprinus carpio	Freshwater	10 000	0.03	Background	Field	(Meng *et al.*, 2019)
	Carassius auratus	Freshwater	4 000	0.03	Background	Field	(Meng *et al.*, 2019)
	Erythroculter dabryi	Freshwater	26 670	0.03	Background	Field	(Meng *et al.*, 2019)
	Hypophthalmichthys molitrix	Freshwater	8 330	0.03	Background	Field	(Meng *et al.*, 2019)
	Siniperca chuatsi	Freshwater	65 000	0.03	Background	Field	(Meng *et al.*, 2019)
Minnow	*Hemiculter lcucisculus*	Freshwater	6 092	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Silver carp	*Hypophtha lmichthys molitrix*	Freshwater	1 761	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Whitebait	*Reganisalanx brachyrostralis*	Freshwater	2 835	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Crucian	*Carassius cuvieri*	Freshwater	15 599	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Lake Saury	*Coilia mystus*	Freshwater	9 190	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Carp	*Cyprinus carpio*	Freshwater	7 623	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Mongolian culter	*Culter mongolicus*	Freshwater	15 088	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Mud fish	*Oriental weatherfish*	Freshwater	10 810	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Chinese bitterling	*Rhodeus sinensis Gunther*	Freshwater	6 444	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Gobies	*Ctenogobius giurinus*	Freshwater	6 144	5.68	Industry/WWTP	Field	(Fang *et al.*, 2014)
Crucian carp	*Carassius auratus*	Freshwater	120 000	0.48	Industry	Field	(Wang *et al.*, 2012)
Silver Perch	*Bidyanus bidyanus*	Freshwater	6 000	10	Reclaimed water	Field	(Terechovs *et al.*, 2019)
Crucian carp	*Carassius carassius*	Freshwater	900 [b]	13-18	Industry/WWTP	Field	(Shi *et al.*, 2018)
Nile Tilapia	*Oreochromis niloticus*	Freshwater	398	0.073-5.6	Industry/WWTP	Field	(Ahrens *et al.*, 2016)
	Labeobarbus megastoma	Freshwater	5 012	0.073-5.6	Industry/WWTP	Field	(Ahrens *et al.*, 2016)
	Labeo- barbus gorguari	Freshwater	3 981	0.073-5.6	Industry/WWTP	Field	(Ahrens *et al.*, 2016)
	Labeobarbus intermedius	Freshwater	794	0.073-5.6	Industry/WWTP	Field	(Ahrens *et al.*, 2016)
Eel	*Anguilla anguilla*	Freshwater	234 – 1 148	20-490	AFFF	Field	(Kwadijk *et al.*, 2014)
Whole fish							
Pike	*Esox lucius*	Freshwater	1 549	340-490	AFFF	Field	(Kwadijk *et al.*, 2014)
Perch	*Perca fluviatilis*	Freshwater	2 344 - 6 310	20-490	AFFF	Field	(Kwadijk *et al.*, 2014)
Perch	*Perca fluviatilis*	Freshwater	6 400	98	AFFF	Field	(Ahrens *et al.*, 2015)
Lake trout	*Salvelinus namaycush*	Freshwater	12 589	0.2-5.9	Background/ unknown		(Furdui *et al.*, 2007)
	Pseudohemiculter dispar	Freshwater	25 670	0.03	Background	Field	(Meng *et al.*, 2019)
Sculpin	*Cottus cognatus*	Freshwater	234 000	2.20	Unknown	Field	(Houde *et al.*, 2008)
Lake trout	*Salvelinus namaycush*	Freshwater	34 000	2.20	Unknown	Field	(Houde *et al.*, 2008)
Herring	*Clupea harengus membras*	Marine	22 000	0.25	Background	Field	(Gebbink *et al.*, 2016)
Sprat	*Sprattus sprattus*	Marine	23 200	0.25	Background	Field	(Gebbink *et al.*, 2016)

[a] The highest BAF reported in the study. No other species-specific values were reported

[b] Value from figure (approximate)

In lake Tyrifjorden, high concentrations of precursors to PFAA, including preFOS (EtFOSE, EtFOSAA, FOSAA, and FOSA; max concentrations of 72.2, 126, 8.6, and 14.6 μg kg^{-1}, respectively) and the parent compound, SAmPAP diester (max 1 872 μg kg^{-1}), were reported for the top (2 cm) lake sediments. These compounds have previously been reported to be used in the paper industry (Martin *et al.*, 2010; Trier *et al.*, 2011, 2017), which confirms the paper industry related PFAS point source in this area. PreFOS have previously been reported to have a higher affinity for sediments compared to PFAA (Lutz *et al.*, 2009), and K_D values (sediment-pore water partitioning coefficient) have been reported to increase with N-alkyl substitution (Benskin *et al.*, 2012). In agreement with this, K_D values for preFOS reported in **Paper III** are higher than for PFOS (shown in Figure 19), indicating that preFOS and parent compounds partition more strongly to sediments than PFOS. Abiotic transformation of SAmPAP and/or preFOS to PFOS is believed to be negligible (Martin *et al.*, 2010; Benskin *et al.*, 2013), however biotic transformation has been reported for perch (Gaillard *et al.*, 2017) and by microbes in freshwater (Zhang *et al.*, 2018) and in marine sediments (Benskin *et al.*, 2013). Based on the combination of the high concentrations of SAmPAP diester and preFOS in lake Tyrifjorden sediments and the potential of these compounds to be biotransformed to PFOS, it was concluded that sediments represent a large source of PFOS to the food chain in lake Tyrifjorden.

The low PFOS concentrations observed in water compared to biota (and thus very high BAF) suggest other major exposure pathways than from surrounding water. Uptake, transport and transformation of PFOS precursor compounds through the food chain is a likely explanation. Similarly, K_D values for long chained FTS (8:2, 10:2, 12:2, and 14:2 FTS) in lake Tyrifjorden sediments were high compared to K_D values for their expected degradation products, PFCA (Wang *et al.*, 2011), shown in Figure 19. The presence of long chained FTS in lake sediments are therefore a likely reason for the relatively high concentrations of PFCA reported in biota, given the fact that PFCA concentrations were below the LOQ in lake water. The reported results indicate that uptake into biota and subsequent biotransformation of large, hydrophobic PFAA precursor compounds present as a result of historic paper production at the site was the reason for the high BAF in lake Tyrifjorden compared to what has been reported elsewhere.

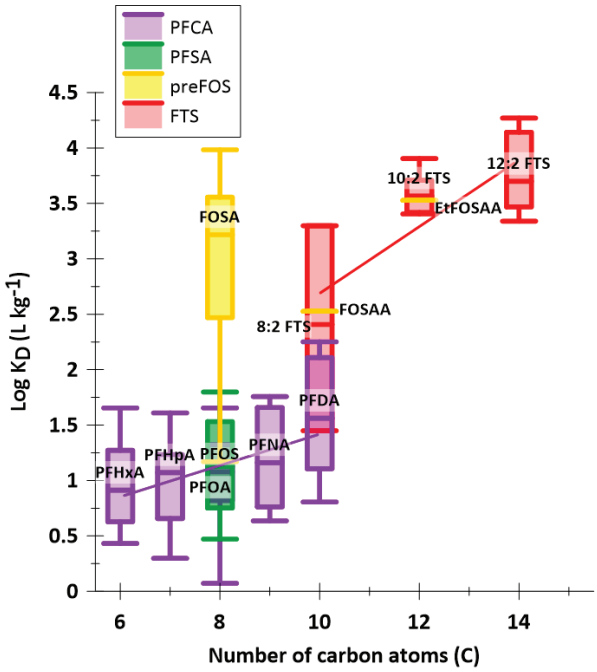

Figure 19. Partitioning coefficients (sediment-pore water, median log K_D values) for different PFAS as a function of number of carbons. Boxes show upper and lower quartiles and whiskers show maximum and minimum values. The purple and red regressions are the relationships between partitioning coefficients and carbon chain length for PFCA (Log K_D=0.14C+0.01; R^2:0.17; p<0.01) and FTS (Log K_D=0.30C-0.32; R^2:0.48; p<0.01), respectively. Only compounds for which at least one concentration above the LOQ was detected in both sediments and pore water for at least one replicate are shown. Concentrations below the LOQ were treated as half the LOQ. Note that some compounds overlap (PFOS and PFOA, 8:2 FTS and FOSAA, 10:2 FTS and EtFOSAA) and are plotted on top of each other. From Paper III.

Conclusion to hypothesis 2a

The results of the work carried out in lake Tyrifjorden support hypothesis 2a: The physiochemical properties, and hence the environmental partitioning, of precursor PFAS might be altered by (bio)transformation, which may affect relationships between concentrations of degradation products in environmental compartments. Therefore, uptake of a specific compound by biota cannot solely be predicted by concentrations of that compound in abiotic compartments such as sediment or water.

The physiochemical properties of precursors are altered by biotransformation as they are taken up into the food chain. Thus, the PFAS product used at a point source may affect the observed distribution of PFAS between different environmental compartments. This information is very important as biota concentrations may be greatly underpredicted if they are solely based on measured water concentrations and BAF from literature related to point sources where a different PFAS mixture were used (such as AFFF). In cases where very little is known about the PFAS source or mixture used, it is important to investigate concentrations in a number of different environmental compartments.

Accounting for factors affecting relationships between PFAS concentrations in sediments and/or water and PFAS concentrations in various biota

Differences in exposure routes for biota with different habitats and diets, including trophic level

Paper III reported that sediment living organisms in lake Tyrifjorden are exposed to high levels of PFAA precursors which are biotransformed into PFAA as they are transported through the food chain. In order to test this hypothesis, potential correlations between concentrations of different PFAS in muscle or liver tissue and trophic level adjusted muscle $\delta^{13}C$ were tested. $\delta^{13}C$ was used as an indicator of an organism's dietary sources. Increased $\delta^{13}C$ in an organism was interpreted as an indication of an increased proportion of benthic organisms in the diet of that organism (see details in **Paper III**). Long chained (C11-C14, and thus hydrophobic) PFCA, preFOS (FOSAA), and 12:2 FTS were positively correlated ($p \leq 0.05$) with $\delta^{13}C$ in the areas where the greatest diversity of

species was sampled. This indicates that concentrations of these PFAS in the investigated biota were positively correlated with increased proportions of benthic organisms in the diet of that biota.

A laboratory study performed after the investigations reported in Paper III strengthens the hypothesis that sediment living organisms accumulate high concentrations of the dominating PFAS in lake Tyrifjorden (Schaanning *et al.*, 2020). Sediments collected in the river downstream the factory were placed in aquaria continuously supplied with clean water. Clams (*Anodonta anatine*) and oligochaete worms (*Tubifex tubifex*) were added to the aquaria and exposed for four weeks. Results showed that the worms, which were exposed to pore water, accumulated higher concentrations compared to the clams, which were not in direct contact with the pore water and feed by filtering water from the water column (Schaanning *et al.*, 2020).

TMF was calculated for the different PFAS. The TMF for PFOS were 3.7 and 9.3 at areas L3 and L6, respectively. In comparison, in two studies similar to Paper III (in Taihu Lake, China), PFOS has been reported to be 2.9 and 3.9 (Fang *et al.*, 2014; Xu *et al.*, 2014). Previously, high TMF for PFOS has been suggested to be due to biotransformation of preFOS as they are transferred through the food chain (Martin *et al.*, 2004b; Kelly *et al.*, 2009; Fang *et al.*, 2014), and a similar mechanism is proposed as the explanation in **Paper III**.

However, mechanisms for exposure through diet are complex and additional laboratory studies are needed that evaluate biomagnification potential and also include the contribution of biotransformation of precursors (Franklin, 2016). To highlight this point, the percentages of EOF explained by the sum of targeted analyses of PFAS (ΣF_{targ}) in perch liver from lake Tyrifjorden were 37-108%, while the percentages in pike liver were much lower (9-30%), shown in Figure 20. EOF concentrations in the two species were comparable, meaning that pike and perch accumulated approximately the same levels of EOF in the liver but that a higher proportion of the EOF in pike livers comes from unknown substances. The two species did not differ in trophic level adjusted $\delta^{13}C$ and relative trophic levels ($p>0.05$), meaning that based on the results it cannot be concluded

that the two species have very different diets. Therefore, differences in diet (and hence differences in dietary PFAS exposure) do not appear to explain the observation, and differences in biotransformation potential were suggested as an explanation.

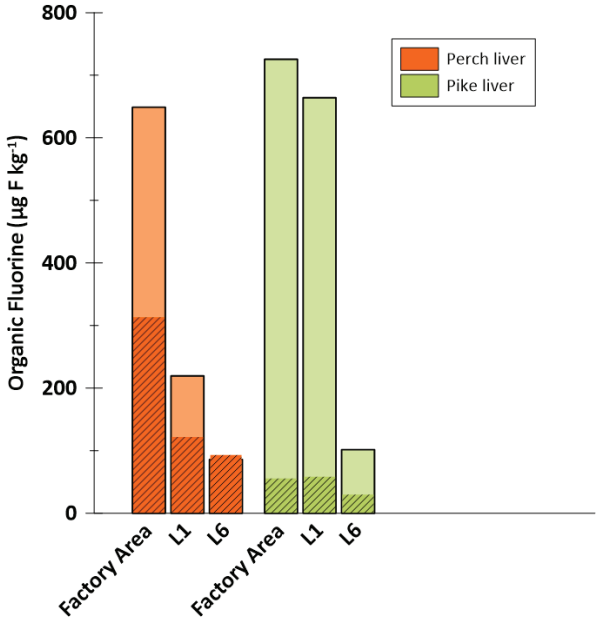

Figure 20. Sum of extractable organic fluorine (EOF, solid bars with black outline i.e. the complete bar) as well as sum fluorine from detected compounds from targeted analysis (hatched bars) in perch and pike livers (w.w.) from areas factory area, L1, and L6 (n=1). From Paper III.

Differences in biotransformation and depuration potential between organisms

In **Paper IV**, accumulation of PFAS arising from the use of AFFF was investigated in the marine food chain outside the military airport in Bodø. The objective was to evaluate potential differences in PFAS accumulation between organisms. Targeted chemical analyses of PFAS were performed on invertebrates (marine snails and crabs), teleost fish, stormwater, leachate water, fjord water (seawater), and marine sediments.

Significant differences in concentrations of 6:2 FTS between teleost fish (Atlantic cod and European place) and invertebrates (green shore crab, great spider crab, and edible crab) sampled in the marine environment outside the military airport in Bodø were

reported ($p<0.05$, shown in Figure 21). 6:2 FTS concentrations in fish were low and mostly below the LOQ: only 3 of 39 fish had 6:2 FTS concentrations above the LOQ and the highest concentration was 3.25 µg kg^{-1} in the liver of a European plaice. This is in agreement with previous studies reporting that 6:2 FTS is rapidly eliminated in teleost fish (Yeung and Mabury, 2013). In contrast to fish, higher concentrations of 6:2 FTS were detected in marine invertebrates with maximum concentrations of 56.3 µg kg^{-1} in snails, 12.3 µg kg^{-1} in green shore crab, and 56.8 µg kg^{-1} in great spider crab, and 26.4 µg kg^{-1} in the hepatopancreas of edible crab. The difference in concentrations between invertebrates and teleost fish was suggested to be due to differences in exposure routes and/or different capabilities for biotransformation and depuration. 6:2 FTS has been reported to be biotransformed to shorter, more water soluble PFAS, including 5:3 fluorotelomer carboxylic acid (5:3 FTCA), PFBA, perfluoropentanoic acid (PFPeA), and PFHxA (Wang *et al.*, 2011). These latter PFAS accumulate in fish to a much smaller extent (Martin *et al.*, 2003a, 2003b; Hoke *et al.*, 2015), likely due to their higher water solubility and this has been suggested as the main mechanism for the rapid elimination of 6:2 FTS (Yeung and Mabury, 2013).

Paper V considered PFAS in the coastal marine environment near Longyearbyen (Svalbard), including the marine environment outside Longyearbyen airport which is a source to PFAS arising from the use of AFFF. The aim of the study was to investigate the contribution of local sources versus long-range transport to PFAS concentrations observed in various media (abiotic and biotic). Targeted chemical analyses of PFAS were performed on leachate/runoff water, seawater, marine sediments, plankton, polychaetes, fish, crabs, and glaucous gulls.

The results indicated a contribution from local sources to the environment near Longyearbyen. Similar to what was reported in Paper IV (Bodø airport), indications of differences in 6:2 FTS concentrations (and thus accumulation potential) between vertebrates and invertebrates were reported for organisms from the marine environment near Longyearbyen (**Paper V**). 6:2 FTS concentrations were very low (mostly below LOQ) in fish liver and muscle and in livers of glaucous gull. In contrast, 6:2 FTS was abundantly detected in zooplankton, and was detected in polychaetes and crabs.

The hypothesis that (some) invertebrate species have a lower capacity for biotransformation of 6:2 FTS has recently been strengthened by a study from Munoz et al. (2020) which reported low levels of PFCA in earthworms despite high accumulated concentrations of 6:2 FTS (Munoz *et al.*, 2020). Further, metabolization of the fluorotelomer sulfonamidoalkyl betaine with 6:2 configuration (6:2 FTAB) was not observed in the exposed earthworms. This was in contrast to previously reported metabolization in fish, suggesting that some invertebrates have limited capabilities to metabolize fluorotelomers that are readily metabolized by vertebrates (Munoz *et al.*, 2020). Although the metabolites formed after biotransformation of 6:2 FTS have been reported to be rapidly depurated in fish, some metabolites, including 5:3 FTCA are reported to have slow clearance in rats and humans (Nilsson *et al.*, 2013; Kabadi *et al.*, 2018, 2020) (5:3 FTCA was not targeted by the chemical analyses in this thesis). Half-lives of months for rats after repeated oral exposure to another precursor to 5:3 FTCA, 6:2 FTOH, have been reported (Kabadi *et al.*, 2020). Many invertebrate species are food sources for vertebrates at higher trophic levels, including humans. Therefore, potential effects of fluorotelomer accumulation in invertebrates and subsequent effects on higher organisms from repeated dietary exposure warrant further investigation.

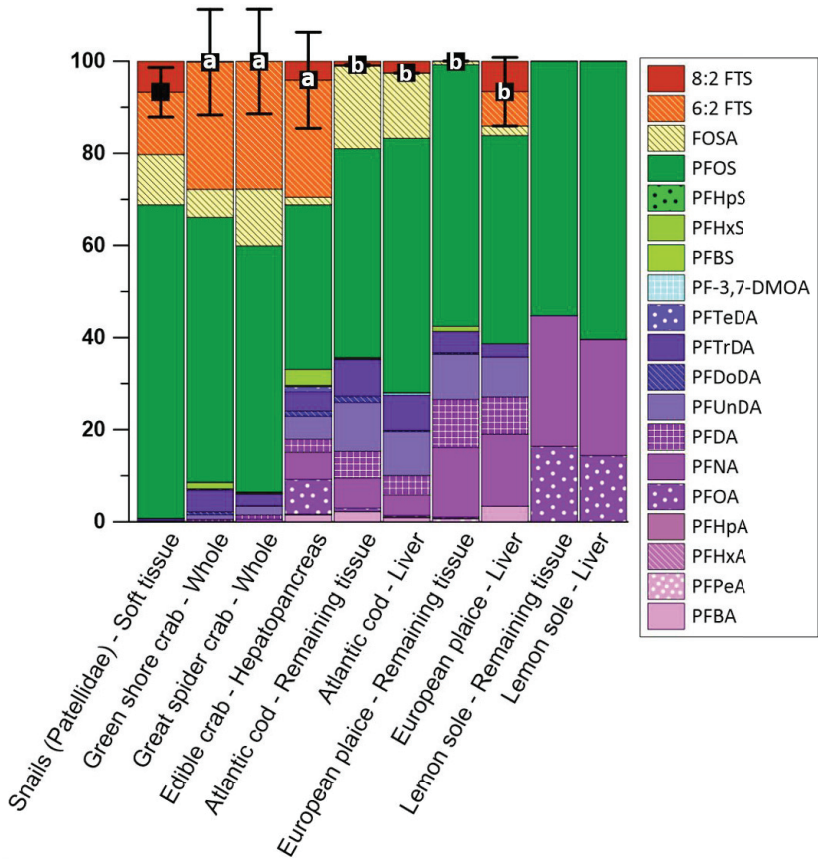

Figure 21. PFAS profiles in different biota tissues sampled near the military airport in Bodø (station A-H). FTS (6:2 and 8:2 FTS) are coloured red, preFOS (FOSA) are yellow, PFSA are green, and PFCA are blue and purple. Profiles are given as relative concentrations (of Σ PFAS 22). Only compounds detected above the LOQ in at least one sample are included in the figure. Error bars show ± standard error of the mean (SEM) for 6:2 FTS (not shown for Lemon sole where n=1). Different letters denote significant differences in 6:2 FTS proportion (Kruskal-Wallis and Bonferroni correction, $p<0.05$). Concentrations below the LOQ were treated as half the LOQ for statistical analyses, while they were set to 0 in the figure. From Paper IV.

Conclusion to hypothesis 2b

The results of the work carried out in lake Tyrifjorden, in the marine environment outside the military airport in Bodø, and the marine environment outside Longyearbyen airport (Svalbard) support hypothesis 2b: Relationships between PFAS concentrations in sediments and/or water and PFAS concentrations in various biota can be better evaluated by accounting for: 1) differences in exposure routes for biota with different habitats and diets, including trophic level; and 2) differences in biotransformation and/or depuration between different species.

Depending on differences such as habitat, diet (including trophic level), physiology, depuration and biotransformation potential, the accumulation of different PFAS may vary greatly between organisms. Differences in bioaccumulation are important to consider when carrying out site investigations and risk assessments of PFAS. For example, organisms in lake Tyrifjorden which are feeding at high trophic levels and/or on the benthic food chain are particularly exposed to the PFAA originating from PFAS released at the factory. From the work in Bodø and Longyearbyen, it is clear that the risk posed by 6:2 FTS in the marine environment might be underestimated if only fish are to be investigated. Thus, to account for differences in accumulation of different PFAS between organisms, investigating biota representing different habitats, diets (including trophic levels), physiology, and phylogenetic groups (e.g. vertebrates and invertebrates) should be considered. This is especially important, when the environmental behaviour of the relevant PFAS, or the PFAS mixture used at the source is unknown.

Approaches that can be used to investigate the fraction of environmental PFAS not accounted for using targeted analyses

The number of individual PFAS in the PFAS mixture at a site polluted by a point source is likely to greatly outnumber the number of individual PFAS that are included in a targeted analysis program. In the following section, two hypotheses are discussed. The first being that PFAS mixtures detected at distances further from point source releases represent older releases composed of smaller fractions of precursors due to more complete transformation to terminal degradation products. The results from the studies carried out at the military airport in Bodø (AFFF point source, Paper IV) and lake Tyrifjorden (paper product point source, Paper III) support the hypothesis, however the number of peer reviewed studies exploring these mechanisms are limited and additional studies are needed. The second hypothesis was that combining targeted analyses with methods to assess the total PFAS to evaluate potential transformation of unknown PFAS to known PFAS is advantageous. This hypothesis was based on the assumptions that samples further from point source releases represent older releases where compounds have undergone more complete transformations, and/or that precursors are transformed as they are transported through the food chain. Results show that the combined use of these approaches provide a useful tool for point source characterization that has a wide application domain.

PFAS mixtures at distances further from point source releases represent older releases composed of smaller fractions of precursors due to more complete transformation to terminal degradation products.

Paper IV (Bodø military airport) reported significant accumulation of 6:2 FTS in invertebrates. Biotransformation of 6:2 FTS has been reported to result in persistent PFCA, including PFBA, PFPeA, and PFHxA, and intermediates such as 5:3 FTCA which over time is expected to be transformed to PFCA (Lee *et al.*, 2010; Wang *et al.*, 2011). The highest 6:2 FTS concentrations were detected in animals from the two sampling areas at the closest proximity to the firefighting training area (56.3 μg kg^{-1} in snails, 12.3 μg kg^{-1} in green shore crab, and 56.8 μg kg^{-1} in great spider crab caught at sampling station F, and 26.4 μg kg^{-1} in the hepatopancreas of edible crab caught at sampling station E). Lower levels were reported for sampling areas further from the main sources. The lower

levels of 6:2 FTS in areas further from the source areas were likely due to biotransformation into the above-mentioned products. In addition, dilution of the PFAS mixture as the distance from the point source increases is an important mechanism for the low concentrations reported further from sources.

Paper III reported that sediments in lake Tyrifjorden were contaminated predominately by preFOS, FTS, and SAmPAP. PreFOS and SAmPAP have been reported to be precursors to PFOS (Benskin *et al.*, 2013; Gaillard *et al.*, 2017; Zhang *et al.*, 2018), and FTS are likely precursors to PFCA (Lee *et al.*, 2010; Wang *et al.*, 2011). In the lake Tyrifjorden source tracking study (**Paper II**), the source of the PFAS pollution was extensively characterized. The different sources had different fingerprints, including different precursors and transformation products. Thus, PFAS concentrations and profiles from the source areas were compared to concentrations and profiles in the river and lake sediments, water, and biota; taking spatial distribution and expected biotransformation into consideration. The shutdown factory that produced PFAS coated paper products was identified as the main source. To simplify the presentation of data, and for statistical analyses, the entire lake was divided into six sampling areas: L1 to L6 (shown in Figure 9, page 25).

Mean ΣPFAS 29 in sediments, were reported to be 2 450 μg kg^{-1} in the river at the factory area and between 6.1 and 207 μg kg^{-1} in the lake (sampling areas L6 and L2, respectively), shown in Figure 22A. A general decrease with distance from the factory was reported for the ΣPFAS 29 concentrations (significantly lower at areas L5 and L6, $p<0.05$). The same was reported for concentrations of the precursors: ΣFTS (6:2, 8:2, 10:2, 12:2, and 14:2 FTS) and ΣpreFOS (EtFOSAA, MeFOSAA, FOSAA, ETFOSE, ETFOSA, MeFOSA, FOSA), however significantly lower concentrations ($p<0.05$) compared to the factory area were only detected for areas L5 and L6 (ΣFTS) and L6 (ΣpreFOS). For distribution profiles in sediments, the same clear decrease in precursors with distance from the factory as shown for concentrations was not reported (see Figure 22B). Nevertheless, the percentage of preFOS as compared to ΣPFAS 29 at area L1 was significantly higher ($p<0.05$) compared to areas L3, L4, L5, and L6, and the percentage of FTS was significantly lower ($p<0.05$) at area L6 compared to the factory area and all the other

sampling areas in the lake. Therefore, sediment concentrations decreased with distance from the factory and the lowest percentages of PFAA precursors (FTS and preFOS) were generally observed furthest from the factory. This finding will be discussed further below in the context of PFAS concentrations and profiles in biota.

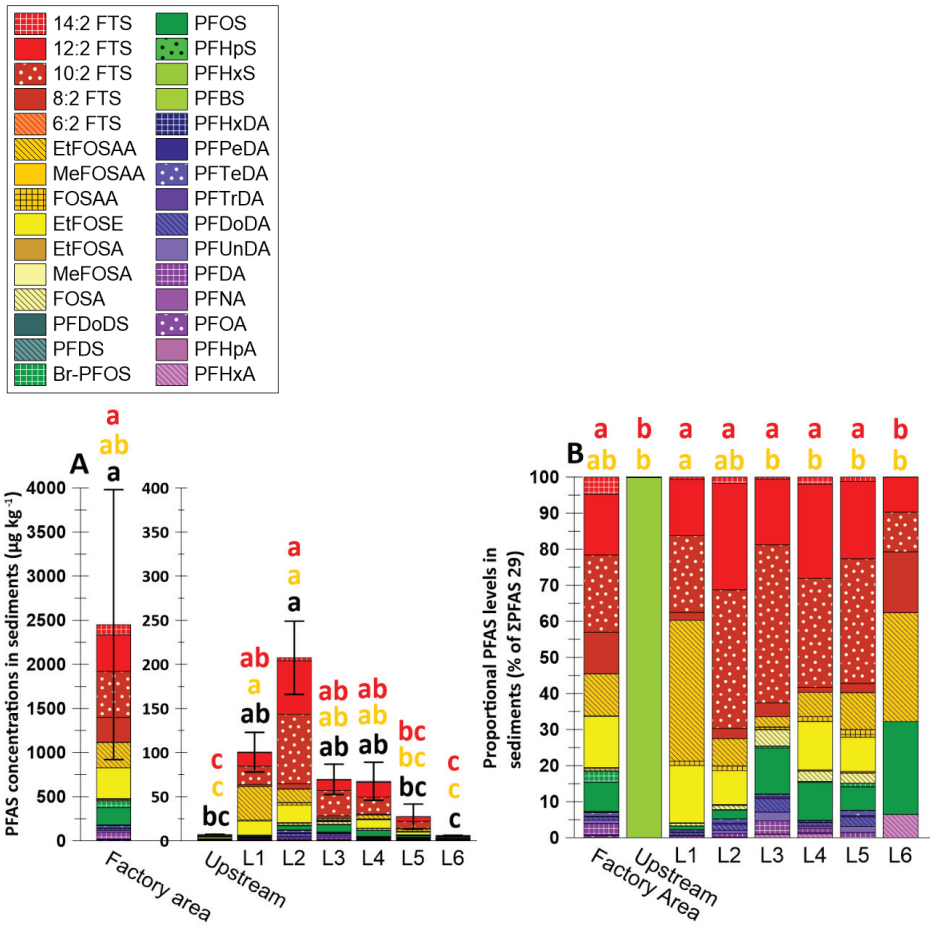

Figure 22. Average PFAS concentrations (d.w.) (A) and distribution profiles (B) in sediments at the different sampling areas in lake Tyrifjorden and the upstream river (n=2-25). Note that in A, the scale on the y axis is different between the sampling locations. Distribution profiles are given as relative concentrations (of ΣPFAS 29). Only compounds detected above the LOQ in at least one sample are included in the data analysis. In samples where compounds were not present above the LOQ, concentrations are taken as half the LOQ for plot A. For the distribution profiles in B, concentrations below the LOQ are treated as 0. For plot A, the different letters denote significant differences in ΣPFAS 29 (bottom, black letters), ΣpreFOS (mid, yellow letters) or ΣFTS (top, red letters), $p<0.05$, (Kruskal-Wallis and Bonferroni correction). For plot B the different letters denote significant differences in percentage preFOS (bottom, yellow letters) or percentage FTS (top, red letters), $p<0.05$, (Kruskal-Wallis and Bonferroni correction). From Paper II.

The mean ΣPFAS 21 in perch liver was 667 µg kg^{-1} at the factory area, 168 µg kg^{-1} at the fire station, and between 181 and 458 µg kg^{-1} in lake Tyrifjorden (sampling areas L1 and L3, respectively), shown in Figure 23A. Compared to the factory area, perch liver ΣPFAS

21 concentrations were significantly lower ($p<0.05$) at sampling areas fire station, L1, and L6. Concentrations of ΣpreFOS and ΣFTS generally decreased with distance from the factory area. ΣpreFOS concentrations were significantly lower ($p<0.05$) at sampling areas fire station, L3, L5, and L6, compared to the factory area, while ΣFTS concentrations were significantly lower ($p<0.05$) in perch livers from sampling areas L3, L5, and L6 compared to the factory area. In addition, ΣpreFOS concentrations were significantly lower at area L6 compared to areas L1 and L3, and ΣFTS concentrations were significantly lower at area L6 compared to areas fire station, L1, and L5. For distribution profiles (Figure 23B), significant lower ($p<0.05$) percentages compared to the factory area were reported for both ΣpreFOS and ΣFTS at areas L3, L5, and L6. In addition, percentages of ΣpreFOS and ΣFTS were significantly lower ($p<0.05$) in several areas further from the factory compared areas closer to the factory, shown in Figure 23B. Thus, ΣpreFOS and ΣFTS concentrations and proportions in perch livers generally decreased with distance from the factory.

The decreasing concentrations and proportions of FTS and preFOS in sediments and biota with distance from the factory likely indicate more complete transformation of these compounds with distance from the source (preFOS to PFOS and FTS to PFCA (Armitage *et al.*, 2009; Paul *et al.*, 2009; Wang *et al.*, 2011; Simonnet-Laprade *et al.*, 2019)). Supporting this was the observed decrease in concentrations of EOF in fish livers in lake Tyrifjorden with distance from the factory, as well as the increase in the sum of organic fluorine in the targeted PFAS as a percentage of EOF in fish livers, as shown in Figure 24. This likely indicates decreasing proportions of unknown precursor compounds (and unknown intermediate transformation products) with distance from the factory due to a more complete transformation of precursors into targeted compounds. However, as EOF was analysed in only a few samples, more samples are needed to evaluate this finding.

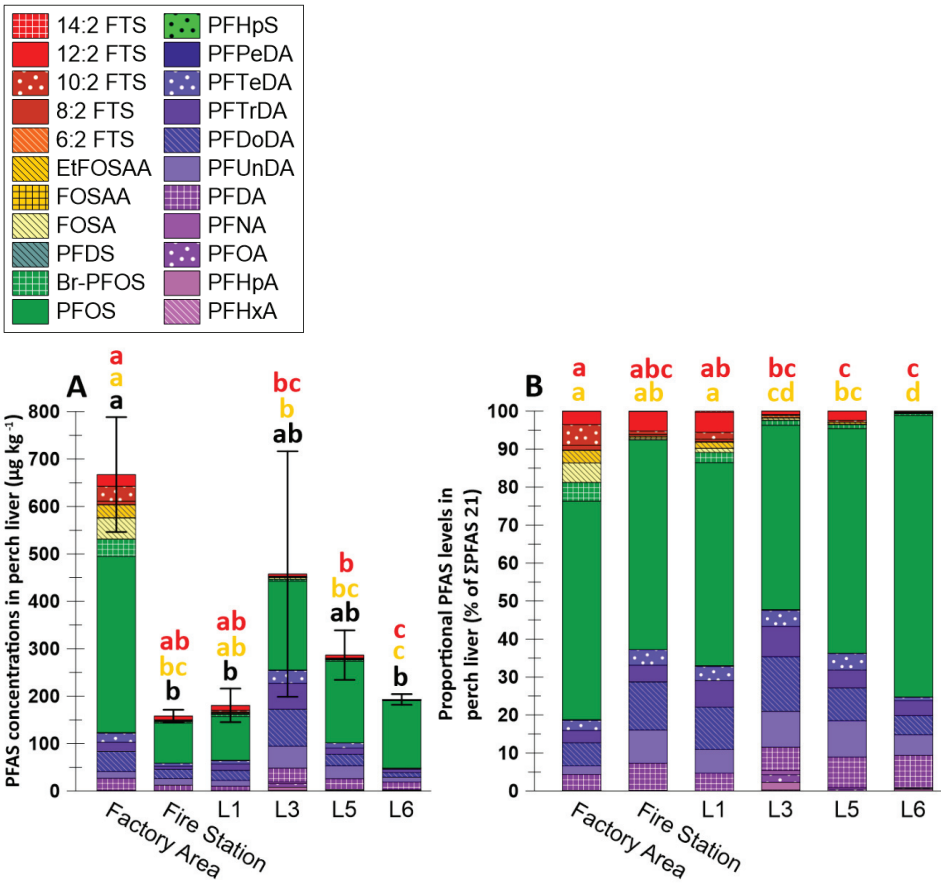

Figure 23. Average PFAS concentrations (w.w.) (A) and distribution profiles (B) in perch livers at the different sampling areas (n=2-5, shown in Table S2). Distribution profiles are given as relative concentrations (of ΣPFAS 21). Only compounds detected above the LOQ in at least one sample are included. For concentrations (A), values below the LOQ are treated as half the LOQ. For distribution profiles (B), values below the LOQ are treated as 0. For plot A, the different letters denote significant differences in ΣPFAS 21 (bottom, black letters), ΣpreFOS (mid, yellow letters) or ΣFTS (top, red letters), $p<0.05$, (Kruskal-Wallis and Bonferroni correction). For plot B the different letters denote significant differences in percentage preFOS (bottom, yellow letters) or percentage FTS (top, red letters), $p<0.05$, (Kruskal-Wallis and Bonferroni correction). From Paper II.

Very few other studies have explored potential gradients of precursor degradation with distance from point sources. Spaan et al. (2020) reported that 7:3 FTCA accounted for a large fraction of the ΣPFAS 36 (64 and 71% in harbor seal and harbor purpoise, respectively), and that a lower percentage of EOF was accounted for in animals sampled from the US Atlantic coast compared to animals sampled in other locations (coasts of

Greenland, Iceland, and Sweden). The authors implied that there are likely more PFAS sources in the US, close to the US Atlantic coast, compared to the other locations. Thus, it was suggested that animals sampled from the US Atlantic coast were located in closer proximity to the source(s) of the unidentified organofluorine, possibly including 7:3 FTCA precursors such as FTOH-based substances (Spaan *et al.*, 2020). 7:3 FTCA is relatively persistent in biota, but is reported to be biotransformed to degradation products, including the terminal end product PFHpA (Butt *et al.*, 2010). Thus, although the study by Spaan et al. (2020) covers much larger geographic distances compared to the papers in this thesis, it indicates similar processes: as precursors travel further from the point source, they are transformed to intermediate and terminal degradation products, and this process takes time.

Conclusion to hypothesis 3a

Results from the work carried out in Bodø and lake Tyrifjorden support hypothesis 3a: PFAS mixtures detected at distances further from point source releases represent older releases composed of smaller fractions of precursors due to more complete transformation to terminal degradation products.

Over time, precursor compounds in the environment are expected to be increasingly transformed to intermediate and terminal degradation products, both due to abiotic transformation and by biotransformation. As the distance between a point source and compounds released from that source (and subjected to environmental transport), in many cases is expected to increase over time, the percentage of precursors (as a percentage of the total sum PFAS) is expected to decrease with distance. The polyfluorinated compounds focused on in this thesis (especially preFOS, SAmPAP, and FTS) are expected to be transformed to PFSA or PFCA, and the percentage of these compounds (as a percentage of the total sum PFAS) were observed to increase with distance from the point sources, supporting the hypothesis. However, there are few previously reported peer reviewed publications that focus on the spatial distribution of degradation products compared to precursors (or estimates of the total environmental concentrations such as EOF) for PFAS pollution from point sources. Therefore, more research is needed to explore this.

Target chemical analyses of a limited number of compounds combined with methods for estimating total environmental PFAS can be used to evaluate potential transformation of unknown PFAS to targeted PFAS

The large number of environmentally relevant PFAS makes it practically impossible to routinely target each individual compound. Therefore, methods for estimating the total environmental PFAS or organofluorine have been developed (McDonough *et al.*, 2019). Such methods include measurements of EOF where the total extractable organic fluorine in a sample is measured and compared to the sum fluorine from compounds detected using targeted analyses, and the TOP assay where a sample is oxidized by an excess of hydroxyl radicals and the concentrations of specific PFAS before and after oxidation are

compared (McDonough *et al.*, 2019). However, these methods do not give information on bioavailability, biotransformation pathways, or the potential for biotransformation (of known and unknown compounds) under site-specific conditions. As such, supplementary strategies are needed to evaluate a PFAS contaminated site.

In **Paper III** (lake Tyrifjorden), the sum of organic fluorine in the targeted PFAS as a percentage of EOF in fish livers were reported to increase with distance from the factory, shown in Figure 24. For the perch liver sampled furthest from the source (area L6), the targeted analyses accounted for 108% of the EOF and the mass balance was considered complete. This indicates that the majority of the bioavailable and bioaccumulative fractions of the environmental PFAS mixture in lake Tyrifjorden has the potential to be transformed into the terminal PFCA and PFSA given the environmental conditions (as all the quantified PFAS are PFCA, PFSA, or precursors to these two groups).

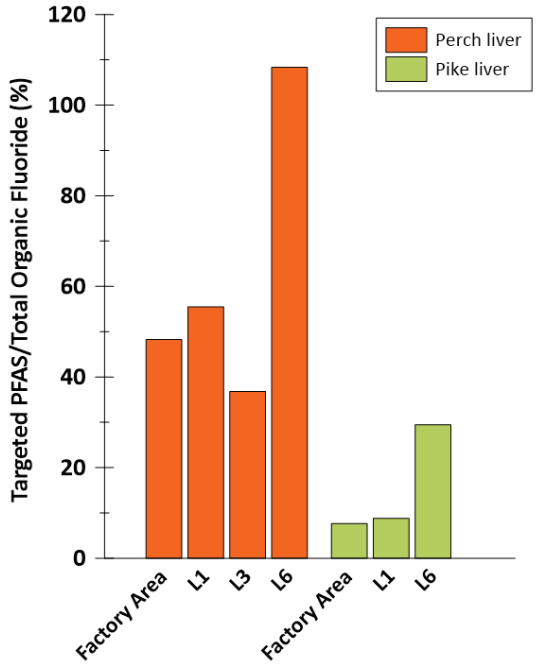

Figure 24. Sum organic fluorine in the targeted PFAS as a percentage of fluorine determined in the extractable organic fluorine (EOF) analysis (n=1).

The work performed in lake Tyrifjorden supports the notion that methods for estimating bulk environmental PFAS (such as EOF or TOP assay) and targeted analyses in samples representing a (relatively) large spatial distribution and/or different levels in the food chain can provide information about (bio)transformation, and therefore be used to characterize PFAS point sources. However, the increasing percentage of EOF accounted for by the sum of targeted analyses with distance from the source reported for lake Tyrifjorden in **Paper III** is based on a limited number of samples, and additional studies are needed in order to verify the results. Further, different physicochemical properties for different PFAS (resulting in differences in environmental transport) can be a confounding factor when using spatial distribution to evaluate transformation over time. As the approach used in lake Tyrifjorden assumes environmental transformation over time, it is only suitable to assess point sources in which the PFAS mixture in question was first released a sufficiently long time ago. Uncertainties related to the methods, including possible organofluorine compounds other than PFAS that are detected using EOF (Spaan *et al.*, 2020), and potential transformation products other than the targeted PFAS for the TOP assay (Houtz and Sedlak, 2012; Harding-Marjanovic *et al.*, 2015), need to be addressed in future studies. One step forward to address this knowledge gap would be to compare different methods for estimating bulk environmental PFAS when applied to the same samples.

Conclusion to hypothesis 3b

The results from the work in lake Tyrifjorden support hypothesis 3b: Targeted chemical analyses of a limited number of compounds in biota from different trophic levels and abiotic media with varying distance from the source can be used to evaluate potential transformation of unknown PFAS to targeted PFAS. The use of methods to estimate bulk environmental PFAS can complement the targeted analyses to give information about quantity and final degradation products of the unaccounted PFAS.

Combined, methods for estimating bulk environmental PFAS and targeted analyses that provide information about (bio)transformation can be used to characterise PFAS point sources. This is a valuable tool that has a role in future PFAS work. However, more studies are needed to explore the usefulness of such approaches for specific cases.

CONCLUSIONS

The results in this thesis provide novel information about PFAS contaminated sites which can be used in future site investigations, monitoring campaigns, risk assessments, site management, and when designing remediation strategies.

The overall objective of this thesis was to investigate how differences in PFAS mixtures released from different point sources (and hence products) can affect fate and transport, in the aquatic environment. The difference in PFAS formulation depending on the year of production was also taken into consideration. In addition, a subsequent objective was to identify optimal approaches for investigations of PFAS contaminated sites. A sound understanding of a polluted site is vital when risk assessments and site remediation strategies are selected. Results from this work support the hypotheses as described below.

Addressing hypothesis 1a:

> The emitted PFAS mixture differs depending on the source. This results in different composition of PFAS (i.e., profiles) in environmental samples depending on which source(s) they are affected by.

Addressing hypothesis 1b:

> The different PFAS profiles in environmental samples depending on source(s) can be used to identify sources of the pollution. Different partitioning and environmental fractionation between different PFAS and isomers must be taken into consideration, including species-specific differences and differences between tissues in accumulation potential.

Addressing hypothesis 2a:

(Bio)transformation can change the physiochemical properties of a compound, and thus its partitioning and exposure route. (Bio)transformation of precursor compounds with different physiochemical properties can be a major factor that controls concentrations of intermediate and terminal degradation products. For this reason, precursors are important to consider when assessing environmental concentrations of persistent end products such as PFCA and PFSA. Further, species-specific accumulation occurs, depending on the specific PFAS, resulting in species-specific PFAS profiles and concentrations. Therefore, without detailed knowledge of the composition of the PFAS mixture released from the source at a specific site, and the behaviour of the dominant PFAS in the relevant species, PFAS burdens in biota cannot necessarily be estimated with sufficient accuracy based solely on concentrations in water or sediments.

Addressing hypothesis 2b:

Differences in environmental distribution between different PFAS, as well as differences in bioaccumulation between species, and contributions from (bio)transformation of precursor compounds to the observed concentrations are reported in this thesis. Therefore, investigating biota that represent different habitats, diets (including trophic levels), physiology, and phylogenetic groups (e.g., vertebrates and invertebrates) will increase the likelihood of identifying those species that accumulate the highest concentrations of the emitted PFAS. Thus, when the environmental behaviour of the relevant PFAS, or the PFAS mixture used at the source is unknown, several species as well as abiotic media should be investigated to assess the environmental PFAS mixture.

Addressing hypothesis 3a:

In the present thesis, the percentage of precursors (as a percentage of the total sum PFAS) is reported to decrease with distance from the PFAS source. Over time, precursor compounds in the environment are generally expected to transform to intermediate and terminal degradation products to a greater extent. As the distance between a point source and compounds released from that source (and subjected to environmental transport), is expected to increase over time in many cases, the percentage of precursors is expected to decrease with distance.

Addressing hypothesis 3b:

Characterising the total environmental PFAS mixture by identifying the most important environmental compartments for partitioning, and the major terminal degradation products is a promising strategy for the investigation of PFAS point sources. However, further studies are needed to explore how this strategy performs.

RECOMMENDATIONS FOR SITE INVESTIGATIONS

A subsequent objective of this thesis was to identify optimal ways in which PFAS contaminated site investigations can be carried out. A number of aspects have been investigated, and a summary of the most important findings for site investigations performed during this study are summarised in the following.

Source identification is important in cases where high concentrations are detected at sites where there is no known point source, or there are several suspected sources. PFAS profiles in environmental samples differ depending on the type of source and can therefore in many cases be used to identify the source(s) of the pollution. Different partitioning and environmental fractionation between different PFAS and PFAS isomers must be taken into consideration, as well as species-specific differences and differences between tissues in accumulation and biotransformation potential.

PFAS burdens in biota cannot necessarily be estimated with sufficient accuracy based solely on concentrations in water or sediments. This is due to factors such as differences in exposure pathways depending on the PFAS mixture emitted from a source (e.g. due to different physiochemical properties between PFAS and contribution from transformation of precursors) and differences in diet, as well as possible differences in biotransformation and depuration capacities, between different organisms. Thus, when the environmental behaviour of the relevant PFAS, or the PFAS mixture used at the source is unknown, several species as well as abiotic media should be investigated in order to assess the environmental PFAS mixture and to identify the most important environmental compartments for partitioning.

The spatial distribution of contaminants originating from a point source (and subjected to environmental transport) is expected to increase over time in many cases. As precursors in the environment are expected to be transformed over time, the percentage of precursors is expected to decrease with distance. Therefore, including a spatial dimension in a sampling program should be considered to evaluate the fate of the emitted PFAS mixture.

The combined approach of including a spatial dimension in the sampling regime and applying both targeted analyses of key PFAS as well as approaches to quantify the total PFAS mixture, deserves attention as it is a promising approach for evaluating environmental transport and the major degradation products (specific for the site).

FURTHER KNOWLEDGE NEEDS

Of the case study sites described in this thesis, lake Tyrifjorden is the one that most clearly warrants further investigation. The production of PFAS coated paper products is a novel and largely unexplored PFAS source. Considering the extensive use of disposable paper products and hence production, such industry is likely to represent significant point sources elsewhere. The dated sediment core proved valuable for exploring historic PFAS emissions at the site. Therefore, several similar cores should be sampled from different parts of the lake, as well as in the river downstream. This would provide information to further explore the extent of the pollution and emission amounts.

Due to the dominance of precursor compounds to PFAA, the fate and transport reported for PFAS from the paper industry in lake Tyrifjorden differed compared to more well-investigated point sources, such as the use of AFFF. A sound understanding of the fate and transport of the pollutants at a site is necessary for performing satisfactory risk assessments and for evaluating potential remediation measures. Thus, the biotransformation potential of the total PFAS mixture, as well as individual key precursor compounds, in sediments should be explored further. Laboratory studies on PFAA and their precursors in sediments, including biotransformation, would be valuable for obtaining a detailed mechanistic understanding. Further, laboratory studies exploring uptake of PFAA precursors from sediments into the food chain and the effect on TMF should also be conducted. Together, these investigations will provide further information about the importance of paper production as a source of PFAA, which is important for future site characterizations.

Most work on potential health effects of elevated exposure to PFAS has focused on PFAA such as PFOS and PFOA. Potential risks for human health and the environment, posed by the precursors before biotransformation has received less attention. Some precursors or intermediate products have been reported to have long elimination half-lives (e.g. 5:3 PFCA, (Kabadi *et al.*, 2020)), or to be more toxic than PFAA (e.g. different length fluorotelomer carboxylic acids (Phillips *et al.*, 2007), or chlorinated polyfluorinated ether

sulfonic acids (Mi *et al.*, 2020)). Therefore, potential toxicity of PFAA precursors before biotransformation into PFAA is an aspect that warrants future investigation.

Most studies on PFAS contamination have applied targeted analyses of a few selected PFAS. This thesis provides a strategy for characterising the total environmental PFAS mixture at PFAS hot spots by combining targeted analyses with the use of methods for quantifying the total PFAS mixture in samples (e.g. EOF and TOP assay). The strategy was used for samples considered to represent different degrees of (bio)transformation. However, as there are uncertainties related to how methods for quantifying the total PFAS mixture perform (e.g. effect of organic fluorine from other substances than PFAS for EOF, or quantity of PFAS not detected by the TOP assay), investigations that compare these methods would be valuable. In order to interpret contamination levels at PFAS polluted sites using results from methods for quantifying the total PFAS, investigations of total PFAS concentrations in different media at different hot spots, as well as in the environment at areas not directly affected by point sources, are needed to establish relevant reference data for comparison.

This work demonstrated the use of spatial distribution to characterize fate and transport properties of the released PFAS mixture. As there are few previous peer reviewed publications on the spatial distribution of precursors and degradation products from point source releases, there is little basis for comparison. Therefore, more studies are needed to evaluate and explore both transformation of precursors with distance from point sources, and environmental fractionation as a result of differing partition between substances due to different physiochemical properties. For example, PFOS isomer profiles in pore water, perch livers, and pike livers in lake Tyrifjorden showed a clear trend (increasing percentages of L-PFOS) with distance from the point source (the factory). This was attributed to the different physiochemical properties between different PFOS isomers (and possibly also due to different biotransformation rates between preFOS isomers) and suggested as a source tracking tool. However, as this study is one of the first to report this pattern, it should be investigated at other sites (e.g. evaluate under which conditions the observed patterns can be reproduced).

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APPENDIX

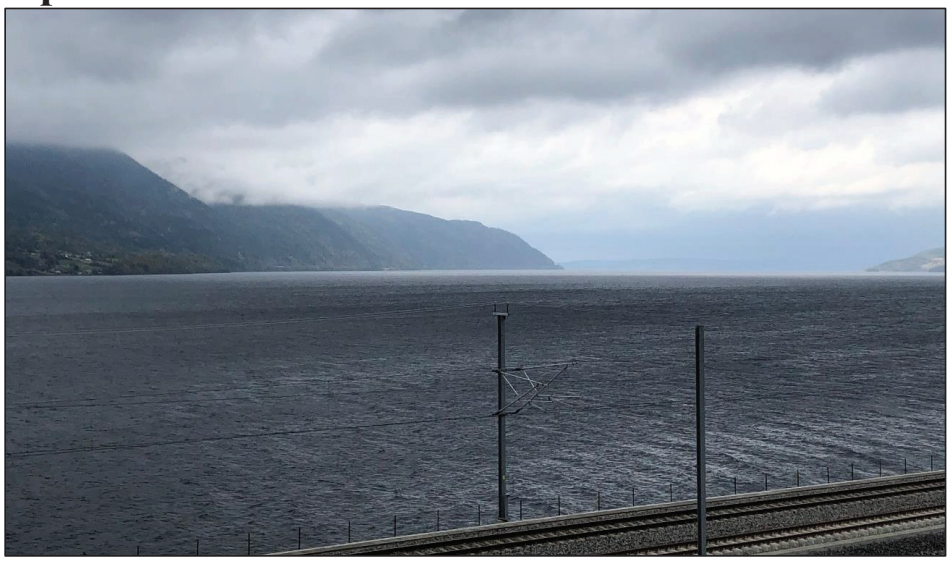
Table of contents

Doctoral theses in Biology, Norwegian University of Science and Technology, Department of Biology

Appendix

Paper I

PFAS fingerprints in fish from Norwegian freshwater bodies subject to different source inputs



Lake Mjøsa. Photo: Morten Jartun

This paper is awaiting publication and is not included in NTNU Open

Paper II

Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: source and historic emission tracking

Lake Tyrifjorden. Photo: Håkon Austad Langberg

Appendix: Paper II

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Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking☆

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ABSTRACT

The entirety of the sediment bed in lake Tyrifjorden, Norway, is contaminated by per- and polyfluoroalkyl substances (PFAS). A factory producing paper products and a fire station were investigated as possible sources. Fire station emissions were dominated by the eight carbon perfluoroalkyl sulfonic acid (PFSA), perfluorooctanesulfonic acid (PFOS), from aqueous film forming foams. Factory emissions contained PFOS, PFOS precursors (preFOS and SAmPAP), long chained fluorotelomer sulfonates (FTS), and perfluoroalkyl carboxylic acids (PFCA). Concentrations and profiles in sediments and biota indicated that emissions originating from the factory were the main source of pollution in the lake, while no clear indication of fire station emissions was found. Ratios of linear-to branched-PFOS increased with distance from the factory, indicating that isomer profiles can be used to trace a point source. A dated sediment core contained higher concentrations in older sediments and indicated that two different PFAS products have been used at the factory, referred to here as Scotchban and FTS mixture. Modelling, based on the sediment concentrations, indicated that 42–189 tons Scotchban, and 2.4–15.6 tons FTS mixture, were emitted. Production of paper products may be a major PFAS point source, that has generally been overlooked. It is hypothesized that paper fibres released from such facilities are important vectors for PFAS transport in the aquatic environment.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals used in cosmetics, household products, medical devices, oil production, pesticides, aqueous film forming foams (AFFF), textiles and paper (Lindstrom et al., 2011; Wang et al., 2017b). Due to adverse environmental and human health effects (Knutsen et al., 2018; Lau et al., 2007; Stahl et al., 2011; Sunderland et al., 2019), PFAS have received attention from the scientific community and regulatory authorities (Directive 2013/39/EU, 2013; Norwegian Government, 2006; Prevedouros et al., 2006; Wang et al., 2017b). The highest PFAS concentrations have been reported for sites contaminated by point sources such as AFFF from firefighting training (Anderson et al., 2016; Filipovic et al., 2015; Hu et al., 2016; Moody and Field, 2000). However, PFAS are ubiquitous in the environment and are even found at remote pristine locations (Ellis et al., 2004; Gao et al., 2019; Houde et al., 2011; Lescord et al., 2015; Liu and Mejia Avendaño, 2013; Tomy et al., 2004). Different data and techniques have been used to characterize sources, emissions, and the spread of PFAS pollution (Dorrance et al., 2017), including fate and transport properties, chemical profiles (where PFAS

☆ This paper has been recommended for acceptance by Charles Wong.

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composition in different samples is compared), spatial distribution, and PFAS history (Dorrance et al., 2017; Hu et al., 2018; Shi et al., 2015; Trier et al., 2011; Zhang et al., 2016).

As will be presented, PFAS mixtures in the environment can potentially be back-tracked to production methods and possibly the application of specific products. Two methods have been used for large scale PFAS production: electrochemical fluorination (ECF) and telomerization. ECF generates a mixture of linear and branched isomers in addition to impurities of other fluorinated compounds (Prevedouros et al., 2006), while telomerization primarily produces linear isomers (Buck et al., 2011). ECF has been used to produce PFOS and perfluorooctanesulfonyl fluoride (POSF) based products (Benskin et al., 2010; Paul et al., 2009; Prevedouros et al., 2006). PFOS and POSF based chemicals were phased-out in some parts of the world in the 2000s (Butenhoff et al., 2006), and PFOS was listed as a persistent organic pollutant (POP) by the United Nations Environment Programme (UNEP) Stockholm Convention in 2009 (UNEP - The Stockholm Convention, 2019). As an example, the use of PFOS in AFFF was phased out between 2006 and 2011 in Norway (Norwegian Government, 2006). Fluorotelomer based PFAS, produced by telomerization, are of the substances that have been used as replacements (Field and Seow, 2017; Hoke et al., 2015; Moe et al., 2012; Place and Field, 2012; The Swedish Chemicals Agency (KEMI), 2015; Wang et al., 2015).

Several commercial PFAS mixtures produced by ECF have been identified that contain compounds that can (bio)transform to PFOS in the environment, including the N-alkyl substituted perfluorooctane sulfonamides ($F_{17}C_8-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-N-R$, R), for simplicity termed preFOS throughout this study, and their parent compounds such as the mono-, di-, and tri-substituted phosphate esters of N-ethyl perfluorooctane sulfonamido ethanol (referred to collectively as SAmPAP) (Armitage et al., 2009; Benskin et al., 2012a, 2012b; Lee and Mabury, 2011; Martin et al., 2010; Olsen et al., 2005; Paul et al., 2009). Due to the preferential biotransformation of branched precursor isomers, producing branched PFOS (Br-PFOS), observation of elevated ratios of Br-PFOS to linear PFOS (L-PFOS) has been suggested to indicate a major contribution from PFOS precursor compounds (Benskin et al., 2009b; Chen et al., 2015a; Peng et al., 2014; Ross et al., 2012). The ratio is therefore suggested to be a useful source tracking tool for precursor based sources (Benskin et al., 2009b; Gebbink et al., 2016). Br-PFOS has been reported to be more water soluble and have a lower depuration half-life in organisms compared to L-PFOS (Benskin et al., 2009a; Chen et al., 2015a; Zhang et al., 2013). This can increase the complexity of PFAS source tracking by leading to variations in branched to linear ratios (Martin et al., 2010).

Depending on the PFAS application and the industrial era, different mixtures of PFAS, with different chemical profiles, have been used (Trier et al., 2011; Wang et al., 2013; Zhang et al., 2016). These profiles can be used to track what mixtures were emitted, when one mixture was substituted for another, and provide information about current and historic sources (Land et al., 2018; Wang et al., 2017b; Xiao, 2017). For example, 6:2 fluorotelomer sulfonate (6:2 FTS), and other fluorinated telomer products with 6:2 configurations have been used as replacements for PFOS in AFFF (Hoke et al., 2015; Moe et al., 2012; Place and Field, 2012; The Swedish Chemicals Agency (KEMI), 2015; Wang et al., 2015). 6:2 FTS is a precursor of perfluoroalkyl carboxylic acids (PFCA) (Wang et al., 2011a), and the same is suspected to be the case for longer FTS (Simonnet-Laprade et al., 2019). Emission history, such as the shift from PFOS to 6:2 FTS in AFFF after the PFOS phase-out has previously been shown to be reflected in sediment cores (Lutz et al., 2009; Mussabek et al., 2019). Only the top 11 cm of sediments from Tokyo Bay, Japan, was found to contain 6:2 FTS which corresponds to sediments settling from 2002 (Lutz et al., 2009).

Langberg et al. (2020) have previously reported that the entirety of the sediment bed in lake Tyrifjorden, Norway, is polluted by hydrophobic precursors (preFOS, SAmPAP, FTS) of perfluorinated alkyl acids (PFAA), resulting in substantial sediments and biota concentrations in all areas of this 138 km^2 lake, whilst concentrations in water are generally near or below detection limits (sum of L-PFOS and Br-PFOS of 0.22−0.28 ng L^{-1} in lake water) (Langberg et al., 2020). The objective of the present study was therefore to identify and better characterize the source of this pollution, as well as estimate the historic input of PFAS to the lake system. The two major likely point sources were a fire station where AFFF was used, and a factory producing PFAS coated disposable paper products. The present study builds on the work presented in Langberg et al. (2020), however as the objective differs from the previous study, data were interpreted using a different approach. In addition, water and sediments from the storm water system at the fire station, water and sediments sampled downstream a landfill filled with waste from the factory, a product from the factory (paper plate), sediment and fish samples from the river directly downstream to the fire station, and a dated sediment core from the lake were included in the present work. The present study uses source tracking methods (spatial distribution, PFOS isomer patterns and sediment core dating) to decipher which point source was responsible for the pollution. PFAS concentrations and profiles from the two source areas were compared to concentrations and profiles in river and lake sediments and water. Following the identification of the main source, a fate and transport model was employed to back-calculate historic emission volumes, to predict future sediment concentrations, and to draw hypotheses related to possible mechanisms that can explain the spreading of PFAS in the lake. This work is the first to use source tracking methods to positively identify the paper production industry as a major PFAS hot spot source and to estimate emission volumes and transport mechanisms from such industrial activity based on an environmental record.

2. Materials and methods

2.1. Case study site and sampling

Lake Tyrifjorden (60.03° N, 10.17° E), Norway is a freshwater lake with a surface area of 138 km^2 and a maximum depth of 288 m. Further details are given in the section *Site description - Lake Tyrifjorden* in the supplemental information (SI). In 2015, elevated PFOS concentrations (mean 183 ± 25 μg kg^{-1}, n = 5) were reported in perch livers (*Perca fluviatilis*) from the lake (sampled close to area L3 in the present study, see the description below) (Fjeld et al., 2016). Follow-up investigations identified two suspected major PFAS sources to the lake: a fire station that opened in the 1980s and used AFFF until 2007, and a shutdown factory that produced paper products from 1964 to 2013 (Slinde and Høisæter, 2017). The fire station and factory are located on the banks of a river flowing into the lake, with the fire station located 11 km upstream from the river mouth, and the factory a further 15 km upstream (Fig. S1 in the SI which shows all sampling locations). To simplify the presentation of data, the entire lake was divided into 6 regions: L1 to L6. L1 is the region closest to the river mouth and L4 to L6 the furthest away. L5 is connected to the outflow of the lake (Fig. S1). The sampling area in the river downstream the factory was termed the factory area. Sampling procedures are described briefly below and more information and details of quality assurance procedures, including sample storage and limit of quantifications (LOQ), are provided in the sections *Sampling and sample preparation* and *Quality assurance*

and sample storage in the SI.

2.2. Abiotic samples

Access to the factory itself was not possible so water and sediments were sampled in November 2018 from a creek located downstream a landfill used by the factory during the late 1980s to the 1990s (Fig. S1). The landfill is now closed. These samples were used to represent the PFAS emission profile of the factory. In addition, a paper plate produced at the factory in 2007 was analysed to determine the PFAS mixture used at that time. At the fire station, water was sampled (n = 2) from intermediate bulk containers and sediments were sampled (n = 2) from containers during cleaning of the storm water system (more information is given in the SI section *Sampling and sample preparation*). Downstream from the landfill, water (n = 1) and sediments (n = 1) were sampled from the creek. Water was sampled by submerging sample-rinsed high-density polyethylene (HDPE) bottles (1 L) directly in the water source. Sediments were sampled using a metal tube attached to a telescopic pole.

River and lake sediments were sampled from two locations upstream from the factory, nine locations in the river downstream the factory, four locations downstream the fire station, and 94 locations in the lake (shown in Fig. S3 and Table S1). Sediments were sampled with either a van Veen sampler or a Kajak-Brinkhurst sediment corer where the top two cm was carefully sampled if visually undisturbed. Sediment samples were transferred into prebaked glass jars with HDPE lids. One core from sampling area L1 was divided in one cm intervals for determination of the vertical PFAS distribution profile and dating of sediments. Sediment traps (plexiglass, 10 cm internal diameter) were used to investigate PFAS concentrations in present day settling sediments (details in the *section Sampling and sample preparation* in the SI). Sediment in the river close to the factory were sampled in August 2018. Lake and river (downstream the fire station) sediment and pore water were sampled in September 2018. Abiotic samples were kept in insulated boxes and brought to the laboratory within 24 h of sampling. The samples were kept in the refrigerator (dark, at 4 °C) until analyses.

2.3. Biota

Fish (perch [*Perca fluviatilis*] and pike [*Esox lucius*]) were collected in the period June–October 2018 using fish nets (35–39 mm mesh size). Sampled biota varied between areas (n = 2–5), shown in Table S2. Whole organisms were carefully wrapped in three layers of clean aluminium foil and put in a clean plastic bag (polyethylene), before being frozen at −20 °C. Frozen biota samples were sent to the laboratory (in sealed, insulated boxes) for sample treatment and analysis.

2.4. Laboratory methods

The analytical methods to quantify extractable organic fluorine (EOF), pore water concentrations, and total organic carbon (TOC) are described fully in the SI section *Laboratory methods*. The sediment core from sampling area L1 was dated using unsupported ^{210}Pb, analysed via gamma spectrometry (details in the section *Laboratory methods* in the SI). Water was extracted using solid-phase extraction (SPE). Biota (fish livers) and sediment were extracted using acetonitrile and ultrasonication. Liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS) was used for PFAS analyses (see all PFAS and acronyms in Tables S3 and S4). Authentic standards (i.e. a standard identical to the targeted substance) and internal standards were used to quantify 44 PFAS, while exact mass and retention time from authentic standards were used to screen for 19 PFAS. In addition to this, peaks for Br-PFOS were identified (confirmed) using a standard mixture of Br-PFOS isomers. As the standards for the Br-PFOS isomers were in the form of a mixture, they could not be used for quantification purposes. Therefore, the standard for L-PFOS was used to quantify the peaks in the chromatogram which were made up of the different Br-PFOS isomers, and the sum of all the Br-PFOS isomers was reported. By using exact mass and estimated retention time, an additional 28 PFAS were screened for. Peaks in the chromatograms were observed at expected retention times for three substances, and these were quantified using the standard for a structurally similar compound (details in the section *Laboratory methods* in the SI). According to the literature, the detected compounds indicated the use of an EtFOSE based PFAS product, and therefore likely that SAmPAPs were one of the parent compound groups (Martin et al., 2010; Trier et al., 2017). The analytical range for most samples (m/z: 150–1100) did not include SAmPAP diester (m/z: 1203) and SAmPAP diester could therefore not be looked for in most samples. However, SAmPAP diester was analysed in the sediment core and the sediment sample used for EOF, described in the SI section *Laboratory methods* (PFAS names, acronyms and more details are given in Table S3).

2.5. Quality assurance

Lab blanks were run following the same procedures as for field samples in each analysis batch. As the whole lake is polluted by PFAS (see Fig. S3), the use of a reference site in the lake system was not possible. Concentrations in the blank samples were low (<0.5 ng g^{-1} or ng L^{-1}) and consistent, indicating little cross contamination. Blank concentrations were subtracted from results when calculating sample concentrations. Recoveries in the present work were satisfactory (within the range of 70–110%, see Table S3). A random sample was selected from each matrix for duplicate analysis to control for repeatability.

2.6. Data handling and statistics

Arithmetic means and the standard error of the mean (SEM) are reported. Differences in PFAS concentrations and profiles for fish livers, sediments, and pore water at the different areas were tested using Kruskal-Wallis and Bonferroni correction. The significance level was set to 0.05. PFAS profiles in sediments and the paper product were compared using principal component analysis (PCA). Details related to the statistical analyses are in the section *Statistics and data analysis* in the SI.

2.7. Modelling

A fate and transport model of PFAS entering the lake was employed based on the previously reported Drammensfjord model (Arp et al., 2014). In principle, this model could be used for any lake/fjord or contaminant, provided the necessary input data is available (Arp et al., 2014; Oen and Arp, 2014). The model is a two-box water-sediment model that allows for changes in emissions of a pollutant within specified time-intervals following a first-order rate constant. The water domain describes all transport and transformation processes in the water phase over the entire lake, the sediment domain describes all transport and transformation processes in the sediment phase, including deep sediment burial (Fig. S6). These domains are modelled following coupled linear differential equations (Schwarzenbach et al., 2003) to account for the interdependency of sediment and water processes. Details are provided in the SI section *Modeling*.

3. Results and discussion

3.1. Lines of evidence for source tracking

3.1.1. Differences in PFAS profiles in samples

Concentrations and profiles of targeted PFAS in the water and sediment samples from the two suspected sources (fire station and paper production) varied (Fig. S7, concentrations in Tables S9–S10).

Water from the storm water system at the fire station was dominated by C5–C8 PFCA and perfluoroalkyl sulfonic acids (PFSA), while sediments were dominated by PFOS in addition to perfluorohexane sulfonic acid (PFHxS), FOSA, and 6:2 FTS. Relatively minor levels of C9 and C10 PFSA and PFCA, other preFOS compounds (FOSAA, EtFOSAA) and 8:2 FTS were detected, likely reflecting impurities, or that small amounts of different AFFF products have been used. PFAS profiles in fire station storm water and sediments are consistent with profiles previously reported for AFFF impacted areas (Backe et al., 2013; Dauchy et al., 2017; Filipovic et al., 2015; Langberg et al., 2019; Prevedouros et al., 2006).

Water from the creek downstream the factory landfill was dominated by PFOA, PFOS and EtFOSAA as well as a smaller proportion of C5–C7 and C9 PFCA, FOSA, and FOSAA. Sediment samples from the creek were dominated by 8:2 FTS and 10:2 FTS, smaller fractions of EtFOSAA and 12:2 FTS, in addition to some 14:2 FTS, FOSAA, EtFOSE, and PFOS. The paper plate was dominated by C6–C10 PFCA with smaller proportions of C12–C14 PFCA, 8:2 FTS, and 10:2 FTS. PFAS profiles in water and sediments in the creek downstream the landfill show the compounds, or their degradation products, that were used in paper production since the 1970s (i.e. SAmPAP and preFOS) (Olsen et al., 2005; Trier et al., 2011, 2017). The creek drains into lake Tyrifjorden and as such is a source of PFAS to the lake. However, as the landfill was filled with waste from the factory it is considered to represent factory emissions. Further, the total amount of PFAS in lake sediments (tons, according to an extrapolation of concentrations in the sediment core discussed below and shown in Table 1) make it difficult to decipher a realistic estimate of the contributions from emissions via the creek to lake sediment concentrations. The national sum 28 PFAS emissions from Norwegian landfills have been estimated to be 0.017 tons per year (average per landfill was reported to be 0.00016 tons per year) (Knutsen et al., 2019). Similarly, other estimates of yearly PFAS emissions via landfill leachate (per landfill) are in ranges far below the volumes needed to account for the masses observed in lake Tyrifjorden sediments (Benskin et al., 2012b; Lang et al., 2017; Masoner et al., 2020). The profile in the paper plate from 2007, which did not contain PFOS above the LOQ, reflects that it is manufactured after the phase out of PFOS and related compounds (Butenhoff et al., 2006). The high percentages of PFCA and FTS might indicate that these substances were used as replacements at the time. The concentrations of PFCA in the paper plate were in the range of 6–7156 μg kg^{-1} (see Table S10), which is comparable to concentrations previously reported by (Xu et al., 2013). It is uncertain if the extraction method used (see description in the *Laboratory methods* section in the SI) extracted all the relevant PFAS (Schaider et al., 2017; Trier et al., 2011), however it is clear that large volumes of PFCA and FTS were used at the time. As a variety of different PFAS products have been used for paper products (Schaider et al., 2017; Trier et al., 2011), the analysed paper product does only represent a snapshot of the production at the factory. Nevertheless, the differences in PFAS profiles from the fire station and paper producing factory provide important source tracking information.

As previously reported, concentrations of targeted PFAS in river and lake water were low (i.e. the sum of L-PFOS and Br-PFOS in lake water was 0.22 and 0.28 ng L^{-1}) (Langberg et al., 2020). Thus, PFAS concentrations in lake water indicate limited ongoing emissions of PFAS to the lake.

Concentrations of targeted PFAS in sediments (dry weight; d.w.) sampled upstream the factory area were low and the only

Table 1
Model output for the two suspected PFAS products using three different log K_{OC} values.

			Scotchban[a]			FTS Mixture[b]		
			log K_{OC}			log K_{OC}		
			5	**7**	**9**	**5**	**7**	**9**
Total emission estimates to lake Tyrifjorden								
Emissions entering the lake		(tons)	189.0	42.2	41.6	15.6	2.5	2.4
Emissions leaving the lake		(tons)	154.0	0.8	0.4	13.7	0.07	0.04
Estimated mass in sediments		(tons)	34.5	41.3	41.2	1.9	2.4	2.4
Mass in sediments extrapolated from the sediment core		*(tons)*	*40.7*			*2.3*		
Predictions								
$C_{Lake,\ sed}$[c]	2017	(ng g^{-1})	11	41	31	104	102	100
	Measured 2018	*(ng g^{-1})*	*25*			*68*		
	2030	(ng g^{-1})	6	24	18	60	58	57
		(% reduction)	44	42	42	43	43	43
	2060	(ng g^{-1})	6	21	16	57	56	55
		(% reduction)	48	48	48	45	45	45
$C_{Lake,w\ (total)}$[d]	2017	(ng L^{-1})	4	0.3	0.1	36	0.8	0.5
	Measured 2018	*(ng L^{-1})*		*0.2*			*<LOQ*	
	2030	(ng L^{-1})	2×10^{-3}	2×10^{-4}	8×10^{-5}	2×10^{-2}	4×10^{-4}	3×10^{-4}
		(% reduction)	~100	~100	~100	~100	~100	~100
	2060	(ng L^{-1})	2×10^{-3}	2×10^{-4}	7×10^{-5}	2×10^{-2}	4×10^{-4}	2×10^{-4}
		(% reduction)	~100	~100	~100	~100	~100	~100

[a] Scotchban is considered sum of all SAmPAP diester, preFOS, PFSA, as well as PFCA (prior to 1990).
[b] FTS mixture is considered the sum of all FTS as well as PFCA (after 1990).
[c] Total sediment concentration i.e. sediment plus freely dissolved porewater (ng g^{-1}), and projected percentage reduction in top sediments in the future (2030 and 2060) compared to the concentration in 2017.
[d] Total water concentration i.e. freely dissolved phase plus particle/colloid bound (ng L^{-1}), and projected percentage reduction in water in the future (2030 and 2060) compared to the concentration in 2017.

substance above the LOQ was PFHxS (max 2.17 μg kg^{-1}). In contrast to this, elevated concentrations were found in sediments from the factory area and in the lake, as shown in Fig. 1A (all PFAS concentrations are listed in Table S11, sediment particle size distribution and TOC are shown in Table S12, and spatial distributions are shown in Figures S3 and S8-S11). The TOC content in river and lake sediments were between 0.3 and 4.5%. A thorough discussion of the effect of sediment characteristics on PFAS concentrations in sediments is provided in Langberg et al. (2020). The mean ΣPFAS 29 in river sediments from the factory area was 2450 μg kg^{-1}, and in lake sediments means ranged between 6.1 and 207 μg kg^{-1} (L6 and L2, respectively). As these areas collectively cover all main parts of the lake, it is clear that PFAS has been spread over the entire lake bed. Maximum concentrations of the dominating PFAS were 688–2150 μg kg^{-1} for C10–C16 FTS, 2455 μg kg^{-1} for EtFOSE, 1831 μg kg^{-1} for EtFOSAA, 1780 μg kg^{-1} for L-PFOS, 677 μg kg^{-1} for Br-PFOS, and 184–665 μg kg^{-1} for C10–C12 PFCA. PFAS profiles in sediments from the lake were dominated by the same compounds as from the factory area (especially FTS and preFOS), as shown in Fig. 1B. The ΣPFAS 29 concentration generally decreased with increasing distance from the factory area (significantly lower in area L5 [$p = 0.02$] and L6 [$p < 0.01$]) compared to the factory area. Concentrations in the sediments sampled in the river downstream the fire station were below the LOQ.

Concentrations of ΣFTS (6:2, 8:2, 10:2, 12:2, and 14:2 FTS) and ΣpreFOS (EtFOSAA, MeFOSAA, FOSAA, ETFOSE, ETFOSA, MeFOSA, FOSA) in sediments followed the same trend as for ΣPFAS 29 where they generally decreased amongst the different lake regions with increasing distance from the factory area, however significantly lower ΣFTS concentrations compared to the factory area were only detected for L5 and L6 (ΣFTS; $p = 0.03$ and $p < 0.01$, respectively) and for L6 for ΣpreFOS (ΣpreFOS; $p < 0.01$). PFAS profiles did not show the same clear pattern, however the percentage of FTS as compared to total PFAS was significantly lower ($p \leq 0.01$) at sampling area L6 compared to the factory area and all other sampling areas in the lake, and the percentage of preFOS at area L1 was significantly higher compared to areas L3 ($p = 0.02$), L4 ($p = 0.02$), and L6 ($p < 0.01$). Concentrations and profiles in the sediment traps in the river downstream both suspected sources and in the lake showed elevated concentrations of preFOS and FTS (Table S14). As previously reported (Langberg et al., 2020), concentrations in pore water were relatively high (the highest mean concentration of L-PFOS was 392.2 ng L^{-1} at area L4), and reflect the higher solubility of PFAA compared to their larger precursors, shown in Table S15.

The low concentrations in sediments upstream the factory indicate that there are no significant PFAS sources further upstream that contributed to the observed PFAS loads in the lake. High concentrations at the factory area and decreasing concentrations with increasing distance into the lake clearly indicate a significant contribution of the PFAS pollution from the factory. Based on this, the concentrations in the sediments outside the fire station that were below the LOQ are unexpected (as the fire station is downstream the factory). One possible explanation could be that the high river current in the area prevented PFAS polluted particles from settling and transported them further into the lake. All PFAS profiles from the sediment samples and the paper plate were compared using PCA (Fig. S13). Samples from the fire station storm water system were grouped separately based on their content of 6:2 FTS and PFSA, while sediments from the factory area, landfill (with waste from the factory), and the lake grouped together. The paper plate did not group with either one, however its PC 1 score (x-axis) was similar to the PC 1 scores for sediments from the factory area, landfill, and the lake. PFAS profiles in the sediments downstream the factory and the landfill are similar to profiles in the lake sediments. The same compounds, that is preFOS (and related compounds) and precursors to FTS (based on their structure, such as FTMAP, also termed S-diPAP), have been reported to be used in paper production (Trier et al., 2011, 2017). PFAS profiles in the sediment traps in the river downstream both suspected sources and in the lake, reflect the dominate compounds in lake sediments, indicating that present day settling sediments are contaminated by the same source as sediments in the lake bed. Therefore, it is concluded that emissions originating from the factory are the main source of PFAS contamination in lake sediments.

3.1.2. PFAS in biota

Concentrations of targeted PFAS for perch livers (wet weight; w.w.) are presented in Fig. 2. Data for the different stations for both perch and pike is shown in the SI (Tables S16–17). 21 PFAS (+Br-PFOS) were detected in perch liver. The same number of PFAS was detected in pike livers, however EtFOSA was detected in pike but not perch, while PFHpA was detected in perch but not pike. The concentrations for PFOS in perch livers at sampling area L3 (188 ± 85 μg kg^{-1}) were comparable to the concentrations reported

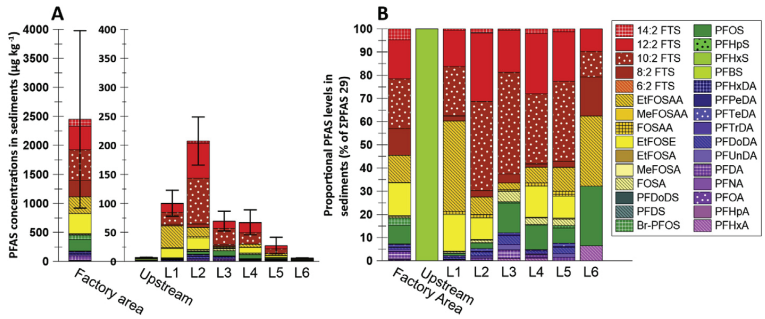

Fig. 1. Average PFAS concentrations (d.w.) (A) and distribution profiles (B) in sediments at the different regional stations (i.e. sampling areas) in the river and lake (n = 2–25, shown in Table S1). FTS (6:2, 8:2, 10:2, 12:2, and 14:2 FTS) are coloured red, preFOS (EtFOSAA, MeFOSAA, FOSAA, ETFOSE, ETFOSA, MeFOSA, FOSA) are yellow, PFSA are green, while PFCA are blue and purple. For concentrations, the scale on the y-axis are different for the factory area and the other sampling areas. Distribution profiles are given as relative concentrations (of ΣPFAS 29). Only compounds detected above the LOQ in at least one sample are included in the data analysis. In samples where compounds were not present above the LOQ, concentrations are taken as half the LOQ for plot A. For the distribution profiles in B, concentrations below the LOQ are treated as 0. Statistically significant differences between areas are shown in Fig. S12. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

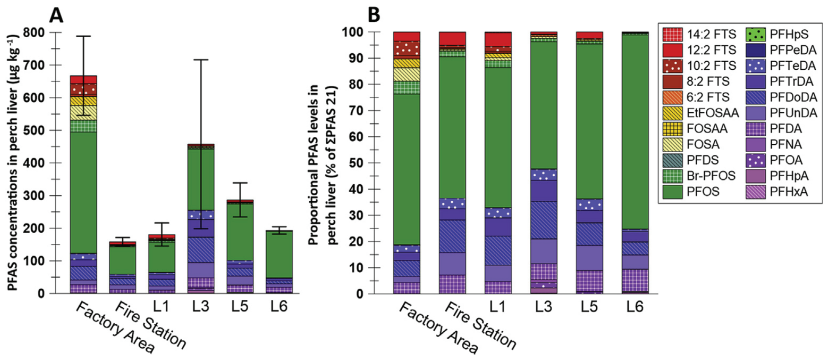

Fig. 2. Average PFAS concentrations (w.w.) (A) and distribution profiles (B) in perch livers at the different sampling areas (n = 2–5, shown in Table S2). FTS (6:2, 8:2, 10:2, 12:2, and 14:2 FTS) are coloured red, preFOS (EtFOSAA, FOSAA, FOSA) are yellow, PFSA are green, while PFCA are blue and purple. Distribution profiles are given as relative concentrations (of ΣPFAS 21). Only compounds detected above the LOQ in at least one sample are included. For concentrations (A), values below the LOQ are treated as half the LOQ. For distribution profiles (B), values below the LOQ are treated as 0. Statistically significant differences between areas are shown in Fig. S14. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

in the study in 2015 (183 ± 25 µg kg^{-1}) (Fjeld et al., 2016). The highest PFAS concentrations were generally found in fish from the factory area, similar to the sediment results. Maximum concentrations of the dominating PFAS in the perch livers from the factory area were 25–96 µg kg^{-1} for C10–C14 PFCA, 640 µg kg^{-1} for L-PFOS, 88 µg kg^{-1} for Br-PFOS, 195 µg kg^{-1} for FOSA, 64 µg kg^{-1} for EtFOSAA, and 14–56 µg kg^{-1} for C10–C14 FTS. Mean ΣPFAS 21 in perch liver was 667 µg kg^{-1} at the factory area, 158 µg kg^{-1} at the fire station, 181 µg kg^{-1} at L1, 458 µg kg^{-1} at L3, 287 µg kg^{-1} at L5, and 193 µg kg^{-1} at L6. Perch liver ΣPFAS 21 concentrations were significantly lower at the fire station ($p = 0.03$), L1 ($p = 0.02$), and L6 ($p = 0.03$), compared to the factory area, shown in Fig. 2A. Similar trends were observed for pike livers (Table S17).

Concentrations of ΣFTS and ΣpreFOS as well as their relative percentages compared to ΣPFAS 21 generally decreased with distance from the factory area (Fig. 2). ΣFTS concentrations as well as relative percentages were significantly lower ($p < 0.01$) in perch livers from sampling areas L3, L5, and L6 compared to perch from the factory area. ΣpreFOS concentrations were significantly lower in the fire station ($p = 0.03$), L3 ($p = 0.01$), L5 ($p < 0.01$), and L6 ($p < 0.01$) areas, compared to the factory area (Fig. 2A). Relative percentages of ΣpreFOS compared to ΣPFAS 21 were significantly lower in perch livers from areas L3 ($p = 0.01$), L5 ($p < 0.01$), and L6 ($p < 0.01$) compared to perch livers from the factory area.

The dominant PFAS in lake perch are consistent with those in factory area perch, in factory area and landfill sediments and water, and in lake sediments. This collectively indicates that the factory is a major source of the observed PFAS in biota. Dominance of PFOS, in addition to the presence of other PFSA and comparatively low concentrations of PFCA have previously been reported for perch sampled at AFFF impacted sites (Ahrens et al., 2015; Kwadijk et al., 2014). There is little evidence for bioaccumulation of C4–C7 PFSA, which if present could be attributed to AFFF used at the fire station. The C7 PFSA (PFHpS), was the only of the C4–C7 PFSA above the LOQ in biota. PFHpS was detected in all perch livers from the factory area (n = 5), in none of the perch from the fire station (n = 2), and in seven perch livers from the lake (n = 20). The C6 and C7 PFSA, PFHxS and PFHpS, are previously reported to bioaccumulate in fish, however bioaccumulation potentials are smaller, and half-lives are shorter, compared to PFOS (Falk et al., 2015; Labadie and Chevreuil, 2011; Lescord et al., 2015; Zhong et al., 2019). The lower bioaccumulation potentials complicate the use of these compounds as indicators of AFFF contamination, however PFHxS has previously been reported in whole fish, fish liver and fish muscle at AFFF polluted sites (Filipovic et al., 2015; Kärrman et al., 2011; Langberg et al., 2019; Lanza et al., 2017). The lack of PFHxS in biota from lake Tyrifjorden, indicates that emissions from the fire station do not result in detectable PFHxS accumulation. The results taken together show that the biota profiles also reflect PFAS emissions from the factory and not the fire station.

The decreasing fish liver concentrations of FTS and preFOS in regions further away from the factory echo the same trend in sediments. This is interpreted as an indication that the fish reflect PFAS concentrations in the abiotic environment in the part of the lake in which they were sampled. The relatively large distances between sampling areas (13–17 km between area L1 and areas L4, L5, and L6, see the section *Sampling and sample preparation* in the SI) and the relatively short (days) depuration half-lives of PFAA in fish (Martin et al., 2003) is likely the explanation for this observation even though fish are expected to move around in the lake. However, the same clear trend for preFOS and FTS was not observed for relative percentages, with a clear decreasing trend for percentages of FTS and preFOS in perch livers but not in sediments. The reason for this discrepancy is unclear but could be due to differences in factors such as partitioning coefficients and exposure pathways between the two media (i.e. perch livers and sediments). The decreasing proportions of FTS and preFOS in perch liver with distance from the factory area could be due to FTS and preFOS being less mobile in the environment compared to the PFAA, or it might indicate more complete transformation of these compounds with distance from the source (preFOS to PFOS and FTS to PFCA (Armitage et al., 2009; Paul et al., 2009; Simonnet-Laprade et al., 2019; Wang et al., 2011a)). A significant proportion of environmental PFAS not covered by targeted analyses, which are potential PFAA precursors are expected to be present (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014). Corresponding to this, as reported previously (Langberg et al., 2020), extractable organic fluorine (EOF) in fish liver decreased with distance from the factory, and the sum of organic fluorine in the targeted PFAS as a percentage of EOF in fish livers generally increased with distance from the factory (Fig. S15 and Table S18). This might indicate lower proportions of unknown precursor compounds (and unknown intermediate transformation products) further from the factory due to a more complete transformation. Thus, biotransformation of PFAA

precursors might explain the high PFAA levels observed in areas furthest from the factory.

3.1.3. Branched and linear PFOS

PFOS products produced by the 3M Company using ECF have been reported to consist of approximately 70% linear and 30% branched isomers (Benskin et al., 2010; Jiang et al., 2015; Vyas et al., 2007). The percentage of L-PFOS (of ΣPFOS) were 68.2% and 64.3% in the lake water from L4 and L6, respectively (Langberg et al., 2020). Percentages of L-PFOS were 74.3–89.3% in pore water, 92.0–99.3% in perch liver, and 97.0–99.6% in pike liver and increased with distance from the factory area ($p < 0.05$) (Fig. S16, individual p values are shown in Table S19). The percentage of L-PFOS in water and fish at the factory area is comparable to previously reported percentages for both point and diffuse sources, including sources where precursor compounds could contribute to PFOS levels (urban runoff and sewage, water from a firefighting training area, and wastewater discharge) (Boulanger et al., 2005; Houde et al., 2008; Kärrman et al., 2011; Labadie and Chevreuil, 2011). The increasing percentages of L-PFOS with distance from the factory area observed in the present study are likely due to the higher water solubility and faster elimination in organisms of most Br-PFOS congeners compared to L-PFOS (Benskin et al., 2009a; Chen et al., 2015a, 2015b; Zhang et al., 2013). These processes result in environmental fractionation whereby L-PFOS is retained in biota and sediments, while Br-PFOS is removed with water exchange. Thus, over time and increasing distance from point sources, the amount of L-PFOS relative to Br-PFOS is expected to increase (for this type of environmental transport scenario). The faster transformation of branched isomers could also contribute to this, i.e. that more Br-PFOS precursors are transformed earlier/closer to the source compared to L-PFOS precursors (as all the ECF based preFOS have both branched and linear compositions) (Benskin et al., 2009b; Chen et al., 2015a,b; Peng et al., 2014; Ross et al., 2012). Thus, PFOS isomer profiles in perch livers, pike livers, and pore water represent further evidence that the factory is the main point source of PFOS to the lake.

3.1.4. Historic concentrations in lake sediments

The dated sediment core at L1 presents PFAS concentrations in sediments that settled between 1934 and 2017 (Fig. 3 and Table S20). High concentrations of SAmPAP diester were detected in the core (max: 3383 μg kg^{-1}), shown in Fig. 3A. This is in agreement with concentrations previously reported for top sediments in Lake Tyrifjorden (max: 1872 μg kg^{-1}), including the sample analysed for EOF (850 μg kg^{-1}) (Langberg et al., 2020). Core data was used to explore the introduction and phase-out of the different PFAS products. Peaks in the sediment core varied for different PFAS substances: PFOS peaked at approximately 1960; preFOS and SAmPAP diester peaked around 1984, with a smaller peak around 1960; PFCA and FTS peaked at the second half of the 1990s. The low concentrations in top (recent) sediments compared to deeper (older) sediments likely reflects lower levels in settling sediments after the factory was shut down in 2013. PreFOS and SAmPAP were detected in sediments dated to the 1950s. Production at the factory began in 1964 and preFOS based phosphate surfactants were commercialised in the late 1960s and introduced for use in food contact paper and packaging in 1974 (Olsen et al., 2005). Concentrations observed in the period between 1950 and 1970 could be due to uncertainties related to the dating, sampling, or bioturbation of PFAS in sediments. The concentration peaks of SAmPAP diester and preFOS in the 1980s correspond well to the history of the factory as well as reported use of PFAS in paper products. Therefore, the accuracy of the dating varies throughout the core, but appears more uncertain with depth.

The PFAS profile observed in sediments dated to pre-1995 corresponds to a 3M product called Scotchban which was used for paper products and contained a mixture of SAmPAP and preFOS (Martin et al., 2010; Trier et al., 2017). As commercial SAmPAP formulations were dominated by diester, with much less mono- and tri-ester (Lee and Mabury, 2011), this compound was prioritized for analysis. However, the presence of SAmPAP mono- and tri-ester in sediments were expected as well, as reported previously (Zhang et al., 2018). The decreasing concentrations of SAmPAP, preFOS, and PFOS from the late 1980s/early 1990s occurs before the phase out of PFOS and related compounds in 2002 (Martin et al., 2010). However, the peak and subsequent decline in PFOS concentrations is in agreement with previous studies (Furdui et al., 2008; Holmström et al., 2005; Kwadijk et al., 2010; Martin et al., 2004; Verreault et al., 2007). In the present study, high levels of FTS were detected downstream the landfill which was filled with waste from the factory during the late 1980s to the 1990s. Concentrations of 10:2 and 12:2 FTS dominate the sediment core between 2000 and 2010, peaking in 2006, indicating that the use of Scotchban was phased out at the site by the late 1990s. Thus, the reported decline of PFOS in the environment before the phase out might be due to a shift from SAmPAP and preFOS to other PFAS mixtures.

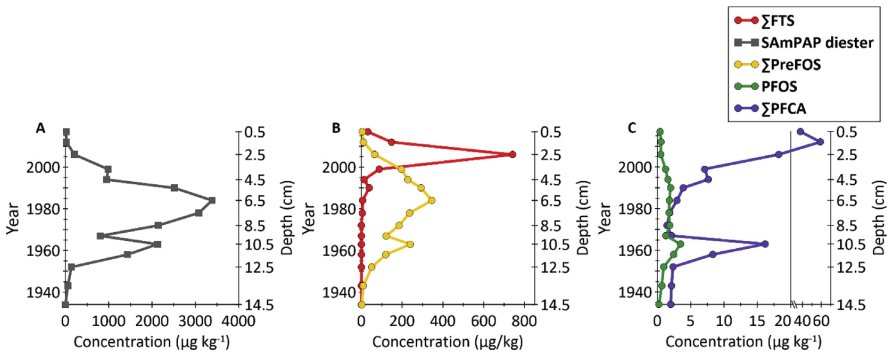

Fig. 3. PFAS concentrations in sediments from the dated core sample from area L1. Panel A: concentrations of SAmPAP diester. Panel B: Concentrations of ΣFTS and ΣpreFOS. Panel C: Concentrations of PFOS, and ΣPFCA (PFOS was the only PFSA above the LOQ). The black vertical line in C shows that the x-axis is split at the interval 20–35 μg kg^{-1}. Concentrations for individual compounds are shown in Fig. S18 and Table S20.

Fluorotelomer mercaptoalkyl phosphate esters (FTMAP, also termed S-diPAP and known by the tradename Lodyne P208E) have been used in food packaging since 1995, and are based on their structure likely precursors to FTS (Lee and Mabury, 2011; Trier et al., 2011). Other possible FTS precursors are groups containing the same (suspected) FTS precursor moiety as FTMAP such as 3-[2-(perfluoroalkyl)ethylthio] propionate (tradename: Zonyl FSA) (Trier et al., 2011), fluorotelomer sulfonamide alkylbetaines (FTAB) (Field and Seow, 2017; Moe et al., 2012), and others (Barzen-Hanson et al., 2017). However, it is not known to what extent these have been used in paper coatings, and research in this area is scarce. The main focus in the literature of FTS compounds are those with 6:2 and 8:2 structure (Field and Seow, 2017); detailed information regarding 10:2, 12:2, and 14:2 FTS and their potential precursors is not currently available. Nevertheless, the results indicate two eras of product emissions: 1) Scotchban (considered sum of all SAmPAP, preFOS, PFSA, as well as PFCA prior to 1990), and 2) the FTS dominated product(s), termed the FTS mixture (considered the sum of all FTS and their precursors as well as PFCA after 1990). Only the targeted compounds were included in calculations and for the modelling (described below), therefore SAmPAP mono- and triester and potential precursors to FTS were not included. Interestingly, another group of ester phosphates reported to be used in paper products, fluorotelomer alcohol (FTOH) mono- and di-substituted phosphates (Trier et al., 2011), were analysed for in water, sediments and biota, but not detected (neither were their expected degradation products, FTOHs), indicating that these compounds were not used at the factory (Table S3).

The sediment core profile corresponding to PFAS used in paper products gives further evidence to that the majority of the PFAS pollution in the lake originates from the factory. To the best of our knowledge, this (together with the results reported by Langberg et al., 2020) is the first-time that production of PFAS coated paper products has been reported to be a significant PFAS point source. Extrapolating the concentrations in the core to the entire lake except area L6 (due to lower concentrations in this area) gives a total mass residing in the sediment bed of 40 660 kg Scotchban and 2341 kg FTS mixture (*equation VII* in the SI). This extrapolation is based on the observation that surface sediments of the core match well with the mean and geometric average of all PFAS in all other surface sediments except area L6 (see Table S13), and this core is therefore assumed to be representative of the lake for the purpose of modelling (as described in the *Modelling* section in the SI). These calculations are based on the results from the targeted analyses, therefore, the unidentified fraction of organic fluorine, which is approximately 50% in the sediment sample which was analysed for EOF (Fig. S15), is not included.

3.2. PFAS fate and transport modelling

To understand how emissions from the factory may have resulted in PFAS pollution over the entire lake bed, a fate and transport model was employed. The purpose of this model was threefold: 1) to back-calculate emission volumes of the two suspected PFAS products, Scotchban and the FTS mixture, 2) to account for how much of the emissions of Scotchban and FTS mixture were likely dissolved or particulate bound, and 3) to extrapolate towards future predictions of emissions and sediment surface concentrations. Emissions in the model assume two eras of pollution that were calibrated to the sediment core data (using the method of least squares): the Scotchban era and the FTS mixture era. The Scotchban era was assumed to begin in 1950, followed by a yearly increase in emissions until 1984. After this, Scotchban emissions were assumed to decrease yearly to the present day. For the FTS mixture, emissions were assumed to begin in 1994, reach a peak in 2006 before being phased out, with emissions declining yearly. Assumptions, as well as details for the modelling are described in the *Modelling* section in the SI.

Details regarding the production methods at the factory are not known, however it is widely acknowledged that the paper industry produces effluent wastewater containing organic, suspended solids, rich in paper/cellulosic fibers (Ali and Sreekrishnan, 2001; Lacorte et al., 2003). As Scotchban and the FTS mixture were used as paper coaters, it is not unreasonable to assume they were sorbed to paper fibres when they were released (and therefore associated with organic carbon, which is a dominant parameter affecting sorption of PFAS (Higgins and Luthy, 2006)). As part of a sensitivity analysis, the model was run assuming three different organic carbon-water partitioning coefficients (Log K_{OC}: 5, 7 and 9), to describe sorption of Scotchban or FTS mixture to the particles entering the lake, as well as sorption to sediments. The value of 5 was chosen as it corresponds to locally measured values for preFOS and FTS in lake Tyrifjorden sediment (Table S21), which dominate the PFAS profile. The value of 9 was chosen to represent the very strong hydrophobic sorption of parent compounds (SAmPAP and FTMAP), which has not yet been measured but could be much higher (Wang et al., 2011b). A value of 7 was chosen as the mid-point.

Modelled emission volumes and sediment and water concentrations are shown in Table 1 for the two eras of product emissions, and for the three log K_{OC} values. When log K_{OC} was 5, emissions of Scotchban and the FTS mixture summed over all modelled years were 189 tons and 15.6 tons, respectively, with 154 and 13.7 tons leaving the lake by the downstream river. However, when log K_{OC} was 7, the back calculated emissions dropped drastically, to 42 and 2.5 tons respectively, and (in comparison) relatively minor emissions downstream: 0.8 and 0.07 tons, respectively. There was no substantial change in calculated emissions when log K_{OC} was 7 or 9, as at this point PFAS are essentially particulate bound (Table 1).

Regardless of the log K_{OC}, predicted total amounts of PFAS in sediments in the lake (ca. 35–41 tons of Scotchban and ca. 1.9–2.4 tons of the FTS mixture) agreed well with the extrapolated amount based on sediment measurements used for calibration (41 and 2.3 tons for Scotchban and the FTS mixture, respectively, see *equation VII* in the section *Modeling* in the SI for the calculation of measured volumes in the sediments). These emission volumes are substantial considering that previous estimates by Wang et al. (2017a) of total global emissions of PFOS, preFOS (*x*FOSA/Es) and POSF between 1958 and 2015 are in the ranges of 1228–4930, 1230–8738, and 670 tons respectively (Wang et al., 2017a). However, these emissions do not cover SAmPAP itself, but rather the building blocks and degradation products thereof (*x*FOSA/Es), and were mostly for air, which are most relevant for global distribution in a short time frame, and not lake sediments (Wang et al., 2017a). Thus, the global emission amounts could be much higher than estimated, when including local SAmPAP emissions and emissions to sediments, as discussed in Wang et al. (2017a). It has been reported that between 1.0 and 1.5% fluorochemical concentrations (based on the dry weight of the fibres) are needed for paper protection, and that approximately 32% of total PFOS produced in the European Union before 2000 was used for paper coating (United Nations Environment Programme Persistent Organic Pollutants Review Committee, 2010). In this context, modelled emissions for log K_{OC} values of 7 or higher seem more realistic, but still imply that the amount of SAmPAP and FTS in lake Tyrifjorden is in the range of 0.5–3% of estimated global *x*FOSA/Es emissions. If correct, this would imply that, globally, local emissions of large PFAS such as SAmPAP in sediments and soils could be much larger than global emissions of *x*FOSA/Es, and therefore represent a continuous source of xFOSA/Es emissions in the future as these degrade.

Projected water concentrations in the years 2030 and 2060 were very low for all scenarios (below present day LOQ), which matches well with the assumption of strong sorption to particles. PFAS in top sediments originating from the use of Scotchban was projected to decrease up to 44% in 2030 and 48% in 2060 when compared to modelled concentrations in 2017. Similarly, the projected decrease was 43% in 2030 and 45% in 2060 for the FTS mixture. Rate constants (change in emission volumes in the lake via river input k_{in}), for the simulations at log K_{OC} 7.0/9.0 (Table S22) when concentrations of Scotchban and FTS mixture increased, were small, indicating near steady-state emissions when these products were used. Rate constants for the periods when concentrations of Scotchban and the FTS mixture, decreased, were larger, indicating a rapid decrease in emissions. Emission half-lives from the peak were on the scale of 4 years for Scotchban and 3 years for the FTS mixture. The extent to which these explain a decrease in direct factory emissions and a transition to diffuse emissions (e.g. from resuspension of river sediments or emissions from landfills) is unclear and should be re-evaluated in the future.

Both diffuse emissions from the landfill and soil as well as resuspension from top sediments are likely sources of long-term pollution to lake Tyrifjorden. Thus, despite the current low aquatic concentrations, PFAA exposure to biota is expected to be an issue for the foreseeable future. This is confirmed by the PFAS profiles seen in the sediment samples and the sediment traps, which exhibit a combination of both Scotchban and the FTS mixture composition, despite the likely shift from Scotchban to the FTS mixture around 1990 and the closure of the factory in 2013. The presence of both PFAS products in present day settling material in all lake sampling areas shows that mobilisation of the sediment is still occurring, resulting in a wide distribution of the PFAS pollution. Field results indicating a more complete transformation of PFAS furthest from the point source suggest that (some of) these legacy sources are subject to very little biotransformation, and that this occurs after PFAS are emitted from these sources.

4. Conclusions

PFAS profiles in samples representing emissions from the factory and PFAS profiles in river sediments directly downstream the factory were similar to PFAS profiles in lake sediments. In contrast, PFAS profiles in samples representing emissions from the fire station differed. PFAS profiles in biota were dominated by the same compounds and/or their expected biotransformation products as in lake sediments. The spatial distribution of concentrations and profiles (including PFOS isomer patterns) showed clear trends with distance from the factory, as expected based on PFAS physiochemical properties and biotransformation governing fate and transport. The dated sediment core showed distinct differences in the emitted PFAS mixture with time of release, and historical PFAS profiles matched well with known historical use of different PFAS for paper products (including SamPAP diester). Therefore, it is concluded that the factory is the main source to the PFAS contamination in lake Tyrifjorden. Results of the model show that emission volumes were very high, however due to strong sorption to particles, aquatic concentrations are low. Concentrations in top sediments will decrease over time, nevertheless, PFAS exposure to biota is expected to be an issue for the foreseeable future.

4.1. Environmental implications

The body of evidence in the present study indicates that production of paper products can be a major, largely overlooked, PFAS source to the environment. Both the overall environmental release, and local impacts on the environment and human health (e.g. from fish consumption) at such sites, point to the need for investigation of similar paper product production sites, as well as paper recycling and disposal facilities where these products might end up. Exploiting similar chemical profiling methods that allow source tracking and identification, as demonstrated here, is recommended. The inclusion of precursor compounds to PFAA in monitoring campaigns is necessary to capture the full environmental load. Based on these findings, there is a clear need for more rigid regulation of the use of PFAS in paper products and their potential release from the paper recycling industry.

Follow up studies should focus on the role that paper fibres can play in the fate, transport, and exposure of PFAS, as this information could be of importance for the assessment of PFAS related risks. There are currently no studies focusing on this specifically, however based on the literature of microplastic fibres (Thompson et al., 2004; Willis et al., 2017), studies on fibres in the oceanic water columns (Bagaev et al., 2017), as well as fluid dynamic theory (Wiens and Stockie, 2015), they appear to be readily suspended throughout the water column and are easily distributed through large water bodies like lakes, and only settle when aggregated. Hall (2003) presented a summary of research related to pulp mill effluent-induced coagulation and flocculation in rivers, showing that suspended solids downstream pulp mill discharges undergo coagulation and flocculation. The sedimentation of effluent fibres and their contaminants by coagulation and flocculation processes results in apparent decreasing concentration gradients in water and increased concentration gradients in sediments with downstream distance from the pulp mill (Hall, 2003). Similar research could not be found for paper production facilities, but it seems largely consistent with that observed in lake Tyrifjorden, warranting further research on the relevant coagulation and flocculation processes. It is reasonable therefore to hypothesize that the main transport mechanism by which the entirety of the sediment bed in lake Tyrifjorden was contaminated by PFAS, was products such as Scotchban and the FTS mixture being sorbed to emitted paper fibres. These fibres could then have been widely distributed throughout the entire volume of the lake until finally settling. Follow-up studies should thus explore if such paper fibres could be a major transport and exposure vector of PFAS pollution.

Associated content

Supporting information

The Supporting Information is available online.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.116259.

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Appendix: Paper II

Supplementary Information

Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: source and historic emission tracking

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Site description - Lake Tyrifjorden

Lake Tyrifjorden (60.03° N, 10.17° E) is a freshwater lake in the southern part of Norway (see Figure S1). The surface area of the lake is 138 km^2. The lake is shaped like the letter *H,* where the mid part and the southeast "arm" are deep (60-288 m), while the remaining parts are relatively shallow (mostly less than 40 m), see Figure S2. The average water retention time in the lake is estimated to be 2.6 years, however it is expected to vary in different areas (Holtan, 1977). The main riverine input is the river Storelva which has an average flow of 151 $m^3\ s^{-1}$ (personal communications, The Norwegian Water Resources and Energy Directorate, [observations for the measuring stations *Strømstøa* and *Kistefoss* between 01.01.1978 and 31.12.2019]). Thus, due to the size of the lake and the riverine input, there is a large potential for dilution of dissolved compounds. The average precipitation is 1.02 $m\ y^{-1}$, the average temperature is 6.2 °C, and the average wind speed is 2.2 $m\ s^{-1}$ ("The Norwegian Meteorological Institute," 2020).

Sampling and sample preparation

The sampling area in the river downstream the factory was termed the factory area. Six lake sampling areas were selected to represent a gradient of increasing distance, and thus likely decreasing PFAS load from the sources (shown in Figure S1). The areas L1 to L6 are named according to their proximity to the PFAS source areas. Area L1 is located at the river mouth and the distance from L1 to the areas expected to be least influenced (L4, L5, and L6) is 13-17 km. Station L6 is located in a part of the lake which is separated by a narrow inlet from the rest of the lake and was expected to be least influenced by the contaminant sources. As the river is the main riverine input to the entire lake, most of the water in all lake sampling areas originates from the river.

Biota in the lake was sampled between June 7th and October 6th, 2018. Lake sediment, and pore water were sampled between September 27th and 31st, 2018. Water and sediments at the fire station and the landfill were sampled during summer 2018. Biota and sediment in the Factory area (the sampling area in the river directly downstream to the factory) were sampled in the period August 21st and 24th, 2018. The total number of analysed samples from each area is shown in Table S1 (abiotic samples) and S2 (biotic samples). Sample storage prior to analysis is described in chapter *Quality assurance and sample storage.*

Source profiles

The storm water system at the fire station and the creek downstream the landfill was considered indicative of the two sources. At the fire station, water was sampled from intermediate bulk containers and sediment containers. The containers were used to temporary store water and sediments that originated from cleaning of the storm water system. The storm water system covers the fire station

area where AFFF has been used (however the extent is unknown). In addition, this area has been used for washing of the fire trucks. At the landfill, water and sediments were sampled from a creek located downstream the site. Water was sampled (n=2 for the fire station, n=1 downstream the landfill) by submerging high-density polyethylene (HDPE) bottles (1L) directly into the water source (approximately 20 cm below the surface). Sediments were sampled (n=2 for the fire station, n=1 downstream the landfill) using a metal tube attached to a telescopic pole.

Sediments

Sediments were sampled from the river at two locations upstream the factory and nine locations in the factory area, and at 94 locations scattered across the lake (shown in Figure S3). A small van Veen grab was used to sample the top 10 cm of fine sediment in the river as there was a high proportion of rocks on the river bed. Lake sediments were sampled using a Kajak-Brinkhurst sediment corer from a vessel equipped with a high-resolution sounder. A closing mechanism was triggered on contact with sediments, collecting a core of approximately 30 cm length and 8.5 cm diameter. The top 2 cm were sliced carefully and transferred to a burnt glass jar. At some locations (those with high water content, coarse sediments, or deep water), it was not possible to take a core sample and a van Veen grab was used. The grab was cautiously lowered on to the sediment surface and an undisturbed sample of the top 10 – 15 cm sediment was collected. A steel spoon was used to transfer a sample of the top 0-2 cm into the glass jars.

Sediments collected for pore water analysis were sampled in triplicate from the same five areas as for water samples (L1, L3, L4, L5, and L6) in the lake and 1 sample (n=1) was collected from the river (shown in Figure S4).

Four custom built sediment traps (internal radius: 0.05 m) were deployed in the river (upstream the factory area, directly downstream the factory (factory area), directly downstream the fire station, and before the river outlet) and 3 traps were deployed in the lake (2 traps at station L1, and 1 trap at station L5). Sediment traps were placed in areas where sedimentation was expected and left for 56-61 days. The locations of the traps are shown in Figure S5.

Biota

Fish (perch [*Perca fluviatilis*] and pike [*Esox Lucius*], were sampled at the areas: factory area, fire station, L1, L3, L5, and L6 using fish nets (35-39 mm mesh size). The nets were stretching from 3 to 15 m below the water surface in the lake and in the river outside the fire station, and between 1 and 2.5 m below surface in the shallower river at the factory area. Fish were killed by a blow to the head. The number of sampled biota varied between areas as shown in Table S2.

Laboratory methods

Sediment traps

Material collected in the sediment traps was dried and weighed before extraction and analysis as for other sediment samples (described below).

Analyses for calculations of organic carbon-water partitioning coefficients (K_{OC})

Detail for analyses for calculations of KOC values are listed below. Details for the calculation of KOC values are shown in chapter *Calculation of organic carbon-water partitioning coefficients (KOC)*.

Pore water

Approximately 30-35 g of wet sediment was centrifuged at 11 000 G for 45 minutes. The pore water (supernatant) and sediments were transferred to different polyethylene test tubes for extraction and analysis.

Total organic carbon content in sediments

The total organic carbon (TOC) content was analysed using thermal oxidation and infrared detection, (LOD of 0.1 %), by ALS Laboratory Group AS according to methods CSN ISO 10694 and CSN EN 13137:2002.

Sediment dating

Sediment dating was performed at the Department of Geosciences and Natural Resource Management (IGN), University of Copenhagen. Sediments were dated using the activity of elements in the natural uranium (^{238}U) radioactive decay series: lead (^{210}Pb) and radium (^{226}Ra), as well as caesium (^{137}Cs) which was analysed via gamma spectrometry. The measurements were carried out on a Canberra ultralow-background Ge-detector. ^{210}Pb was measured via its gamma-peak at 46,5 keV, ^{226}Ra via the granddaughter ^{214}Pb (peaks at 295 and 352 keV) and ^{137}Cs via its peak at 661 keV.

The dating is based on that sediments contain a background level of ^{210}Pb. The ^{210}Pb isotope has a half-life of 22 years, however levels remain relatively stable because of radioactive decay of ^{226}Ra to ^{210}Pb from rocks, which replaces the ^{210}Pb which is lost. Excess or unsupported ^{210}Pb is present in young sediments because uranium in the earth's crust produces ^{222}Rn (radon gas), which decays to ^{210}Pb in the atmosphere. ^{210}Pb is precipitated back to the ground, adsorbed to particulate matter, transported to water and becomes part of the sediments. By analysing the remaining excess isotope in the sampled sediment, the year of sediment deposition can be determined.

The sediment core was divided into 15 parts (1 cm slices), and the same slices were both dated and analysed for target PFAS. The surface contents of unsupported ^{210}Pb in the core was approximately

120 Bq kg^{-1} with an exponential decline with depth. CRS-modelling was applied on the profile using a modified method where the activity below the lowermost sample is calculated based on regression (Andersen, 2017; Appleby, 2002). Contents of ^{137}Cs peaked in sediments dated to shortly after the Chernobyl accident in 1986 (Figure S17). The distinct ^{137}Cs peak and the exponential decline in unsupported ^{210}Pb with depth indicates that mixing is very limited. The chronology is therefore considered to be reliable.

Extractable organic fluorine

Extractable organic fluorine (EOF) in sediment and fish liver was analysed by Örebro University. A separate portion of the samples were extracted exactly as described for targeted PFAS analysis but PFAS standards were not added to the extract. Therefore, procedural losses could not be accounted for, which introduces a source of error. In a previous study in which biota samples were spiked with NaF and then extracted with acetonitrile (as in the present study), no inorganic fluoride was extracted (Spaan et al., 2020). Thus, it was assumed that extraction of inorganic fluoride was negligible here. An exact volume was obtained by diluting samples with acetonitrile utilizing 10 mL metric flasks.

EOF content was measured using a combustion ion chromatography (CIC) system. The CIC consists of a combustion module (Analytik Jena, Germany), a 920 Absorber Module and a 930 Compact IC Flex ion chromatograph (both from Metrohm, Switzerland). Separation of anions was performed on an ion exchange column (Metrosep A Supp 5 – 150/4.0) using carbonate buffer (64 mmol/L sodium carbonate and 20 mmol/L sodium bicarbonate) as eluent for isocratic elution. In brief, the sample extract (0.1 mL) was injected on to a quartz boat, which was pushed into the furnace by the autosampler. The furnace was kept at 1000-1050 °C for combustion, during which, all organofluorine compounds were converted into hydrogen fluoride (HF). A carrier gas (argon) was constantly pumped through the combustion tube, the gas carries all formed HF into the absorber module where MilliQ water is used to capture the HF. A 2 mL aliquot of the absorber solution was then injected on a pre-concentration column and then injected on the ion chromatograph. The concentration of F^- ions in the solution was measured using ion chromatography.

Quantification of samples was based on an external calibration curve. For both calibration and samples, the peak area of the preceding combustion blank was subtracted from peak area of the sample to correct for the background contamination.

Fluoride signal was observed in combustion blanks even when no sample was analysed. Prior to sample analysis, multiple combustion blanks were performed until stable fluoride signals were reached; the relative standard deviation of the three most recent combustion blanks was lower than 5 %.

The limit of quantification (LOQ) was determined separately for each sample preparation batch as the procedural blank of the batch plus three times the pooled standard deviation of the procedural blanks. The reported values were not corrected for extraction blanks.

Combustion blanks (CIC analysis cycle without a sample) were made between sample injections to evaluate the presence of carryover between samples and to obtain a reliable estimate of the background fluorine levels. The repeatability of the instrument was tested by triplicate analysis of dilutions made from an anion SRM solution (product code 89886, Sigma-Aldrich). The five dilutions were in the range of 60 ng F g^{-1} to 1200 ng F g^{-1} and the relative standard deviation at all five dilution levels were below 25%. Combustion of 100 ng and 500 ng of SRM 2143 – *p*-Fluorobenzoic (NIST) resulted in recoveries of between 90 - 98%. Combustion of 500 ng of PFOS resulted in recoveries ranging from 89 to 92% and combustion 500 ng of PFOA resulted in 85 to 90% recoveries. Combustions of 100 ng PFOS standard (n=4) before, during and at the end of analysis were found to be 85 ng with a relative standard deviation of 9%.

Extraction and target PFAS analysis

Isotope labelled and authentic standards (i.e. standards identical to the targeted substance) were obtained from Wellington, with a few exceptions: 6:2 FTOH, 8:2 FTOH, 10:2 FTOH were obtained from Chiron, while 4:2 F53B, 6:2 F53B, 8:2 F53B, FHxSA and MeFHxSA were from other research labs via project connections.

For all samples, a mixture of isotope labelled PFAS (MPFAC-MX_C-ES purchased from Wellington Laboratories: M8FOSA, M2-6:2FTS, M2-8:2FTS, d5-N-MeFOSA-M, d9-N-etFOSE-M, d5-N-EtFOSAA-M, M4-8:2 diPAP) was added as internal standards (IS) for quantification before extraction. For sediments, approximately 5 grams of wet sediment was weighed and IS was added. The remaining sample was weighed before and after drying to determine the water content, and this was used to calculate the dry weight of the extracted material. Extraction was performed twice using acetonitrile (8+6 mL), ultrasonic bath (30+30 min) and shaking (30+30 min). The paper plate was extracted as described for sediment samples with the following changes. 2x2 cm of the paper plate (0.1 g) was extracted using methanol (6 mL), followed by heating at 70 °C for 2 hours. For biota samples, approximately 2 grams of biota sample was weighed and IS was added. Extraction was carried out twice using acetonitrile (5+4 mL), ultrasonic bath (30+30 min) and shaking (30+30 min). Extracts were concentrated under a nitrogen flow. 500 mL of lake and river water samples, and smaller volumes of pore water were extracted using Waters HLB solid-phase extraction (SPE) columns.

PFAS were analysed using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS). An Acquity Ultra Performance HPLC system (Waters) was used to inject aliquots of 7 µL

extract onto a Waters Acquity BEH C8 reversed phase column (100 x 2.1 mm, 1.8 µm particles. The target compounds were separated at a flow rate of 0.5 mL min^{-1} using acetonitrile (A) and 5.2 mM NH_4OAc in water (B). The following binary gradient was applied: 0-1.5 min, 12% of A; 1.5-11 min, linear change to 99% of A; 11-13 min, 99% of A. The Acquity system was coupled to a Xevo G2-S Q-ToF-HRMS instrument (Waters) using negative ion electrospray ionization (ESI(-)). Mass spectra were registered in full scan mode (mass range m/z of 150-1100 for initial samples, however it was increased to 150-1300 to include SAmPAP diester (m/z: 1203) in later analyses as described below). The following optimized parameters were applied: Capillary voltage, 0.7 kV; desolvation temperature, 500 °C; source temperature, 120 °C; nitrogen desolvation gas flow, 800 L h^{-1}. Quantitative analysis was performed employing extracted mass chromatograms from full scan recording using the m/z (typical mass tolerance of 0.03 µ) for the different analytes.

Initially, 44 PFAS were analysed using authentic standards (i.e. a standard identical to the targeted substance) and internal standards, while peaks for Br-PFOS were identified using a standard mixture of Br-PFOS isomers and quantified against the standard for L-PFOS. 19 PFAS were screened for using exact mass and retention time from authentic standards. An additional 28 PFAS were screened for using exact mass and estimated retention time (using MassLynx Mass Spectrometry Software). Peaks at expected retention times were observed for three PFAS, and they were quantified using the standard for a structurally similar compound: PFPeDA was quantified using the standard for PFHxDA, and 12:2 FTS and 14:2 FTS were quantified using the standard for 10:2 FTS. All PFAS and acronyms are shown in Table S3 and Table S4. The detected compounds indicated the presence and thus use of an EtFOSE based PFAS product, which according to the literature could indicate that SAmPAPs were of the parent compounds (Martin et al., 2010; Trier et al., 2017). Therefore, SAmPAP diester was screened for using exact mass and estimated retention time in a few samples (the sediment core, and sediment samples used for analyses of EOF), and quantified against the standard for PFOS. An authentic standard for SAmPAP diester was acquired later but SAmPAP diester (m/z: 1203) was outside the analytical range for most samples (m/z: 150-1100) and SAmPAP diester could therefore not be looked for in these data. Concentrations using the authentic standard were 17 times as high compared to when using the standard for PFOS. This difference in ionization efficiency between PFOS and SAmPAP diester is consistent with a factor of about 17, and concentrations in the samples where PFOS was used as the standard was therefore corrected by using this factor. In a previously performed study (Langberg et al., 2020), we reported results from additional sampling and analyses (using the standard for SAmPAP diester) and the presence and concentrations of SAmPAP diester in lake sediments were confirmed (not reported in the present study).

The 45 PFAS (+ Br-PFOS) which were analysed using authentic and internal standards (including SAmPAP diester), the 19 PFAS which were screened for using exact mass and retention time from authentic standards, and the three PFAS that were quantified using the standard for a similar compound are shown in Table S3. The 25 PFAS which were screened for using exact mass and estimated retention times, but not detected are shown in Table S4.

In addition to SAmPAP diester (which was only analysed for in a few samples), 30 compounds and Br-PFOS were detected and quantified. The quantified compounds included 12 perfluorocarboxylic acids (PFCA): perfluoro-n-pentanoic acid (PFPA); perfluoro-n-hexanoic acid (PFHxA); perfluoro-n-heptanoic acid (PFHpA); perfluoro-n-octanoic acid (PFOA); perfluoro-n-nonanoic acid (PFNA); perfluoro-n-decanoic acid (PFDA); perfluoro-n-undecanoic acid (PFUnDA); perfluoro-n-dodecanoic acid (PFDoDA); perfluoro-n-tridecanoic acid (PFTrDA); perfluoro-n-tetradecanoic acid (PFTeDA); perfluoro-n-pentadecanoic acid (PFPeDA); perfluoro-n-hexadecanoic acid (PFHxDA), 6 perfluorosulfonic acids (PFSA): perfluoro-1-butanesulfonate (PFBS); perfluoro-1-hexanesulfonate (PFHxS); perfluoro-1-heptanesulfonate (PFHpS); linear and branched perfluoro-1-octanesulfonate (PFOS); perfluoro-1-decanesulfonate (PFDS); perfluoro-1-dodecansulfonate (PFDoDS); 7 preFOS compounds: perfluoro-1-octanesulfonamide (FOSA); N-methylperfluoro-1-octanesulfonamide (MeFOSA); N-ethylperfluoro-1-octanesulfonamide (EtFOSA); 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (EtFOSE); perfluoro-1-octansulfonamidoacetic acid (FOSAA); 2-(N-methylperfluoro-1-octansulfonamido)acetic acid (me-FOSAA); 2-(N-ethylperfluoro-1-octansulfonamido)acetic acid (EtFOSAA), and 5 fluorotelomer sulfonates (FTS): 6:2 FTS; 8:2 FTS; 10:2 FTS; 12:2 FTS; 14:2 FTS.

Quality assurance and sample storage

Lab blanks were run, following the same procedures as for field samples. Blank samples were used for each batch of samples for analyses (20-25 samples). Each batch contained only samples of the same media, and samples for standard addition. Concentrations in the blank samples were low (<0.5 ng g^{-1} or ng L^{-1}) and consistent regardless of different equipment, indicating little cross contamination. Blank values were subtracted from results when calculating concentrations in samples. No significant carry-over was detected between samples, even when sample concentrations were extremely high (e.g. for SAmPAP diester). The autosampler was set up with a stainless-steel needle and a washing program using MeOH/Isopropyl alcohol (IPA) as a strong washing solution. Instruments were cleaned daily, and blank samples were run before and after each analysis batch (typically 20-30 samples). A random sample was selected from each matrix for duplicate analysis to control for repeatability. Samples from the river bed upstream the factory (which were unpolluted except for low levels of PFHxS, see Figure 1 in the main manuscript) were used for spiking experiments to calculate recoveries. Standards and

internal standards were added in small volumes (150 ul in total) to wet sediment. Acetonitrile was added after ten minutes for extraction. Recoveries of QA samples (matrix matched standard addition samples) in the present work were satisfactory (within the range of 70-110%). Recoveries and LOQ for individual PFAS are reported in Table S3. LOQ were between 0.1-0.5 ng g^{-1} or ng L^{-1} except for the sulfonamido/fluorotelomer alcohols, where the LOQ were higher, i.e. 2 ng g^{-1}. LOQ for PFAS screened for using exact mass and retention times from authentic standards were assumed based on closely related analogues.

As the whole lake is polluted by PFAS (see Figure S3), the use of a reference site in the lake system was not possible. The bottles for the water samples were rinsed with water from the sampling area before taking the sample. Water samples were stored in clean and closed HDPE bottles. Sediment samples were kept in clean and closed burnt glass jars. Abiotic samples were kept in an insulated box and brought to the laboratory within 24 hours of sampling. For biota samples, whole organisms were carefully wrapped in three layers of clean aluminium foil and put in a clean plastic bag (polyethylene), before being frozen at - 20 °C. Frozen biota samples were sent to the laboratory (in a sealed, insulated box) for further sample treatment and analysis. Dissections were performed in the laboratory to avoid contamination during sampling and transport. Clean nitrile gloves were used during sampling. Outdoor clothes that could contain PFAS in the fabric and equipment with Teflon surfaces were avoided.

Statistics and data analysis

The data is presented as means along with standard error of the mean (SEM). Concentrations below the LOQ were assigned values of half the LOQ unless otherwise stated.

Sediment-water partitioning coefficients (K_D values)

Sediment-water partitioning coefficients (K_D values, L kg^{-1}) were calculated for pore water and sediments, as follows:

$$K_d = \frac{C_S}{C_{PW}} \qquad \text{(eq I.)}$$

Where C_S is the sediment concentration (µg kg^{-1} d.w.) and C_{PW} is the pore water concentration (µg L^{-1}). K_D values were calculated from sediment and pore water (extracted from the same sediments) specific for the sample location.

Calculation of organic carbon-water partitioning coefficients **(K_{OC})**

K_{OC} values (L kg^{-1}) were calculated using linear regression to calculate the relationship between PFAS concentrations in pore water and content of organic carbon in sediments as reported previously (Milinovic et al., 2015), and shown in equation II.

$$K_d = K_{OC} \times f_{OC} + K_{d,MINERAL} \quad \text{(eq II.)}$$

302

303 Fluorine mass balance

304 Extractable organic fluorine (EOF) was compared against the sum of fluorine from target PFAS to
305 evaluate the extent of PFAS not accounted for by target analysis. Concentrations of targeted PFAS were
306 converted into fluorine concentrations using equation III:

$$C_F = n_F \frac{MW_F}{MW_{PFAS}} C_{PFAS} \quad \text{(eq III.)}$$

307 Where C_F is the fluorine concentration of the specific PFAS (μg kg^{-1}), n_F is the number of fluorine atoms
308 in the specific PFAS, MW_F is the molecular weight of fluorine (g mol^{-1}), MW_{PFAS} is the molecular weight
309 of the specific PFAS (g mol^{-1}), and C_{PFAS} is the detected concentration of the specific PFAS (μg kg^{-1}).

310 Statistics

311 Statistical analysis was carried out using R version 3.4.2; R Core Team; Vienna, Austria (R Core Team,
312 2017), Packages olsrr (Hebbali, 2018), agricolae (de Mendiburu, 2019), factoextra (Kassambara and
313 Mundt, 2017) and FactoMineR (Lê et al., 2008).

314 Σ detected PFAS in sediment and fish livers, proportions of FTS and preFOS in perch livers and fractions
315 of L-PFOS in pore water and perch livers were not normally distributed according to the Shapiro-Wilk
316 w-test (function: shapiro.test). Therefore, the non-parametric Kruskal-Wallis test and Bonferroni
317 correction (package: agricolae (de Mendiburu, 2019), functions: shapiro.test, kruskal.test, kruskal)
318 were used to test significant differences.

319 Differences in PFAS profiles between sediments from different areas (and the paper plate) were
320 evaluated using Principal Components analysis (PCA) (packages factoextra (Kassambara and Mundt,
321 2017) and FactoMineR (Lê et al., 2008), functions: prcomp, fviz_pca_ind, and fviz_pca_var).

322 Concentrations in biota are given on wet weight basis (w.w.). Averages in the present work are
323 reported with the standard error of the mean (SEM). Concentrations below the LOQ were assigned
324 values of half the LOQ except for PFAS profiles (i.e. percentages of the sum detected PFAS) for which
325 values below the LOQ were set to 0 (including for the PCA).

326 Modeling

327 *The Tyrifjorden model*

328 The model is referred to as the Tyrifjorden model. It is a simplified model of the Drammensfjord model
329 (Arp et al., 2014), which is a two-box water-sediment model that allows PFAS (or other contaminant)

emissions to change within specified time-intervals following a first-order rate constant. The water domain describes all transport and transformation processes in the water phase over the entire lake, including interaction with the atmosphere, the sediment domain describes all transport and transformation processes in the sediment phase, including deep sediment burial. These domains are modelled following coupled linear differential equations (Schwarzenbach et al., 2003) to account for the interdependency of sediment and water processes:

(eq IV.)

$$\frac{\mathrm{d}C^{\mathrm{w}}_{\mathrm{w}\,total}}{\mathrm{d}t} = k_{\mathrm{w}}C^{\mathrm{in,river}}_{\mathrm{w\,total}} + \frac{C_{\mathrm{p}}F_{\mathrm{p\,dep}}}{h} + k_{\mathrm{aw}}\frac{C_{\mathrm{a}}}{D_{\mathrm{aw}}} - (k_{\mathrm{w}} + k^{*}_{\mathrm{aw}} + k^{*}_{\mathrm{s}} + k_{\mathrm{sedex}} + k^{\mathrm{w}}_{\mathrm{r}})C^{\mathrm{w}}_{\mathrm{w\,total}} + \frac{k_{\mathrm{sedex}}}{f^{\mathrm{w}}_{\mathrm{w}}K_{\mathrm{D}}}C^{\mathrm{s}}_{\mathrm{sed}}$$

(eq V.)

$$\frac{\mathrm{d}C^{\mathrm{s}}_{\mathrm{sed}}}{\mathrm{d}t} = \left(\frac{1}{m_{\mathrm{sed}}}\right)(v_{\mathrm{sed}}f^{\mathrm{w}}_{sus\ sed} + v_{\mathrm{sedex}})C^{\mathrm{w}}_{\mathrm{w\,total}} - \left(\beta\frac{v_{\mathrm{sed}}}{m_{\mathrm{sed}}}r^{\mathrm{w}}_{\mathrm{sus\,sed}} + \frac{v_{\mathrm{sedex}}}{m_{\mathrm{sed}}f^{\mathrm{w}}_{\mathrm{w}}D_{\mathrm{D}}} + k^{\mathrm{sed}}_{\mathrm{r}}\right)C^{\mathrm{s}}_{\mathrm{sed}}$$

Where $C^{\mathrm{w}}_{\mathrm{w\,total}}$ (µg L^{-1}) and $C^{\mathrm{s}}_{\mathrm{sed}}$ (µg kg^{-1}) represent the *total* water concentration (freely-dissolved phase plus particle/colloid bound) and *total* sediment concentration (sediment plus freely-dissolved porewater), averaged over the entire water volume in the lake without area L6 and first 1 cm of sediment of the entire lake except area L6, respectively. As equations IV and V are coupled, the equations are solved so that the value of $C^{\mathrm{w}}_{\mathrm{w\,total}}$ are the same in equations IV and V at any given time point, and the same applies for $C^{\mathrm{s}}_{\mathrm{sed}}$. Explanations for the different components of the model are shown in Table S5 and Figure S6.

In equation IV, the kinetic rate constants (s^{-1}) k_{w}, k_{aw}, k^{*}_{aw}, k^{*}_{s}, k_{sedex}, $k^{\mathrm{w}}_{\mathrm{r}}$ describe respectively the water flushing rate (i.e. Q_{river}/V, where Q_{river} is the flow rate of the inflowing river, and V is the water volume of the lake), air-water transfer rate, air-water transfer rate at steady state, sediment deposition removal rate at steady state, net sediment-water exchange rate due to diffusion and resuspension, and finally ($k^{\mathrm{w}}_{\mathrm{r}}$) is the transformation rate in water (set to 0 for PFAS), respectively.

In equation V, which describes changes in $C^{\mathrm{s}}_{\mathrm{sed}}$ with time, the kinetic terms are the velocity of particle settling (v_{sed} (m s^{-1}) sediment-water-exchange due to diffusion and sediment suspension (v_{sedex}) (m s^{-1}, and the sediment transformation rate constant ($k^{\mathrm{sed}}_{\mathrm{r}}$). Additional terms are the mass of sediments in the sediment-mixing zone, m_{sed} (kg m^{-2}), the ratio of PFAS in suspended sediment compared to

water ($f_{\mathrm{sus\,sed}}^{\mathrm{w}}$), and the fraction of sediment bound contaminant that gets buried, β. More information about how these values are calculated are previously reported (Arp et al., 2014).

Regarding aerosol deposition, C_p describes the air-particle concentration and F_p the aerosol deposition flux. C_p was chosen arbitrarily to be low, as no air samples were obtained and atmospheric PFAS was assumed to be negligible.

Emissions were defined as the *total* (particulate-bound plus aqueous) PFAS concentration in inflowing water from the river, $C_{\mathrm{w\,total}}^{\mathrm{in,river}}$, and changes in emissions over time were defined as:

$$\frac{\mathrm{d}C_{\mathrm{w\,total}}^{\mathrm{in,river}}}{\mathrm{d}t} = k_{\mathrm{in}} C_{\mathrm{w\,total}}^{\mathrm{in,river}} \qquad \text{q VI.)}$$

Where k_{in} is a first-order rate constant describing changes in $C_{\mathrm{w\,total}}^{\mathrm{in,river}}$ with time (s^{-1}), resulting from changes in source emissions that drain into the fjord.

Here both of these terms are unknown and were therefore determined by calibration with the sediment core data from sampling area L1. The use of a single sediment core as representative of the entire lake is a large assumption that should be verified by additional sediment core data. However, the average of most compounds in the top two slices of the sediment core (0.5 and 1.5 cm below surface) is comparable to concentrations in top sediments from areas L1, L2, L3, and L4 (see Table S11, Table S13, and Figure S3, Figure S8, Figure S9, Figure S10, and Figure S11). The average and geometric mean for ΣPFCA, PFOS, preFOS, and ΣFTS in the entire lake without area L6 is comparable to the top two slices from the core, shown in Table S13. SAmPAP diester was not analysed for in most samples, as described above, and the distribution could therefore not be evaluated as the other PFAS. However, as previously reported (Langberg et al., 2020), additional analyses of SAmPAP diester was performed in a few samples in different areas: ranges of concentrations were 75.6-1872 and 2.1-16.1 in sediment samples from areas L1 and L3, respectively (Langberg et al., 2020). In comparison, SAmPAP diester concentrations were 20.4 and 23.8 μg kg^{-1} at 0.5 and 1.5 cm below the sediment surface respectively in the core. Variations in depth profiles in the different parts of the lake are not known, and the best assumption is that they are comparable to the core from area L1, as sediment core data provides information about historical emissions. Therefore, concentrations in top sediments indicate that extrapolation of the depth profile from the core to the entire lake is a reasonable assumption, however due to the proximity to the river mouth and the higher concentration compared to area L5, this likely represents an upper range of PFAS contamination in the lake.

Two eras of product emissions were modelled. The first era represents the use of Scotchban (sum of all SAmPAP diester, FOSE, PFSA, as well as PFCA prior to 1990) and the second the use of an FTS mixture

(sum of all FTS as well as PFCA after 1990). Each era of product emissions was divided into two phases: the time from introduction to the peak in emissions (phase 1) and start of the phase out followed by decreasing emissions (phase 2). For Scotchban, use started in 1950 (based on the sediment core) and peaked in 1990 (phase 1). Even though the use of PFAS in the production is believed to have started in the 1970s, deeper sediments (i.e. starting at 1950) was included to account for the major parts of the pollution, as the reason for the elevated PFAS levels in deeper sediments is believed to be due to factors such as sediment mixing or inaccuracies in dating. Following this, Scotchban was phased out and there was a lag in the decrease in emissions (phase 2, 1990-2017). For FTS, use began in 1994 and reached a peak in 2006 (phase 1) before being phased out and emissions declining (phase 2, 2006-2017).

This was done by scanning a range of different $C_{\mathrm{w\,total}}^{\mathrm{in,river}}$ and k_{in} values to match the sediment core values as close as possible, as determined by giving the least square in difference between the predicted and measured values.

PFAS and environmental properties used in the model are listed in Table S6 and Table S7. The concentrations used as input are presented in Table S8. This table presents the sum of compounds attributed to SAmPAP, EtFOSE and degradation products (termed Scotchban) as well as FTS and their related compounds (FTS mix). Also shown in this table is the extrapolated mass in the entire sediment basin of lake Tyrifjorden, based on the assumption that the concentration in the core is representative of the entire lake, using equation VII:

$$M_{\mathrm{Tyrifjord,sed}}\ (\mathrm{kg}) = \sum_{layer\ i}^{n} C_{sed,layer\ i}\, h_{layer\ i} A_{fjord} \rho_{\mathrm{bulk}} \qquad \text{(eq VII.)}$$

[kg in Tyrifjord sediment = $\sum 10^{-9}$ (concentration in layer (µg kg^{-1}))*(thickness of layer (m) * Area of the lake without area L6 (m^2) * bulk density (g m^{-3}))]

Supplementary tables

Table S1. Number of analysed abiotic samples from the lake and river

	River				Lake					
Sample type	Upstream	Factory area [a]	Downstream Fire station	River downstream sources	L1	L2	L3	L4	L5	L6
Sediment	2	9	4		14	15	21	12	7	25
Pore water and sediment				1	1 [b]	3		3	3	[b]
Sediment core					1					
Sediment trap	1	1		2	2				1	

[a] The sampling area downstream the factory is referred to as the factory area

[b] Water samples could not be analysed due to high levels of organic material

Table S2. Number analysed samples of fish liver from each sampling area

Species	**Factory area**	**Fire station**	**L1**	**L3**	**L5**	**L6**
Perch (*Perca fluviatilis*)	5	2	5	5	5	5
Pike (*Esox lucius*) [a]	4		2	3		5

[a] The data for perch are shown in the main paper while pike results are only shown in the SI as more individuals of perch were sampled and concentrations were higher than for pike.

Table S3. 45 PFAS quantified using authentic and internal standards (+ Br-PFOS), 19 PFAS screened for using exact mass and retention time from authentic standards, and three PFAS which were detected using exact mass and estimated retention time and quantified using the standard for a similar compound. Rows with PFAS that were detected in this work are filled with grey.

PFAS group	Acronym	Name	CAS	LOQ			Recovery [a]	
				Water (ng L^{-1})	Sediment (µg kg^{-1})	Biota (µg kg^{-1})	Mean (%)	St.dev
PFCA	PFBA	Perfluoro-n-butanoic acid	375-22-4	0,5	1,0	1,0	96.9	14.3
	PFPA	Perfluoro-n-pentanoic acid	2706-90-3	0.5	0.5	0.5	103.1	5.8
	PFHxA	Perfluoro-n-hexanoic acid	307-24-4	0.5	0.5	0.5	101.6	3.0
	PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.5	0.5	0.5	103.4	3.4
	PFOA	Perfluoro-n-octanoic acid	335-67-1	0.5	0.5	0.5	97.4	3.7
	PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.4	0.4	0.4	100.6	3.9
	PFDA	Perfluoro-n-decanoic acid	335-76-2	0.4	0.4	0.4	102.4	3.2
	PFUnDA	Perfluoro-n-undecanoic acid	2058-94-8	0.4	0.4	0.4	98.3	1.4
	PFDoDA	Perfluoro-n-dodecanoic acid	307-55-1	0.4	0.4	0.4	97.0	2.3
	PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	0.4	0.4	0.4	94.9	2.0
	PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	0.4	0.4	0.4	95.9	3.1
	PFPeDA [b, c]	Perfluoro-n-pentadecanoic acid			0.4	0.4		
	PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5		0.4	0.4	82.4	5.3
	PFODA	Perfluoro-n-octadecanoic acid	16517-11-6		0.4	0.4	69.8	4.4
PFSA	PFPrS [d]	Perfluoro-1-propanesulfonate		0.2	0.2	0.2		
	PFBS	Perfluoro-1-butanesulfonate	59933-66-3	0.1	0.1	0.1	96.1	2.0
	PFPeS	Perfluoro-1-pentanesulfonate	22767-49-3	0.1	0.1	0.1	95.1	4.8
	PFHxS	Perfluoro-1-hexanesulfonate	355-46-4	0.1	0.1	0.1	94.3	3.2
	PFHpS	Perfluoro-1-heptanesulfonate	22767-50-6	0.1	0.1	0.1	93.1	1.7
	PFOS	Perfluoro-1-octanesulfonate	4021-47-0	0.1	0.1	0.1	98.5	3.2
	PFNS	Perfluoro-1-nonanesulfonate	98789-57-2	0.1	0.1	0.1	94.2	2.3
	PFDS	Perfluoro-1-decanesulfonate	335-77-3	0.1	0.1	0.1	81.7	2.1
	PFDoDS	Perfluoro-1-dodecansulfonate	79730-39-5		0.2	0.2	74.4	3.5
	ipPFNS [d]	Perfluoro-7-methyloctanesulfonate		0.2	0.2	0.2		
	Br-PFOS [e]	PFOS branched isomers		0.2	0.2	0.2		
PreFOS	FOSA	Perfluoro-1-octanesulfonamide	754-91-6	0.1	0.1	0.1	98.3	4.9
	MeFOSA	N-methylPerfluoro-1-octanesulfonamide	31506-32-8	0.2	0.2	0.2	78.3	5.7
	EtFOSA	N-ethylPerfluoro-1-octanesulfonamide	4151-50-2	0.2	0.2	0.2	91.0	3.4
	MeFOSE	2-(N-methylPerfluoro-1-octanesulfonamido)-ethanol	24448-09-7	2	2	2	78.5	6.1
	EtFOSE	2-(N-ethylPerfluoro-1-octanesulfonamido)-ethanol	1691-99-2	2	2	2	90.9	3.8
	FOSAA	Perfluoro-1-octansulfonamidoacetic acid	2806-24-8	0.3	0.3	0.3	89.8	3.9
	MeFOSAA	2-(N-methylPerfluoro-1-octansulfonamido)acetic acid	2355-31-9	0.3	0.3	0.3	90.8	3.5
	EtFOSAA	2-(N-ethylPerfluoro-1-octansulfonamido)acetic acid	2991-50-6	0.3	0.3	0.3	97.9	3.3
FTS	4:2 FTS	1H,2H-Perfluorohexan sulfonate (4:2)	757124-72-4	0.3	0.3	0.3	95.7	3.7
	6:2FTS	1H,2H-Perfluorooctane sulfonate (6:2)	27619-97-2	0.3	0.3	0.3	93.0	3.6
	8:2 FTS	1H,2H-Perfluorodecan sulfonate (8:2)	39108-34-4	0.3	0.3	0.3	99.8	2.1
	10:2 FTS	1H,2H-Perfluorododecan sulfonate (10:2)	120226-60-0	0.3	0.3	0.3	86.5	2.5
	12:2 FTS [b, f]	1H,2H-Perfluorotetradecan sulfonate (12:2)		0.3	0.3	0.3		

	14:2 FTS[b, f]	1H,2H-Perfluorohexadecan sulfonate (14:2)		0.3	0.3	0.3		
	8-ClPFOS	8Cl-Perfluoro-1-octanesulfonate		0.2	0.2	0.2	94.5	4.6
	8:2 F53B	C_{10} H F_{16} Cl O_4 S		0.3	0.3	0.3	98.2	4.6
	6:2 F53B	C_8 H F_{16} Cl O_4 S	73606-19-6	0.3	0.3	0.3	93.5	3.6
	4:2 F53B	C_6 H F_{12} Cl O_4 S		0.3	0.3	0.3	96.4	1.8
	PFBPA	Perfluoro butylphosphonic acid	52299-24-8	0.5	0.5	0.5	97.0	4.3
	PFHxPA	Perfluoro hexyl phosphonic acid	40143-76-8	0.5	0.5	0.5	93.4	4.1
	PFPOA[d]	Perfluoro octyl phosphonic acid	40143-78-0	0.5	0.5	0.5		
	PFDPA[d]	Perfluoro decyl phosphonic acid	52299-26-0	0.5	0.5	0.5		
	6:2 PAP[d]	1H,1H,2H,2H-Perfluorooctyl phosphate	57678-01-0	0.5	0.5	0.5		
	8:2 PAP[d]	1H,1H,2H,2H-Perfluorodecyl phosphate	57678-03-2	0.5	0.5	0.5		
	6:2 diPAP	Bis (1H,1H,2H,2H-Perfluorooctyl phosphate)	57677-95-9	0.5	0.5	0.5	101.6	3.0
	8:2 diPAP	Bis (1H,1H,2H,2H-Perfluorodecyl phosphate)	678-41-1	0.5	0.5	0.5	109.7	6.0
	6:2/8:2 diPAP	Comb of 6:2 and 8:2 Perfluoroalkyl phoshate	943913-15-3	0.5	0.5	0.5	103.3	3.0
	10:2 diPAP[d]	Bis (1H,1H,2H,2H-Perfluorododecyl phosphate)	1895-26-7	0.5	0.5	0.5		
Other	6:2 FTOH[d]	2-Perfluorohexyl ethanol	647-42-7		2	2		
	8:2 FTOH[d]	2-Perfluorooctyl ethanol	678-39-7		2	2		
	10:2 FTOH[d]	2-Perfluorododecyl ethanol	865-86-1		2	2		
	6:2 FTCA[d]	2-Perfluorohexyl ethanoic acid (6:2 FTA)	53826-12-3	2	2	2		
	8:2 FTCA[d]	2-Perfluorooctyl ethanoic acid (8:2 FTA)	53826-12-3	2	2	2		
	10:2 FTCA[d]	2-Perfluorodecyl ethanoic acid (10:2 FTA)	53826-13-4	2	2	2		
	6:2 FTUCA[d]	2H-Perfluoro-2-octenoic acid (6:2 FTUA)	70887-88-6	2	2	2		
	8:2 FTUCA[d]	2H-Perfluoro-2-decenoic acid (8:2 FTUA)	70887-84-2	2	2	2		
	10:2 FTUCA[d]	2H-Perfluoro-2-dodecenoic acid (10:2 FTUA)	70887-94-4	2	2	2		
	PFHxSA[d]	Perfluoro-1-hexansulfonamide	41997-13-1	0.5	0.5	0.5		
	MeFHxSA	Perfluoro-1-hexansulfonamide	68259-15-4	0.5	0.5	0.5	93.4	6.8
	Gen X[d]	Perfluoro(2-methyl-3-oxahexanoate)	62037-80-3	0.5	0.5	0.5		
	ADONA[d]	Dodecafluoro-3H-4,8-dioxanonanoat	958445-44-8	0.5	0.5	0.5		
	PFECHS	Perfluoroethylcyclohexanesulfonate	67584-42-3	0.5	0.5	0.5	95.2	3.1
	SAmPAP diester[g]	bis[2-[N-ethyl(heptadecafluorooctane)-sulfonylamino]ethyl] phosphate	30381-98-7	0.5	0.5	0.5	77.4	12.9

[a] Recoveries shown in the table were calculated based on spiking of sediment samples, n=5.
[b] Standard was not available, detected using exact mass and estimated retention time.
[c] Quantified using the standard for PFHxDA.
[d] Screened for using exact mass and retention time from an authentic standard. The LOQ was assumed similar to the LOQ for a closely related as PFAS with similar physiochemical properties (as the authentic standard was not available when performing the spiking experiment for calculating recoveries).
[e] Quantified using the standard for L-PFOS.
[f] Quantified using the standard for 10:2 FTS.
[g] Detected using exact mass and estimated retention time in the sediment core and the sediment samples used for analyses of EOF. A standard was acquired later and used for quantification, see materials and methods.

412 Table S4. 25 PFAS screened for using exact mass and estimated retention time, but not detected

Acronym	Name	CAS
PFHpDA	Perfluoro-n-heptadecanoic acid	
PFUnDS	Perfluoro-1-undecansulfonate	
PFTrDS	Perfluoro-1-tridecansulfonate	
PFTeDS	Perfluoro-1-tetradecansulfonate	
6:2 53B	C8 H F17O4 S	754925-54-7
12:2 FTOH	2-Perfluorododecyl ethanol	39239-77-5
PFBSA	Perfluoro-1-butansulfonamide	30334-69-1
PFPeSA	Perfluoro-1-pentansulfonamide	82765-76-2
PFHpSA	Perfluoro-1-heptansulfonamide	82765-77-3
MeFBSA	Perfluoro-1-butansulfonamide	68298-12-4
MeFPeSA	Perfluoro-1-pentansulfonamide	68298-13-5
MeFHpSA	Perfluoro-1-heptansulfonamide	68259-14-3
EtFBSA	Perfluoro-1-butansulfonamide	40630-67-9
EtFPeSA	Perfluoro-1-pentansulfonamide	162682-16-8
EtFHpSA	Perfluoro-1-heptansulfonamide	68957-62-0
MeFBSE	2-(N-mehylperfluoro-1-butansulfonamido)-ethanol	34454-97-2
MeFPeSE	2-(N-methylperfluoro-1-pentansulfonamido)-ethanol	68555-74-8
MeFHxSE	2-(N-methylperfluoro-1-hexansulfonamido)-ethanol	68555-75-9
MeFHpSE	2-(N-methylperfluoro-1-heptansulfonamido)-ethanol	68555-76-0
EtFBSE	2-(N-ethylperfluoro-1-butansulfonamido)-ethanol	34449-89-3
EtFPeSE	2-(N-ethylperfluoro-1-pentansulfonamido)-ethanol	68555-72-6
EtFHxSE	2-(N-ethylperfluoro-1-hexansulfonamido)-ethanol	34455-03-3
EtFHpSE	2-(N-ethylperfluoro-1-heptansulfonamido)-ethanol	68755-73-7
EtFHxSA	Perfluoro-1-hexansulfonamide	87988-56-5
FOSE	Perfluoro-1-octanesulfonamido-ethanol	10116-92-4

413 Table S5. Components of the two-box linear water-sediment model.

Term	Explanation	*Figure S6*	Simplified Symbol
	Water box (Equation III)		
$k_{\mathrm{w}} C_{\mathrm{w\ total}}^{\mathrm{in,river}}$	gain in water concentration from the river	1a+b	J_T
$\frac{C_{\mathrm{p}} F_{\mathrm{p\ dep}}}{h}$	gain in water concentration from deposition of air particles	2a	(µg m^{-3} y^{-1})
$k_{\mathrm{aw}} \frac{C_{\mathrm{a}}}{K_{\mathrm{aw}}}$	gain or loss in water concentration due to air-water exchange of freely-dissolved compounds	2b	sum of all water input and atmosphere exchange
$(k_{\mathrm{w}} + k_{\mathrm{aw}}^{*} + k_{\mathrm{s}}^{*} + k_{\mathrm{sedex}} + k_{\mathrm{r}}^{\mathrm{w}})$	Rate constants for dynamic processes influencing the water concentration, which are from left to right a) water in the lake renewing itself, b) air-water exchange at steady state, c) sediment deposition, d) sediment exchange by diffusion and resuspension and e) transformation reactions	3g, 2b, 3a, 3b+c+d, 3e	k_{11} (y^{-1}) sum of water rate constants influencing $C_{w\ total}^{w}$
$\frac{k_{\mathrm{sedex}}}{f_{\mathrm{w}}^{\mathrm{w}} K_{\mathrm{D}}}$	Gain or loss in water concentration due to sediment-water exchange through diffusion and resuspension reactions	3b+3c+3d	k_{12} (kg m^{-3} y^{-1}) sum of sediment rate constants influencing $C_{w\ total}^{w}$
	Sediment box (Equation IV)		
$\left(\frac{1}{m_{\mathrm{sed}}}\right)(v_{\mathrm{sed}} f_{\mathrm{sus\ sed}}^{\mathrm{w}})$	gain or loss in sediment concentration due to deposition from water phase	3a	k_{21} (kg^{-1} m^{3} y^{-1}) sum of kinetic factors in water influencing on C_{sed}^{s}
$\left(\frac{1}{m_{\mathrm{sed}}}\right)(v_{\mathrm{sedex}})$	gain or loss in sediment concentration due to sediment-water exchange or sediment resuspension	3b + 3d	
$(\beta \frac{v_{\mathrm{sed}}}{m_{\mathrm{sed}}} r_{\mathrm{sus\ sed}}^{\mathrm{w}}) C_{\mathrm{sed}}^{\mathrm{s}}$	loss in sediment due to permanent burial	4a	k_{22} (y^{-1}) sum of kinetic factors in sediment influencing C_{sed}^{s}
$\frac{v_{\mathrm{sedex}}}{m_{\mathrm{sed}} f_{\mathrm{w}}^{\mathrm{w}} K_{\mathrm{D}}} C_{\mathrm{sed}}^{\mathrm{s}}$	gain or loss in sediment due to exchange with water	3b + 3d	
$(k_{\mathrm{r}}^{\mathrm{sed}}) C_{\mathrm{sed}}^{\mathrm{s}}$	loss in sediment due to transformation reactions	4c	

414 Table S6. Scotchban and FTS mix properties used in the model

Parameter	Units	Scotchban	FTMAP	Reference / Comments
M.W.	(g mol^{-1})	585	628	EtFOSAA (585), SAmPAP diester (1204), 10:2 FTS (628), 10:2 FTMAP (1250)
log K_{aw}	(-)	-12	-13.5	Air-water partitioning is essentially negligible, value for Scotchban based on that of PFOS and FTMAP from 10:2 FTS (Wang et al., 2011), adjusted for pH 7 (pKa -3.41 for PFOS and -2.86 for 10:2 FTS)
log K_{ow}	(-)	See D_{TOC}		Assumed same as D_{TOC}
log K_{TOC}	(L kg$^{-1}_{\mathrm{TOC}}$)	5.0, 7.0, 9.0		Ranging from that measured in lake Tyrifjorden for EtFOSAA and 10:2 FTS in this study (both 5.0) to larger values for SAmPAP diester/commercial Scotchban mixture and 10:2/12:2 FTMAP
D_{w}	(cm^2 s^{-1})	2.93E-06	2.78E-06	(Schwarzenbach et al., 2003) p814, based on M.W.
Sc_{w}	(-)	3.05E+03	3.21E+03	(Schwarzenbach et al., 2003) p919, based on M.W.
v_{a}	(cm s^{-1})	2.02E-01	2.02E-01	(Schwarzenbach et al., 2003) p919, based on M.W.
v_{w}	(cm s^{-1})	2.88E-04	2.81E-04	(Schwarzenbach et al., 2003) p919, based on M.W.
v_{aw}	(cm s^{-1})	1.76E-13	1.76E-13	(Schwarzenbach et al., 2003) p919, based on M.W.
$k_{\mathrm{r}}^{\mathrm{w,surface}}$	(1 h^{-1})	0	0	Assumed negligible
$k_{\mathrm{r}}^{\mathrm{w,deep}}$	(1 h^{-1})	0	0	Assumed negligible
$k_{\mathrm{r}}^{\mathrm{sed}}$	(1 h^{-1})	0	0	Assumed negligible

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417 Table S7. Model properties and uncertainties

Parameter	Units	Value	Error	Reference	Comments
		Sediment Box Properties			
A_{fjord}	m^2	125000000	12500	Present study	Determined with arcmap
$A_{\text{fjord\_60m}}$	m^2	58400000	5840	Present study	Determined with arcmap
$F_{\text{sed}}^{\text{fjord}}$	$kg_{sed}\ m_{sed}^{-2}\ y^{-1}$	0.47	0.14	present study	
$f_{\text{TOC}}^{\text{s, fjord}}$	$kg_{TOC}\ kg_{sed}^{-1}$	0.029	0.006	present study	
ρ_{sed}	$kg_{sed}\ m_{sed}^{-3}$	2600	100	Assumed	typical value
n_{sed}	-	39%	22%	present study	
ρ_{bulk}	$kg_{sed}\ m_{sed}^{-3}$	1620	890	present study	
$z_{\text{mix}}^{\text{fjord}}$	m	0.1	0.01	Defined	1 cm mixing depth for conformity with sediment core resolution
$\delta_{\text{bl}}^{\text{fjord}}$	m	7.00E-04	2.00E-04	(Eek et al., 2010)	
$\mu_{\text{res}}^{\text{fjord}}$	$kg_{sed}\ m_{sed}^{-2}\ y^{-1}$	0.00E+00	0.00E+00		Assumed negligible
β	-	9.00E-01	3.00E-02		typical value
		Water Box Properties			
h_{fjord}	m	93	18.6		
h_{rain}	$m\ y^{-1}$	1.02	0.65		Asker station (19710, Jan '83-Jan'20)
Q_{river}	$(m^3 s^{-1})$	151.3	95.2	Present study	River inflow from Storelva (used data from stations in the two rivers upstream, Begna and Randselva - average between 01.01.1978 and 31.12.2019)
$Q_{\text{run-off}}^{\text{fjord}}$	$(m^3 s^{-1})$	2.65	1.69	www.eklima.no	Calculated from h_{rain} and A_{fjord}
$r_{\text{sus sed}}^{\text{river}}$	$g\ m^{-3}$	1.7	1.5		Assummed similar to nearby Drammen river
$r_{\text{sus sed}}^{\text{runoff,fjord}}$	$g\ m^{-3}$	0	0		
$r_{\text{sus sed}}^{\text{w,surface,fjord}}$	$g\ m^{-3}$	5	4.9	(Arp et al., 2014)	Assummed similar to nearby Drammen river

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Table S8. Input concentrations and total mass of PFAS in lake Tyrifjorden sediment (area L6 is not included in calculations of total mass)

Depth of sediment (cm)	Sediment thickness (cm)	Date (y)	Concentration in core		Total mass in lake bed	
			Scotchban[a)] ($ng\ g^{-1}$)	FTS mix[b)] ($ng\ g^{-1}$)	Scotchban[a)] (kg)	FTS Mix[b)] (kg)
0-1	1.00	2017	24.9	68.1	25	139
1-2	1.00	2012	35.0	206.3	71	420
2-3	1.00	2006	274.8	760.1	559	1547
3-4	1.00	1999	1181	94.1	2404	192
4-5	1.00	1994	1182	21.7	2404	44
5-6	1.00	1990	2811	0.0	5720	0
6-7	1.00	1984	3730	0.0	7591	0
7-8	1.00	1978	3315	0.0	6746	0
8-9	1.00	1972	2329	0.0	4740	0
9-10	1.00	1967	931.9	0.0	1896	0
10-11	1.00	1963	2368	0.0	4820	0
11-12	1.00	1958[c)]	1552	0.0	3158	0
12-13	1.00	1952[c)]	189.4	0.0	385	0
13-14	1.00	1943[c)]	66.3	0.0	135	0
14-14.5	0.50	1934[c)]	2.4	0.0	5	0
0-14.5	**14.40**	**all years**	**-**	**-**	**40 660**	**2 341**

a) Scotchban is considered sum of all SAmPAP diester, preFOS, PFSA, as well as PFCA (prior to 1990)

b) FTS is mix is considered the sum of all, FTS as well as PFCA (after 1990)

c) It is unlikely/not possible that so much PFAS was used at this time, PFAS in this interval may be due to inaccuracy of dating or (less likely) vertical migration in the sediment core

Table S9. Concentrations in water from the creek downstream the landfill and the storm water system at the fire station (ng L^{-1}). For the fire station, concentrations are shown as mean ± the standard error of mean (SEM). Only PFAS showing a concentration above the LOQ in at least one sample are shown.

	Landfill (n=1)	Fire Station (n=2)
PFPA	41	4199 ±1735
PFHxA	41	9892 ±6168
PFHpA	99	2210 ±1645
PFOA	473	3260 ±1253
PFNA	34	155 ±50
PFDA	7.6	12 ±0.7
PFBS	5.6	701 ±260
PFPeS	2.7	695 ±231
PFHxS	12	2811 ±364
PFHpS	4.9	873 ±57
L-PFOS	214	3741 ±3034
Br-PFOS	119	3854 ±211
PFNS	<0.1	85 ±46
PFDS	<0.1	10 ±6.8
FOSA	107	154 ±50
EtFOSA	15	<0.3
FOSAA	67	4.0 ±1.6
EtFOSAA	343	0.5 ±0.5
6:2 FTS	1.1	149 ±1.0
8:2 FTS	4.2	3.6 ±2.3
10:2 FTS	3.8	<0.3
12:2 FTS	0.6	<0.3

Table S10. Concentrations in sediment from the creek downstream the landfill, the storm water system at the fire station, and concentrations in a product from the factory (paper plate) (μg kg^{-1} d.w.). For the fire station, concentrations are shown as mean ± the standard error of mean (SEM). Only PFAS showing a concentration above the LOQ in at least one sample are shown.

	Landfill (n=1)	Fire station (n=2)	Paper plate (n=1)
PFPA	<0.5	<0.5	255
PFHxA	<0.5	<0.5	3713
PFHpA	<0.5	<0.5	742
PFOA	<0.5	2.5 ±2.5	7156
PFNA	<0.4	<0.4	349
PFDA	<0.4	<0.4	4285
PFUnDA	<0.4	<0.4	139
PFDoDA	<0.4	<0.4	1255
PFTrDA	<0.4	<0.4	57
PFTeDA	<0.4	<0.4	659
PFPeDA	<0.4	<0.4	5.6
PFHxDA	<0.4	<0.4	179
PFBS	<0.1	1.4 ±1.2	<0.1
PFPeS	<0.1	1.6 ±1.3	<0.1
PFHxS	<0.1	19 ±17	<0.1
PFHpS	<0.1	2.3 ±2.0	<0.1
PFOS	5.2	285 ±228	<0.1
Br-PFOS	1.1	57 ±48	<0.1
PFNS	<0.1	1.5 ±1.3	<0.1
PFDS	<0.1	1.1 ±0.9	<0.1
PFDoDS	<0.1	0.7 ±0.5	<0.1
FOSA	1.4	17 ±14	<0.1
EtFOSA	0.7	<0.3	<0.3
EtFOSE	10	<0.2	<0.5
FOSAA	4.6	<0.3	<0.3
EtFOSAA	35	0.7 ±0.7	<0.3
6:2 FTS	0.0	6.3 ±5.3	71
8:2 FTS	389	<0.3	1091
10:2 FTS	107	2.0 ±1.5	399
12:2 FTS	28	1.6 ±1.2	81
14:2 FTS	3.5	<0.3	10

Table S11. Concentrations in sediments at the different sampling areas, and the top two slices from the sediment core from area L1 (mean concentrations at depth 0.5 and 1.5 cm shown in Table S20) (μg kg^{-1} d.w.). Concentrations are shown as mean ± the standard error of mean (SEM). LOQ/2 is reported for values below the LOQ. Missing values for SEM denotes that no concentrations above the LOQ were detected for the specific substance at that sampling area.

PFAS	Sampling areas									Core L1
	Upstream Factory Area		Fire Station	L1	L2	L3	L4	L5	L6	
PFHxA	0.3	1.1±0.5	0.3	0.3	0.6±0.2	0.8±0.2	0.9±0.3	0.3	0.3±0.1	3.2±0.01
PFHpA	0.3	1.4±0.8	0.3	0.3	0.3	0.3	0.3	0.3	0.3	17.9±2.0
PFOA	0.3	10.3±8.9	0.3	0.3	0.3	0.3	0.3	0.3	0.3	20.9±7.5
PFNA	0.2	7.7±7.3	0.2	0.2	0.2	0.2	0.4±0.1	0.2	0.2	1.7±0.3
PFDA	0.2	77.1±73.5	0.2	0.5±0.1	2.0±0.4	2.5±0.4	0.9±0.3	0.5±0.1	0.2	1.5±0.6
PFUnDA	0.2	22.1±20.5	0.2	0.3±0.1	1.7±0.3	1.6±0.3	0.5±0.2	0.5±0.2	0.2	0.8±0.2
PFDoDA	0.2	23.3±20.3	0.2	0.9±0.2	3.3±0.6	2.5±0.5	0.7±0.2	0.7±0.3	0.2	1.1±0.5
PFTrDA	0.2	3.5±2.7	0.2	0.3±0.0	0.9±0.1	0.5±0.1	0.2±0.03	0.3±0.1	0.2	0.6±0.04
PFTeDA	0.2	25.9±22.3	0.2	0.7±0.2	2.5±0.4	0.7±0.3	0.4±0.1	0.5±0.2	0.2	0.5±0.2
PFPeDA	0.2	1.6±1.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
PFHxDA	0.2	3.1±2.6	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
PFBS	0.1	0.1	0.1	0.1	0.1±0.01	0.1	0.1	0.1	0.1	0.1
PFHxS	1.8±0.3	0.4±0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
PFHpS	0.1	2.4±2.4	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
PFOS	0.1	198.7±197.7	0.1	1.0±0.3	4.9±1.2	8.4±1.6	6.7±2.0	1.5±0.7	0.3±0.02	0.5±0.1
Br-PFOS	0.1	75.5±75.2	0.1	0.1±0.02	0.3±0.1	0.4±0.1	0.2±0.1	0.2±0.1	0.1	[a]
PFDS	0.1	0.7±0.7	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
PFDoDS	0.1	0.3±0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
FOSA	0.1	15.1±12.2	0.1	0.7±0.2	2.4±0.8	3.0±0.5	1.8±1.2	0.7±0.4	0.1	0.1
MeFOSA	0.2	0.2	0.2	0.2	0.2±0.02	0.2	0.2	0.2	0.2	0.2
EtFOSA	0.2	7.6±5.4	0.2	0.2±0.03	0.5±0.1	0.2±0.03	0.3±0.1	0.2±0.1	0.2	0.2
EtFOSE	1.0	348.0±268.6	1.0	15.8±5.6	19.6±5.8	1.0	9.2±5.9	3.1±2.1	1.0	2.5
FOSAA	0.2	3.0±2.1	0.2	1.2±0.2	2.8±0.6	0.5±0.1	1.0±0.4	0.6±0.3	0.2	2.2±0.7
MeFOSAA	0.2	0.2	0.2	0.2	0.2±0.02	0.2	0.2	0.2	0.2	0.2
EtFOSAA	0.2	286.2±206.4	0.2	37.9±11.6	15.4±3.8	1.9±0.4	4.4±2.0	2.5±1.6	0.4±0.1	5.2±2.6
6:2 FTS	0.2	1.0±0.7	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.9±0.8
8:2 FTS	0.2	281.3±235.0	0.2	2.2±0.5	5.9±1.2	2.6±0.7	0.9±0.3	0.7±0.4	0.3±0.1	31.4±20.3
10:2 FTS	0.2	524.4±294.5	0.2	20.7±5.9	78.6±17.9	28.9±9.7	19.2±7.6	8.0±5.5	0.2±0.04	28.9±19.9
12:2 FTS	0.2	410.9±197.9	0.2	15.2±4.1	60.6±16.5	12.0±3.6	16.6±5.9	5.0±3.1	0.2±0.04	23.5±14.8
14:2 FTS	0.2	117.2±75.1	0.2	0.7±0.2	3.5±1.2	0.5±0.2	1.3±0.4	0.4±0.2	0.2	4.3±2.6
∑PFAS 29	7.1±0.3	2450.2±1530	5.3 [b]	100.5±22.4	207.5±41.5	69.6±17.2	67.4±21.6	27.4±14.3	6.1±0.2	148.8±72.3

[a] Not analysed for Br-PFOS

[b] No PFAS were detected above the LOQ, and LOQ/2 was used for all PFAS in these samples.

Table S12. Sediment particle size distribution and total organic carbon content determined after extraction of pore water (locations of sampling stations are shown in Figure S4).

Sediment characteristics		Sample station										
		River	L1	L3-1	L3-2	L3-3	L4-1	L4-2	L4-3	L5-1	L5-2	L5-3
Sand (>63 µm)	(%)	99.8	47.6	84.5	20.1	75.8	22.4	8.4	4.4	96.9	92.0	86.1
Silt (63-2 µm)	(%)	0.2	52.0	15.4	79.2	24.1	76.6	75.4	77.0	3.0	8.0	13.8
Clay (<2 µm)	(%)	0.1	0.3	0.1	0.6	0.1	1.0	16.1	18.5	0.1	0.1	0.1
TOC [a]	(%)	0.4	4.5	1.0	3.7	1.4	3.9	0.4	0.4	0.3	0.5	0.9

[a] TOC denotes percent organic carbon (dry weight)

Table S13. Comparison between sediment samples from the entire lake bed except area L6, and the top two samples from the core (0.5 and 1.5 cm below sediment surface) used to extrapolating PFAS mass in the lake and modelling (µg kg^{-1} d.w.).

	Lake		Core	
	Arithmetic mean	Geometric mean	0.5 cm	1.5 cm
ΣPFCA [a]	7.2 ±0.7	5.3	38.2	59.6
PFOS [b]	5.2 ±0.7	2.0	0.41	0.55
preFOS	27.1 ±4.8	11.7	9.6	16.1
ΣFTS	61.9 ±10.8	19.5	30.9	148

[a] Concentrations of the C6-C8 PFCA are higher in top slices from the core compared to the other sediment samples and the reason for this is not known

[b] PFOS was the only PFSA above the LOQ in the core

Table S14. Concentrations (μg kg^{-1} d.w.) in sediment traps. Only PFAS detected above the LOQ in at least one sample are included. LOQ/2 is reported for values below the LOQ. Missing values for SEM denotes that no concentrations above the LOQ.

PFAS	Sampling area				
	Upstream factory (n=1)	Factory area (n=1)	River downstream sources (n=2)	L1 (n=2)	L5 (n=1)
PFHxA	0.3 [a]	0.3 [a]	0.7 ±0.5	0.3 [a] ±0.0	0.3 [a]
PFHpA	0.3 [a]	0.3 [a]	1.8 ±1.6	1.2 ±0.2	0.3 [a]
PFOA	0.3 [a]	0.3 [a]	2.7 ±2.5	3.7 ±1.2	8.4
PFNA	0.2 [a]	0.2 [a]	0.8 ±0.6	0.2 [a] ±0.0	0.2 [a]
PFDA	0.2 [a]	0.2 [a]	0.5 ±0.3	1.8 ±0.1	2.4
PFUnDA	0.2 [a]	0.2 [a]	0.2 [a] ±0.0	1.4 ±0.1	1.2
PFDoDA	0.2 [a]	0.2 [a]	0.2 [a] ±0.0	2.2 ±0.2	1.8
PFHxS	3.1	0.1 [a]	0.1 ±0.0	0.1 [a] ±0.0	0.1 [a]
PFOS	0.1 [a]	1.0	0.5 ±0.3	2.3 ±0.0	2.3
FOSA	0.1 [a]	0.1 [a]	0.1 [a] ±0.0	0.4 ±0.1	0.1 [a]
EtFOSE	1.0 [a]	1.0 [a]	4.4 ±1.4	8.4 ±1.1	2.6
EtFOSAA	0.2 [a]	0.2 [a]	0.3 ±0.1	0.2 [a] ±0.0	0.2 [a]
8:2 FTS	0.2 [a]	0.2 [a]	0.2 [a] ±0.0	0.6 ±0.5	0.2 [a]
10:2 FTS	0.2 [a]	0.2 [a]	0.2 [a] ±0.0	2.6 ±0.7	0.2 [a]
12:2 FTS	0.2 [a]	0.2 [a]	3.5 ±1.1	16 ±1.2	6.4
14:2 FTS	0.2 [a]	0.2 [a]	1.4 ±0.4	6.5 ±0.4	0.2

[a] Concentration(s) below the LOQ

Table S15. Concentrations (ng L^{-1}) in pore water at the different sampling areas. Mean ± the standard error of mean (SEM) for triplicate samples (locations of sampling stations are shown in Figure S4). Only PFAS showing a concentration above the LOQ in at least one sample are shown.

PFAS	Sampling area				
	River	L1	L3	L4	L5
PFPA	9.9 ±2.9	112.2 ±0.1	14.3 ±3.8	43.4 ±9.3	60.0 ±17.8
PFHxA	17.7 ±6.6	146.3 ±17.0	32.1 ±5.7	85.5 ±18.6	65.1 ±15.7
PFHpA	34.3 ±11.3	356.2 ±39.4	80.6 ±7.2	260.9 ±48.3	104.9 ±13.9
PFOA	53.4 ±9.5	1245.9 ±64.4	122.3 ±12.2	262.3 ±51.5	298.9 ±70.7
PFNA	4.1 ±0.4	18.2 ±1.3	10.2 ±1.7	44.4 ±9.4	32.8 ±6.9
PFDA	2.2 ±0.6	29.3 ±2.5	2.9 ±0.7	14.9 ±4.4	22.4 ±4.6
PFBS	0.3 ±0.1	0.4 ±0.3	0.5 ±0.1	1.0 ±0.2	2.0 ±0.4
PFHxS	0.2 [a]	8.4 ±5.2	1.3 ±0.2	3.8 ±0.5	0.3 ±0.1
PFHpS	<0.1 [b]	1.0 ±0.5	1.0 ±0.1	3.8 ±1.2	0.1 ±0.03
PFOS	6.4 ±1.1	61.1 ±19.0	135.7 ±19.7	392.3 ±52.9	65.0 ±10.2
Br-PFOS	2.4 ±0.3	12.3 ±3.5	24.9 ±1.9	85.6 ±4.8	6.8 ±0.4
FOSA	0.2 [a]	4.8 ±0.6	<0.1 [b]	0.7 [a]	3.4 [a]
FOSAA	<0.3 [b]	13.6 ±5.2	<0.3 [b]	<0.3 [b]	<0.3 [b]
EtFOSAA	<0.3 [b]	47.8 ±1.4	<0.3 [b]	<0.3 [b]	<0.3 [b]
8:2 FTS	<0.3 [b]	16.6 ±1.4	<0.3 [b]	5.3 [a]	<0.3 [b]
10:2 FTS	<0.3 [b]	8.5 ±2.8	<0.3 [b]	1.1 [a]	<0.3 [b]
12:2 FTS	<0.3 [b]	5.3 ±0.5	<0.3 [b]	<0.3 [b]	<0.3 [b]

[a] Only one concentration above LOQ

[b] All concentrations below the LOQ

458 Table S16. Concentrations in perch livers (μg kg^{-1} w.w.).

	Sampling area					
PFAS	Factory area	Fire Station	L1	L3	L5	L6
PFHxA	0.8 ±0.2	0.3 [b]	0.3 [b]	1.2 ±0.6	0.3 [b]	0.3 [b]
PFHpA	0.3 [b]	0.3 [b]	0.3 [b]	7.1 ±2.7	0.3 [b]	1.2 ±1.0
PFOA	0.3 [b]	0.3 [b]	0.3 [b]	7.3 ±3.0	1.9 ±1.0	1.0 ±0.7
PFNA	0.3 [b]	0.3 ±0.1	0.3 [b]	3.6 ±1.2	1.2 ±0.3	0.5 ±0.2
PFDA	25 ±4.2	11.5 ±6.4	9.3 ±3.9	29 ±17	23 ±3.8	16 ±0.8
PFUnDA	14 ±2.9	14 ±4.1	12 ±4.8	47 ±29	27 ±8.1	10 ±0.3
PFDoDA	42 ±14	20 ±5.2	21 ±7.1	78 ±52	24 ±5.7	9.4 ±1.1
PFTrDA	20 ±3.9	6.3 ±3.7	13 ±4.9	54 ±42	13 ±3.4	7.4 ±0.7
PFTeDA	19 ±8.5	6.2 ±0.6	6.9 ±2.1	27 ±21	10.9 ±1.5	1.7 ±0.2
PFPeDA	0.6 ±0.1	0.2 [b]	0.5 ±0.2	0.7 ±0.3	0.2 [b]	0.2 [b]
PFHpS	0.7 ±0.3	0.1 [b]	0.1 ±0.04	0.2 ±0.04	0.1 [b]	0.1 [b]
PFOS	371 ±74	85 ±7.1	92 ±16	188 ±85	172 ±38	142 ±9.4
Br-PFOS	36.6 ±13.7	3.2 ±0.9	4.8 ±1.1	3.7 ±0.9	2.9 ±0.6	1.0 ±0.1
PFDS	0.1 [b]	0.1 ±0.1	0.1 [b]	0.4 ±0.3	0.1 [b]	0.1 [b]
FOSA	44 ±37.8	0.6 ±0.05	1.5 ±0.6	2.9 ±1.9	0.6 ±0.3	0.2 ±0.1
EtFOSA[a]	0.2 [b]	0.2 [b]	0.2 [b]	0.2 [b]	0.2 [b]	0.2 [b]
FOSAA	0.4 ±0.1	0.2 [b]	0.2 ±0.04	0.2 [b]	0.2 [b]	0.2 [b]
EtFOSAA	28 ±13.2	0.7 ±0.4	2.3 ±0.7	0.6 ±0.1	1.1 ±0.4	0.2 ±0.1
6:2 FTS	0.3 ±0.2	0.2 [b]	0.2 ±0.1	1.2 ±0.3	0.3 ±0.1	0.2 [b]
8:2 FTS	7.0 ±1.9	0.7 ±0.6	1.1 ±0.5	0.2 [b]	0.2 [b]	0.2 ±0.1
10:2 FTS	31 ±4.0	1.3 ±0.9	3.0 ±0.6	1.0 ±0.6	1.1 ±0.3	0.3 ±0.04
12:2 FTS	24 ±8.4	7.5 ±2.8	10 ±2.8	4.3 ±2.6	6.1 ±1.1	0.4 ±0.04
14:2 FTS	0.5 ±0.2	0.3 ±0.1	0.5 ±0.1	0.2 [b]	0.2 ±0.04	0.2 [b]
Sum	667±121	158±13	181±35	458±259	287±52	193±11

459 [a] EtFOSA was not detected in perch (however low concentrations were detected in pike)

460 [b] All concentrations below the LOQ

461 Table S17. Concentrations in pike livers (µg kg^{-1} w.w.).

PFAS	Sampling area							
	Factory area		L1		L3		L6	
PFHxA	0.8	±0.3	0.3 [b]		0.3 [b]		0.3 [b]	
PFHpA [a]	0.3 [b]		0.3 [b]		0.3 [b]		0.3 [b]	
PFOA	0.3 [b]		0.6	±0.4	1.1	±0.8	0.3 [b]	
PFNA	0.4	±0.1	0.7	±0.4	0.5	±0.2	1.4	±0.7
PFDA	4.3	±1.0	12.1	±3.4	6.3	±0.4	11	±3.2
PFUnDA	2.9	±1.0	26	±13	8.7	±1.1	7.2	±2.9
PFDoDA	2.8	±1.6	28	±5.6	12	±1.2	5.2	±2.0
PFTrDA	4.9	±1.8	9.1	±4.0	5.2	±2.8	5.8	±2.9
PFTeDA	2.7	±0.4	8.4	±2.9	4.3	±0.7	0.9	±0.4
PFPeDA	0.2 [b]		0.4	±0.2	0.2 [b]		0.2 [b]	
PFHpS	0.1 [b]		0.2	±0.1	0.1 [b]		0.1 [b]	
PFOS	48	±13	47	±18	36	±11	68	±12
Br-PFOS	1.5	±0.6	1.3	±0.2	0.6	±0.1	0.3	±0.1
PFDS	0.1 [b]		0.2	±0.1	0.1 [b]		0.1 [b]	
FOSA	98	±34	7.9	±2.8	1.7	±1.0	1.7	±0.2
EtFOSA	0.5	±0.3	0.2 [b]		0.2 [b]		0.2 [b]	
FOSAA	0.2	±0.1	0.2 [b]		0.2 [b]		0.2 [b]	
EtFOSAA	3.7	±1.1	0.2 [b]		0.2	±0.05	0.2	±0.03
6:2 FTS	0.2 [b]		0.2 [b]		0.2 [b]		0.2 [b]	
8:2 FTS	1.1	±0.3	0.2	±0.3	0.2 [b]		1.7	±0.2
10:2 FTS	4.1	±1.0	0.6	±0.4	0.3	±0.1	0.4	±0.3
12:2 FTS	3.7	±0.7	2.3	±1.3	1.6	±0.6	0.4	±0.1
14:2 FTS	0.2 [b]		0.2 [b]		0.2 [b]		0.2 [b]	
Sum	182	±45	146	±1	79	±15	105	±23

462 [a] PFHpA was not detected in pike (however it was detected in perch)

463 [b] All concentrations below the LOQ

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Table S18. Extractable organic fluorine (EOF), sum of target PFAS (µg F kg^{-1}) and sum fluorine from the targeted analysis (ΣF_{targ}) as a percent of EOF, n=1.

Sampling area	Sample type	EOF (µg F kg^{-1})	ΣF_{targ} (µg F kg^{-1})	ΣF_{targ} /EOF (%)
L1	Sediments	963.7	518.4	53.8
Factory area	Perch liver	648.9	313.1	48.3
L1	Perch liver	219.5	121.8	55.5
L3	Perch liver	1347.9	496.1	36.8
L6	Perch liver	85.8	93.0	108
Factory area	Pike liver	725.5	55.5	7.6
L1	Pike liver	664.1	58.4	8.8
L6	Pike liver	101.5	29.9	29.5
L3	Trout liver	373.9	124.3	33.2
L3	Char liver	330.9	75.3	22.8

465

Table S19. Probability values (p values, Kruskal-Wallis and Bonferroni correction) for comparison of linear PFOS (expressed as a percent of total PFOS, i.e sum of branched and linear isomers) in the different sampling areas in pore water, perch liver, and pike liver. Percentage L-PFOS and letters denoting significant differences are shown in Figure S16.

Medium	Sampling areas for comparison		P value
Pore water	L1	River	0.80
	L1	L3	1.00
	L1	L5	0.41
	L3	L5	0.92
	L4	River	0.71
	L4	L1	1.00
	L4	L3	1.00
	L4	L5	0.20
	River	L3	0.15
	River	L5	0.01
Perch liver	Fire station	Factory area	0.35
	Fire station	L1	1.00
	Fire station	L3	1.00
	Fire station	L5	0.11
	Fire station	L6	0.00
	L1	Factory area	1.00
	L1	L3	0.02
	L1	L5	0.00
	L1	L6	0.00
	L3	Factory area	0.00
	L3	L5	1.00
	L5	Factory area	0.00
	L6	Factory area	0.00
	L6	L3	0.00
	L6	L5	0.11
Pike liver	L1	Factory area	1.00
	L1	L3	0.70
	L1	L6	0.01
	L3	Factory area	0.31
	L6	Factory area	0.00
	L6	L3	0.08

Table S20. Concentrations (µg kg^{-1} d.w.). and year of deposition according to sediment dating for different depths in the core from sampling area L1.

Depth (cm)	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	8.5	9.5	10.5	11.5	12.5	13.5	14.5
Year	2017	2012	2006	1999	1994	1990	1984	1978	1972	1967	1963	1958	1952	1943	1934
PFHxA	3.2	3.2	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.2	0.8	<0.5	<0.5	<0.5
PFHpA	16	20	4.6	3.0	2.6	2.0	2.0	1.9	1.5	1.3	7.8	4.2	2.3	2.1	2.0
PFOA	13	28	5.0	2.2	2.9	<0.5	<0.5	<0.5	<0.5	<0.5	6.2	2.2	<0.5	<0.5	<0.5
PFNA	2.0	1.4	0.9	<0.4	0.4	0.5	<0.4	<0.4	<0.4	<0.4	0.8	0.6	<0.4	<0.4	<0.4
PFDA	0.9	2.1	1.9	0.7	0.6	0.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
PFUnDA	0.6	1.0	0.9	<0.4	1.1	1.0	1.0	<0.4	<0.4	0.8	<0.4	0.6	<0.4	<0.4	<0.4
PFDoDA	0.7	1.6	2.4	0.7	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
PFTrDA	0.6	0.5	0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
PFTeDA	0.4	0.7	1.3	0.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
PFOS	0.4	0.6	0.5	1.2	1.6	2.0	1.8	1.8	1.9	1.3	3.5	2.4	0.9	0.7	0.2
FOSA	<0.1	<0.1	0.8	1.5	1.4	1.6	1.5	1.1	0.7	0.7	1.6	0.5	0.3	<0.1	<0.1
EtFOSA	<0.3	<0.3	<0.3	1.0	1.1	1.5	1.8	1.4	1.0	0.7	1.1	0.4	<0.3	<0.3	<0.3
EtFOSE	<5	<5	10	46	43	51	61	46	37	25	31	14	10	<5	<5
FOSAA	1.5	2.8	3.4	4.0	4.0	3.4	2.7	2.1	6.2	3.1	1.4	0.7	<0.3	<0.3	<0.3
MeFOSAA	<0.3	<0.3	0.4	0.8	1.0	1.0	1.3	1.8	1.3	0.6	0.7	0.1	<0.3	<0.3	<0.3
EtFOSAA	2.6	7.8	50	143	178	235	278	185	140	91	205	105	41	9.5	2.2
6:2 FTS	<0.3	1.7	4.2	0.9	0.9	1.0	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
8:2 FTS	11	52	266	28	3.5	11	2.4	1.9	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
10:2 FTS	9.1	49	244	37	5.0	16	2.0	1.5	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
12:2 FTS	8.7	38	197	18	3.8	8.6	1.7	1.4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
14:2 FTS	1.7	6.9	31	3.5	0.8	1.4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
SAmPAP diester [a]	20	24	209	984	952	2516	3383	3077	2142	809	2125	1430	138	56	<5.1

[a] Standard and calibration curve for SAmPAP diester in the core were acquired post analyses and used to correct the results.

Table S21. K_{OC} values (L kg^{-1}) from linear regression for PFAS detected in both pore water and sediments. Data are shown ±SEM.

PFAS group	Compound	K_{OC} (L kg^{-1})	
PFCA	PFHxA	86	±257
	PFHpA	23	±245
	PFOA	142	±254
	PFNA	683	±359
	PFDA	2 206	±1048
PFSA	PFOS [a]	1 965	±548
preFOS	FOSA	42 454	±71 198
FTS [b]	12:2 FTS	249 882	±109 655

[a] A statistically significant relationship between K_D and OC was found for PFOS only.
[b] K_{OC} regression values for 8:2 FTS and 10:2 FTS were negative and not included.

475

Table S22. Calibrated input parameters and changes in emission rates

Tyrifjord model input			**Scotchban Mix**			**FTS mix**		
			log K_{oc} = 5	**log K_{oc} = 7**	**log K_{oc} = 9**	**log K_{oc} = 5**	**log K_{oc} = 7**	**log K_{oc} = 9**
Calibrated input concentrations			t1 = 1950, t2 = 1984, t3 = 2017			t1 = 1994, t2 = 2006, t3 = 2017		
$C_{river,w\ (total)}$	Phase1:t1 [a]	(ng L^{-1})	201.3	200.0	200.0	30.0	30.0	30.0
	Phase1:t2 [b]	(ng L^{-1})	1404.8	251.1	238.9	281.8	39.8	37.6
	Phase2:t2 [c]	(ng L^{-1})	1282.0	50.22	30.07	247.5	9.9	7.7
	Phase2:t3 [d]	(ng L^{-1})	2.0	0.28	0.17	20.1	0.75	0.57
k_{in} [e]	t1 - t2	(y^{-1})	-0.057	-0.0067	-0.0052	-0.19	-0.024	-0.019
	t2 - t3	(y^{-1})	0.20	0.16	0.16	0.23	0.23	0.24
Corresponding data to the input								
$C_{fjord,sed}$	t1	(ng g^{-1})	0.0	0.0	0.0	0.0	0.0	0.0
	t2	(ng g^{-1})	3509.0	3951.0	3963.0	730.0	758.0	764.0
	t3(2017)	(ng g^{-1})	10.9	40.6	31.1	104.0	102.1	100.5
$C_{fjord,w\ (total)}$	t1	(ng L^{-1})	0.0	0.0	0.0	0.0	0.0	0.0
	t2	(ng L^{-1})	1216.9	30.3	18.0	253.1	5.8	3.5
	t3 (2017)	(ng L^{-1})	3.8	0.3	0.1	36.0	0.8	0.5
$t_{1/2}$								
$C_{river,w\ (total)}$ [f]	t1 - t2	(y)	-12.1	-103.5	-132.5	-3.7	-29.3	-36.9
	t2 - t3	(y)	*3.5*	4.4	4.4	3.0	*3.0*	*2.9*

a) Phase1:t1 = Scotchban: Use and direct emissions at 1950, FTS mixture: Use and direct emissions at 1994

b) Phase1:t2 = Scotchban: Use and direct emissions at 1984, FTS mixture: Use and direct emissions at 2006

c) Phase2:t2 = Scotchban: Phase out of followed by decrease lag emissions at 1984, FTS mixture: Phase out of followed by decrease lag emissions at 2006

d) Phase2:t3 = Scotchban: decrease lag emissions at 2017, FTS Mixture: decrease lag emissions at 2017

e) k_{in} is a first-order rate constant describing changes in $C_{\mathrm{w\ total}}^{\mathrm{in,river}}$ with time (y^{-1}), resulting from changes in source emissions that drain into the lake. Positive values indicate increasing emission volumes, while negative values indicate decreasing emission volumes

f) *(half life for the emission rates)*

Supplementary figures

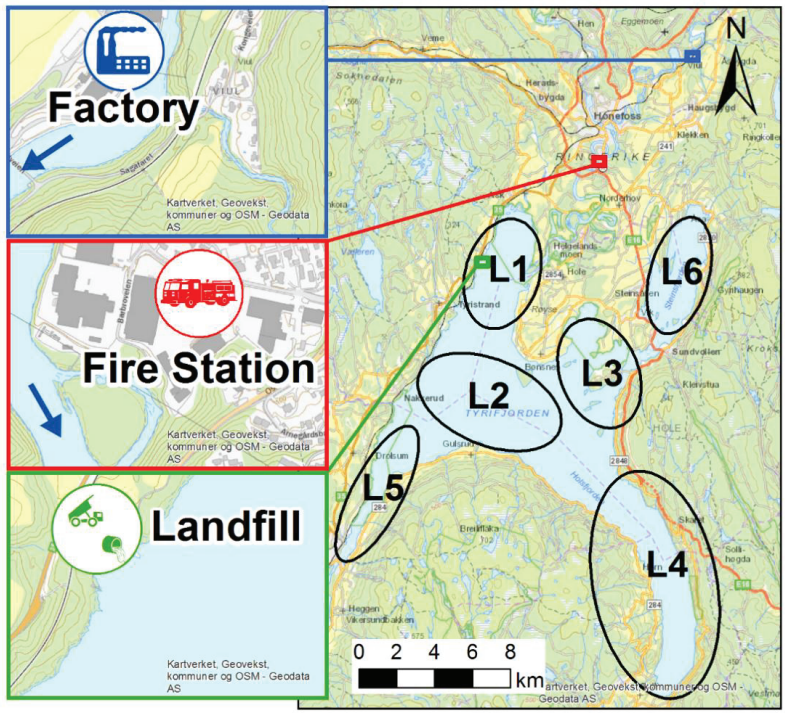


Figure S1. Geographical location of source areas and lake sampling areas (L1-L6). Arrows are indicating directional river flow. The main outlet from the lake is southwest of area L5.

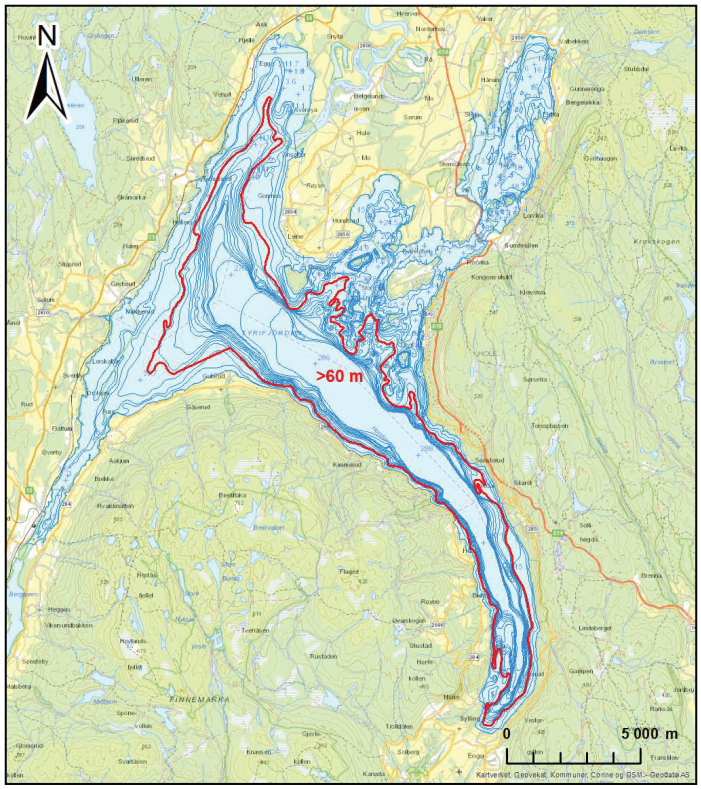
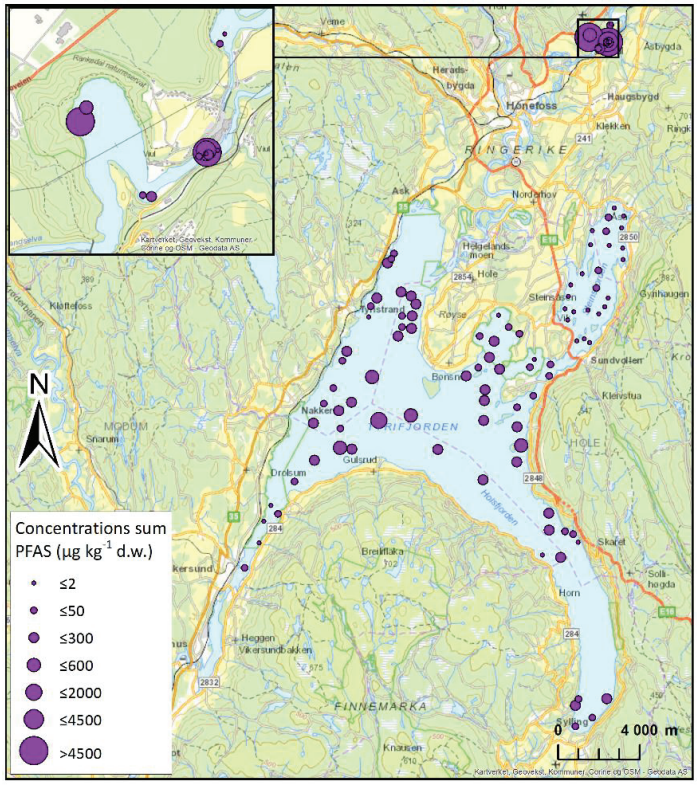
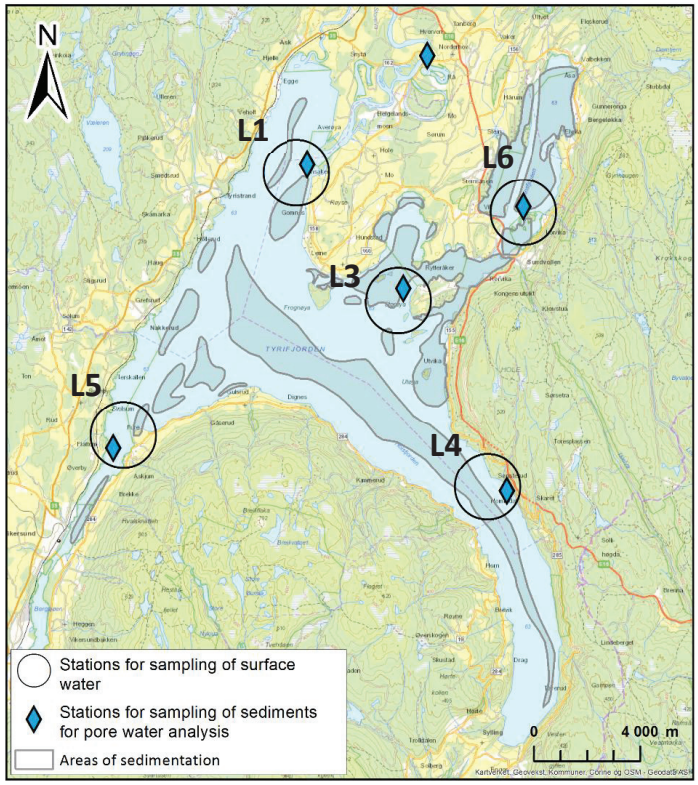


Figure S2. Map showing the depth of different areas of lake Tyrifjorden. Area deeper than 60 m is outlined in red.



497 *Figure S3. Sediment sampling areas and corresponding sum concentrations of detected PFAS (Σ_{29}PFAS).*
498 *No concentrations above the LOQ were detected in sediments sampled in the river downstream to the*
499 *fire station and these samples are not shown.*

500



501 *Figure S4. Sampling sites for surface water and sediments used for pore water analysis.*

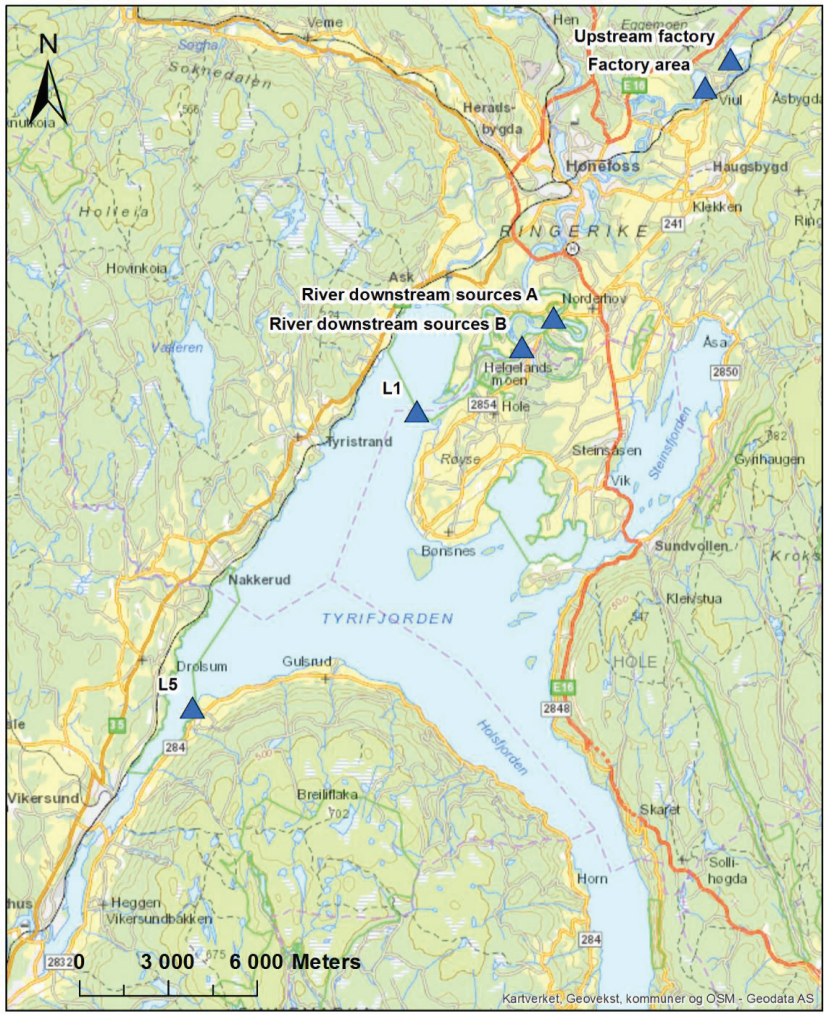


Figure S5. Sediment trap locations in the river and lake Tyrifjorden

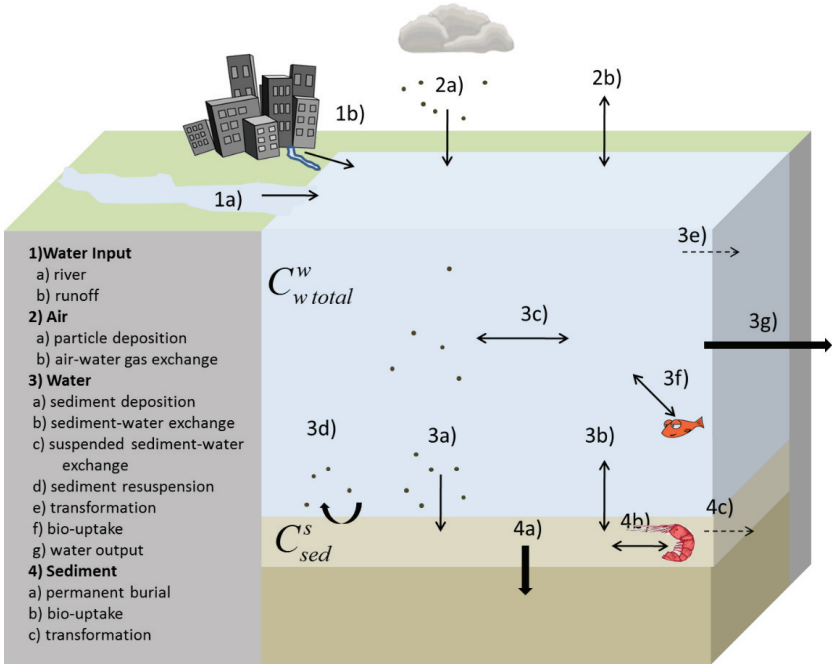


Figure S6. Schematic of processes accounted for in the two-box linear water-sediment model. Reprinted from Arp et al. (2014).

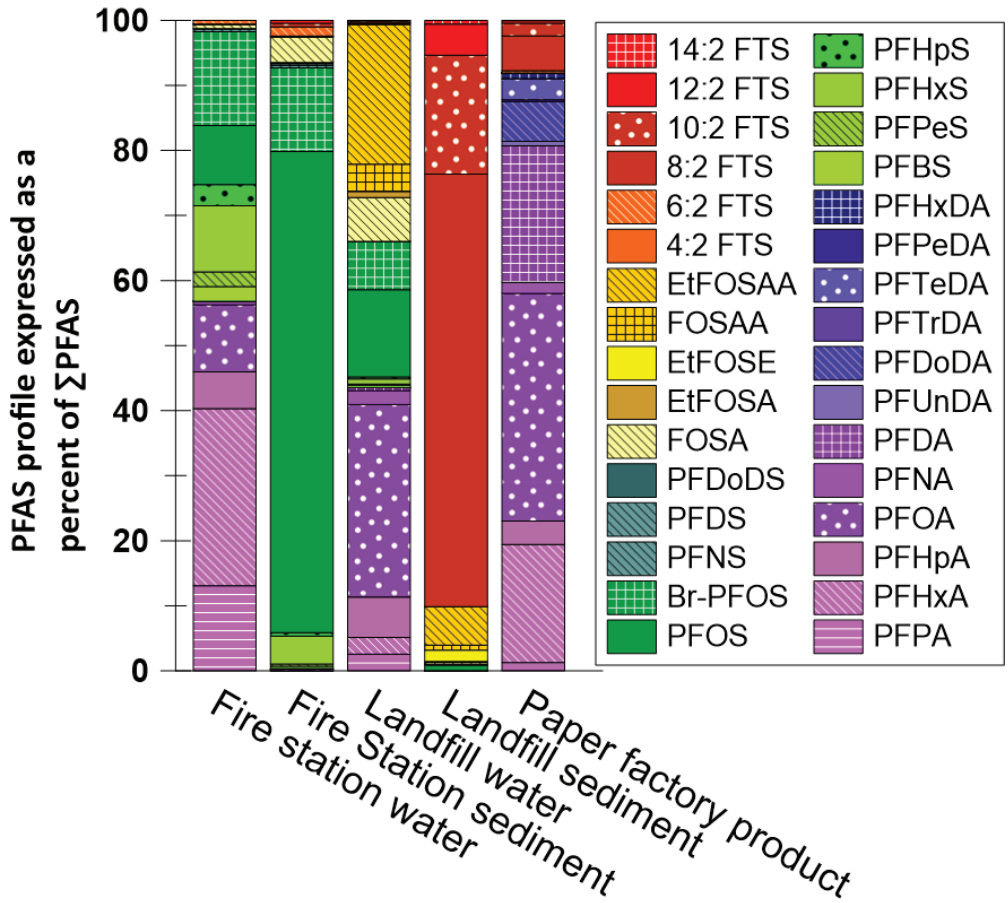
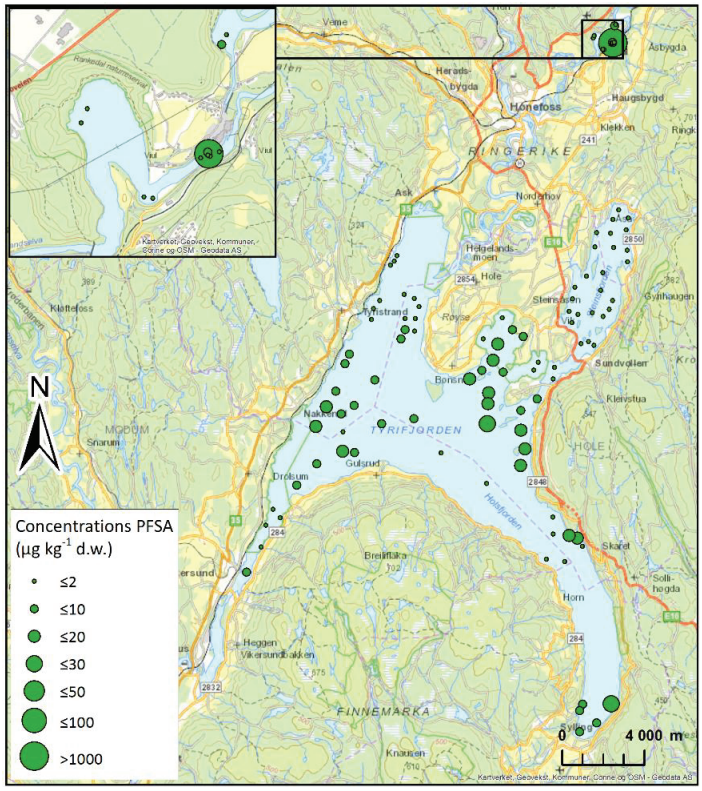
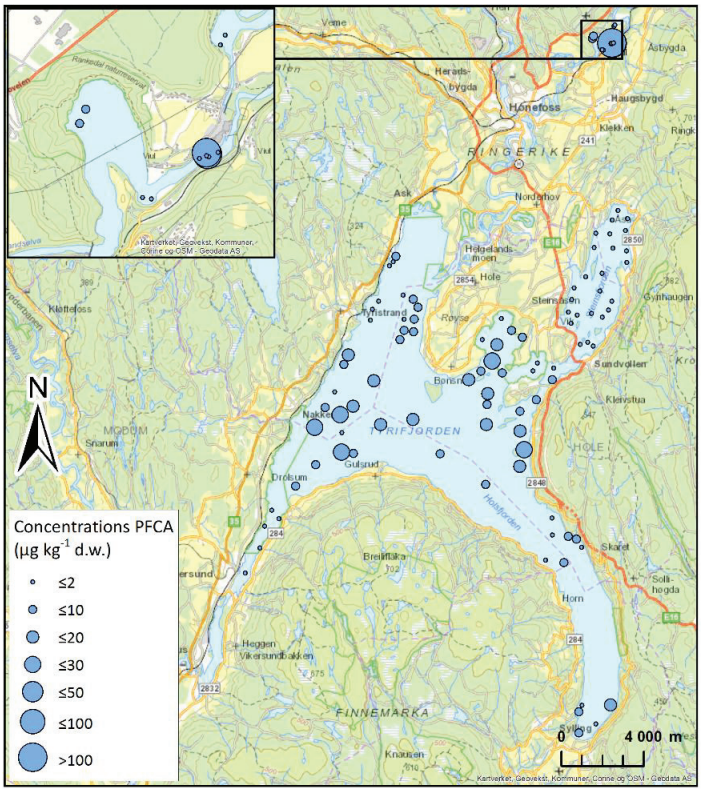


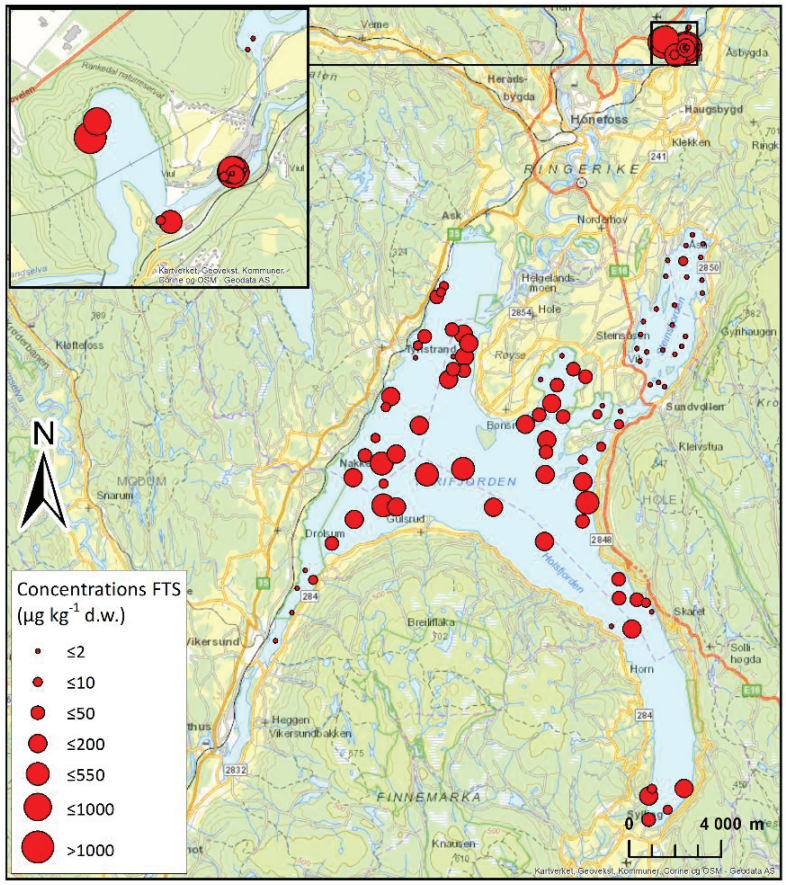
Figure S7. PFAS profiles in water and sediments from the storm water system at the fire station, water and sediments in the creek downstream the landfill, and a paper plate produced at the factory. Only compounds detected above the LOQ in at least one sample are included. Values below the LOQ were treated as 0.



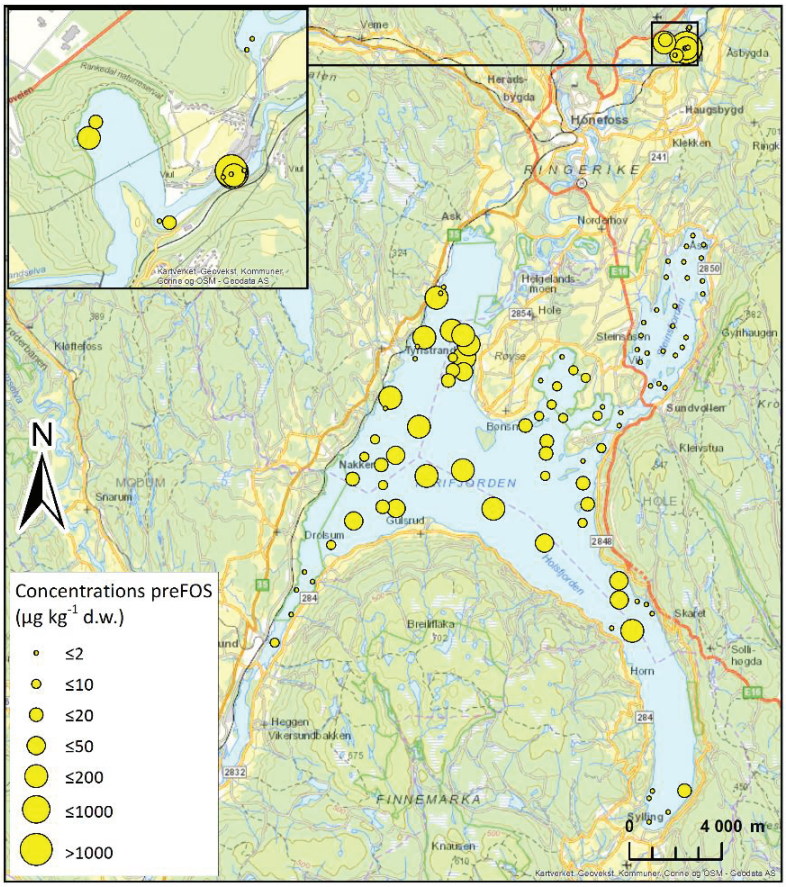
514 *Figure S8. Sediment sampling areas and corresponding PFSA concentrations.*



515 *Figure S9. Sediment sampling areas and corresponding PFCA concentrations*



516 *Figure S10. Sediment sampling areas and corresponding FTS concentrations.*



517 *Figure S11. Sediment sampling areas and corresponding preFOS concentrations.*

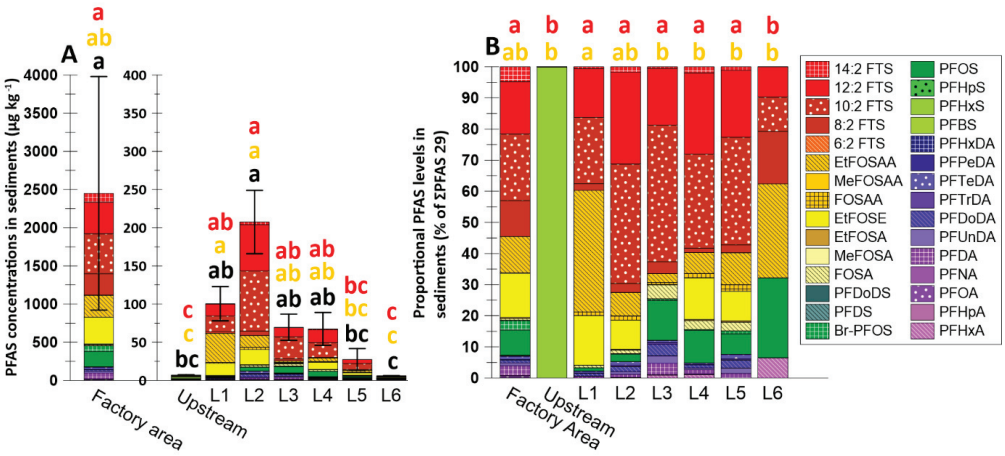


Figure S12. Average PFAS concentrations (A) and distribution profiles (B) in sediments at the different stations in the river and lake. For concentrations, the scale on the y-axis are different for the factory area and the other sampling areas. Distribution profiles are given as relative concentrations (of ΣPFAS 29). Only compounds detected above the LOQ in at least one sample are included in the data analysis. In samples where compounds were not present above the LOQ, concentrations were taken as half the LOQ for plot A. For the distribution profiles in B, concentrations below the LOQ were treated as 0. For plot A, the different letters denote significant differences in ΣPFAS 29 (bottom, black letters), ΣpreFOS (mid, yellow letters) or ΣFTS (top, red letters), p<0.05, (Kruskal-Wallis and Bonferroni correction). For plot B the different letters denote significant differences in percentage preFOS (bottom, yellow letters) or percentage FTS (top, red letters), p<0.05, (Kruskal-Wallis and Bonferroni correction).

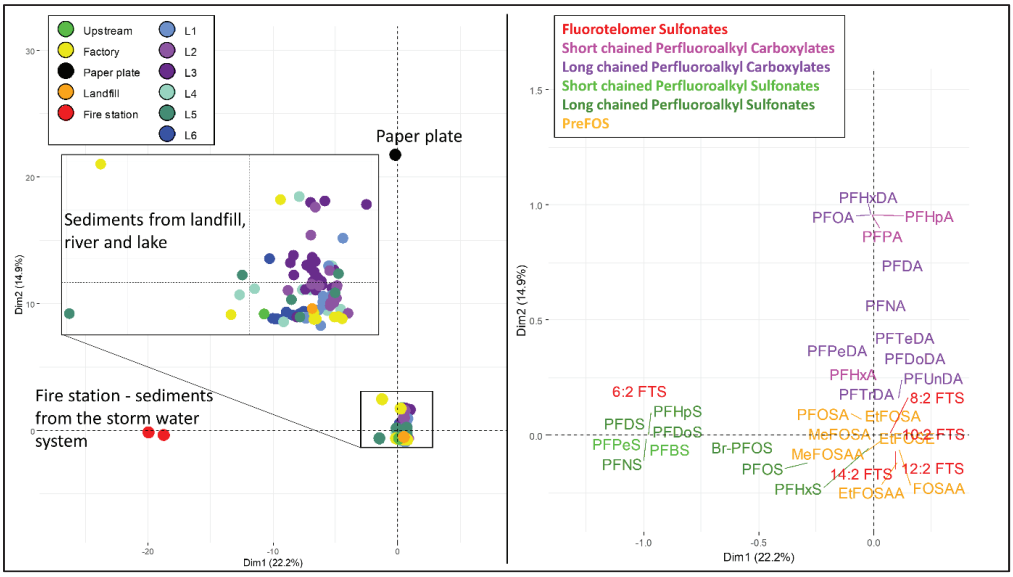


Figure S13. Principal Component Analysis (PCA) for sediment samples and the product from the factory (paper plate). In the score plot (left), sediments from the factory area, landfill, and the lake grouped together close to the centre (0,0), while sediments from the storm water system at the fire station grouped towards the left. In the loading plot (right), FTS longer than 6:2 FTS and preFOS grouped close to the centre (0,0), while PFCA were plotted along the y-axis. PFSA and 6:2 FTS grouped towards the left. Concentrations below the LOQ were treated as 0.

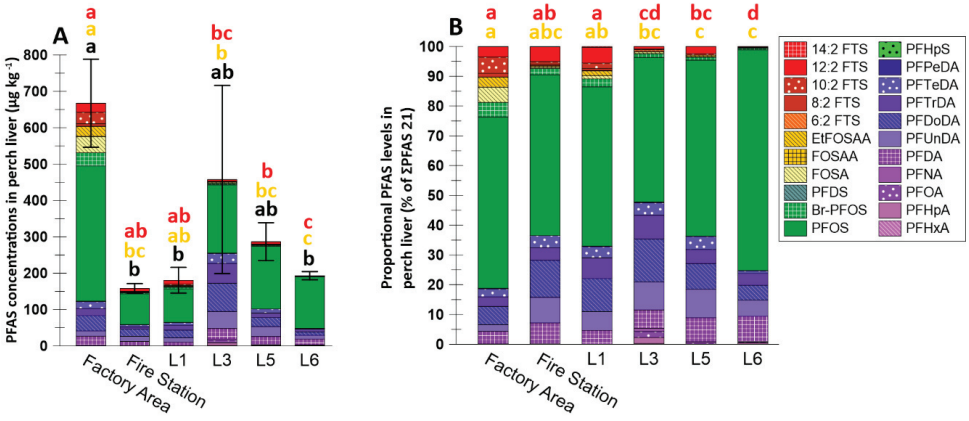
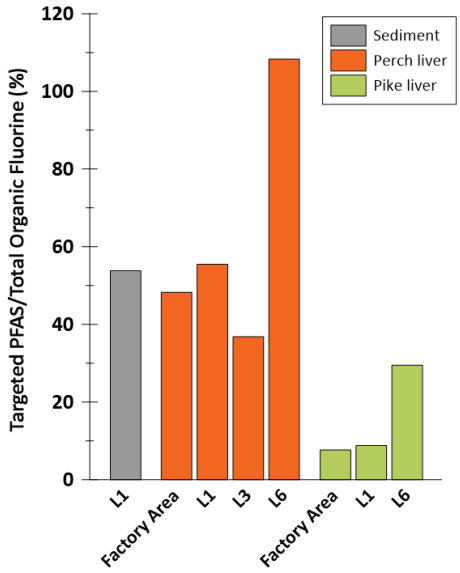


Figure S14. Average PFAS concentrations (A) and distribution profiles (B) in perch livers at the different stations. Distribution profiles are given as relative concentrations (of ΣPFAS 21). Only compounds detected above the LOQ in at least one sample are included. For concentrations (A), values below the LOQ were treated as half the LOQ. For distribution profiles (B), values below the LOQ were treated as 0. Different letters denote significant differences in Σ_{21} PFAS (bottom, black letters), Σ preFOS (mid, yellow letters) or Σ FTS (top, red letters), p<0.05, (Kruskal-Wallis and Bonferroni correction). For distribution profiles (B), values below the LOQ are treated as 0. For plot A, the different letters denote significant differences in ΣPFAS 21 (bottom, black letters), ΣpreFOS (mid, yellow letters) or ΣFTS (top, red letters), p<0.05, (Kruskal-Wallis and Bonferroni correction). For plot B the different letters denote significant differences in percentage preFOS (bottom, yellow letters) or percentage FTS (top, red letters), p<0.05, (Kruskal-Wallis and Bonferroni correction).



548 *Figure S15. Sum organic fluorine in the targeted PFAS as a percentage of fluorine determined in the*
549 *extractable organic fluorine (EOF) analysis (n=1).*

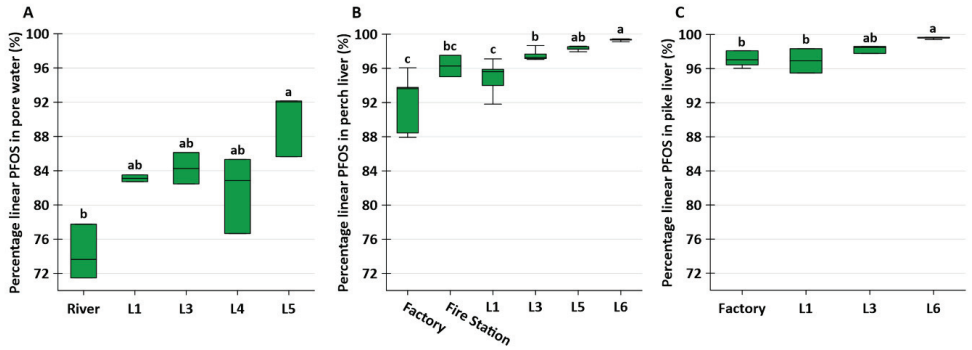


Figure S16. Linear PFOS in pore water (A), perch liver (B), and pike liver at the different stations expressed as a percent of total PFOS (sum of branched and linear isomers. Whiskers show maximum and minimum values, boxes show lower and upper quartile, and the mid black line shows the median. Different letters denote significant differences, p<0.05 (Kruskal-Wallis and Bonferroni correction. Pore water: n=2-3, perch livers: n=2-5, pike livers=2-5). Y-axis starts at 70%.

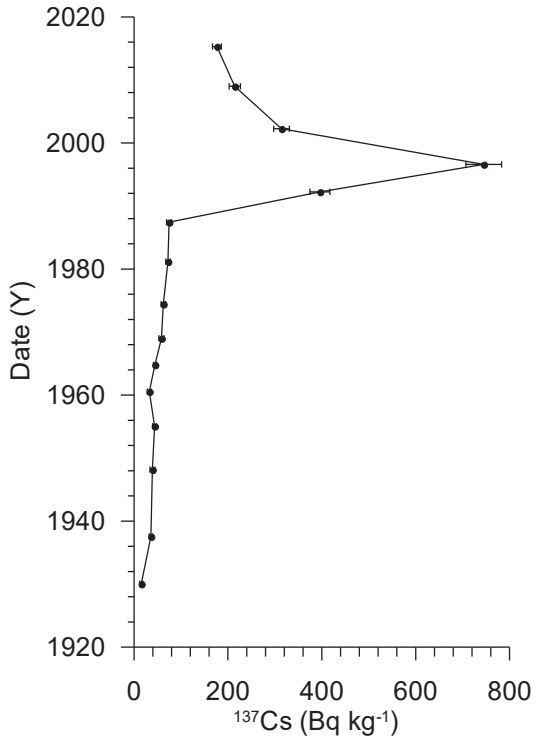


Figure S17. Activity of ^{137}Cs at the different dated depths in the core from area L1

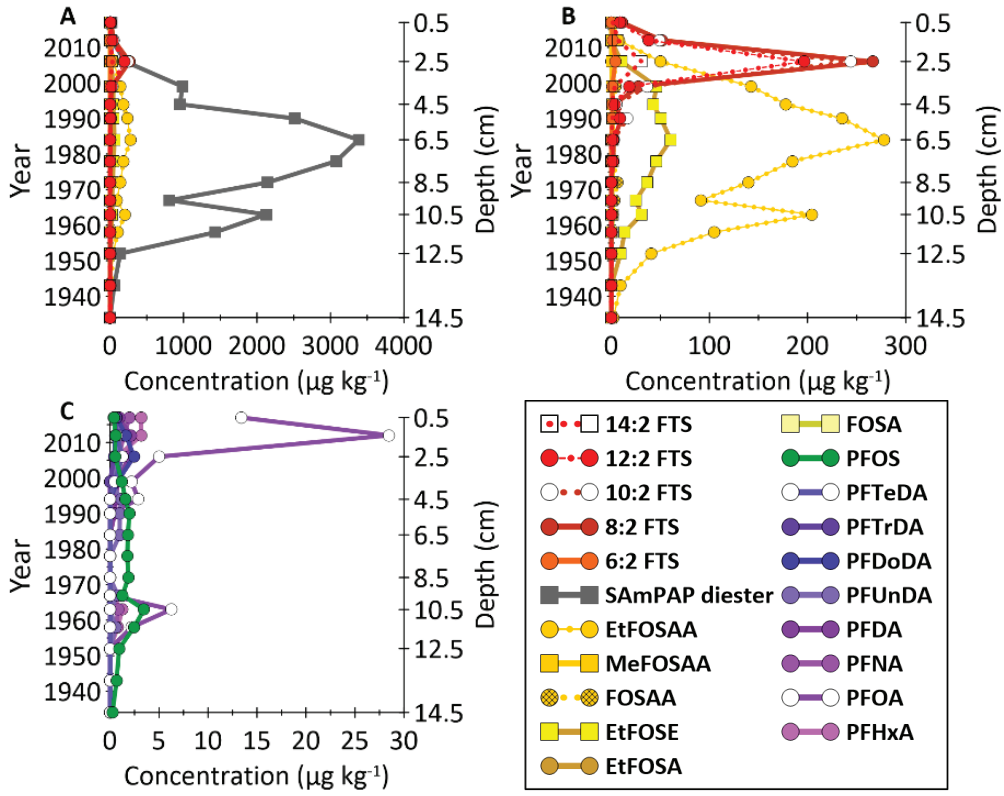


Figure S18. Individual PFAS concentrations at the different depths in the sediment core from area L1

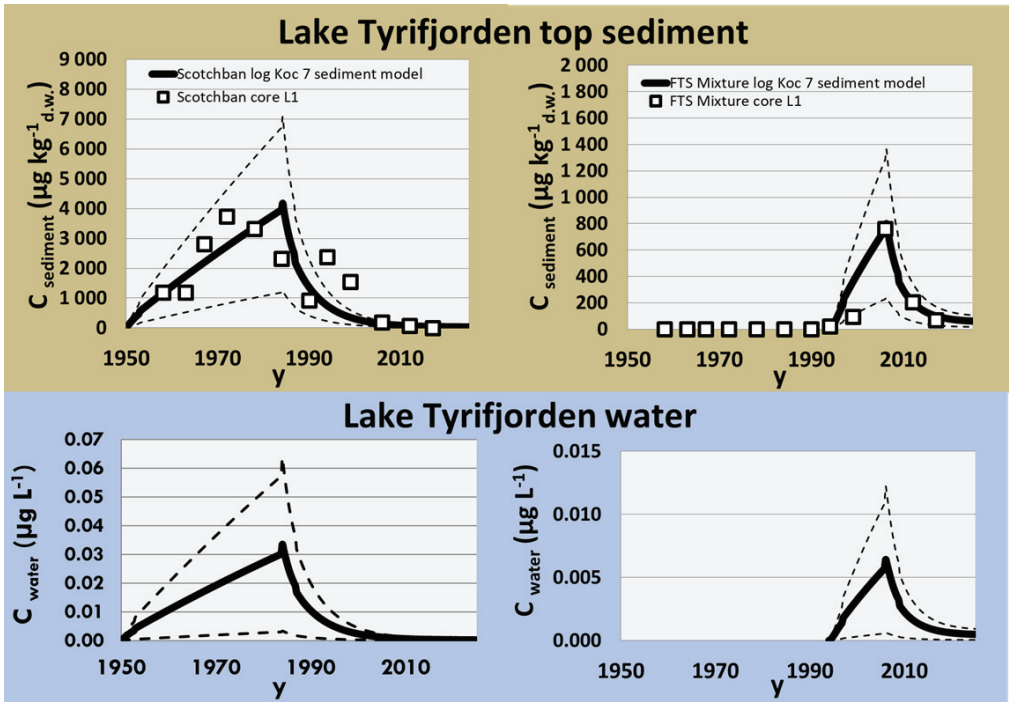


Figure S19. Results from the Tyrifjorden model for K_{OC} 7.0. Top panel: concentrations in the top 1 cm of sediment over time. Bottom panel: corresponding water concentrations for lake Tyrifjorden over time.

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Appendix: Paper II

Paper III

Fluorinated precursor compounds in sediments as a source of Perfluorinated Alkyl Acids (PFAA) to biota

Sampling of perch, lake Tyrifjorden. Photo: Håkon Austad Langberg

Appendix: Paper III

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Article

Fluorinated Precursor Compounds in Sediments as a Source of Perfluorinated Alkyl Acids (PFAA) to Biota

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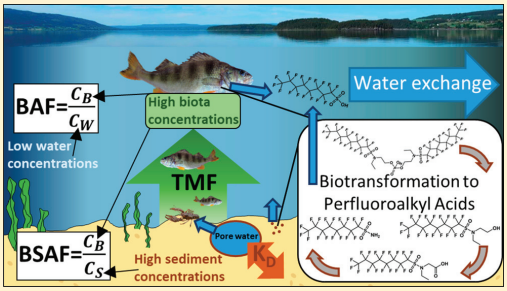
ABSTRACT: The environmental behavior of perfluorinated alkyl acids (PFAA) and their precursors was investigated in lake Tyrifjorden, downstream a factory producing paper products coated with per- and polyfluorinated alkyl substances (PFAS). Low water concentrations (max 0.18 ng L^{-1} linear perfluorooctanesulfonic acid, L-PFOS) compared to biota (mean 149 $\mu g\ kg^{-1}$ L-PFOS in perch livers) resulted in high bioaccumulation factors (L-PFOS $BAF_{Perch\ liver}$: 8.05 × 10^5−5.14 × 10^6). Sediment concentrations were high, particularly for the PFOS precursor SAmPAP diester (max 1 872 $\mu g\ kg^{-1}$). Biota-sediment accumulation factors (L-PFOS $BSAF_{Perch\ liver}$: 22−559) were comparable to elsewhere, and concentrations of PFAA precursors and long chained PFAA in biota were positively correlated to the ratio of carbon isotopes ($^{13}C/^{12}C$), indicating positive correlations to dietary intake of benthic organisms. The sum fluorine from targeted analyses accounted for 54% of the extractable organic fluorine in sediment, and 9−108% in biota. This, and high trophic magnification factors (TMF, 3.7−9.3 for L-PFOS), suggests that hydrophobic precursors in sediments undergo transformation and are a main source of PFAA accumulation in top predator fish. Due to the combination of water exchange and dilution, transformation of larger hydrophobic precursors in sediments can be a source to PFAA, some of which are normally associated with uptake from water.



KEYWORDS: *PFAS, PFOS, SAmPAP diester, extractable organic fluorine (EOF), sediment−pore water partitioning coefficients (K_D), trophic magnification, bioaccumulation factors (BAF)*

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) refer to a class of anthropogenic chemicals that have been produced since the late 1940s and used for a variety of industrial processes and consumer products including firefighting foams, in oil production and mining, pesticides, cosmetics, household products, textiles, as well as food contact materials.[1] Due to the potential for adverse health effects,[2,3] sources, transport pathways, and environmental fate of well-known PFAS such as perfluorinated alkyl acids (PFAA) have received increasing attention from the scientific community.[1,4] PFAA are very persistent at environmentally relevant conditions.[5] Highly elevated concentrations have been reported at contaminated source areas including firefighting training facilities.[6−8] Lower, but detectable levels of PFAA have been reported in areas far from point sources,[9−11] and long-range atmospheric transport and subsequent degradation of precursor compounds is suggested to be one important mechanism for their global distribution.[12−14] The partitioning of PFAA and their precursors between air, water, sediment/soil, and biota phases provides information related to the environmental fate of these compounds. Differences in structure, including molecule size and functional hydrophilic group result in differing physiochemical properties among compounds and thus different partitioning between environmental media. In the environment, PFAS exist as anions, zwitterions, cations or neutral compounds.[15] Generally, ions are more hydrophilic compared to neutral compounds of comparable size, and larger PFAS are generally more hydrophobic and have higher affinities for sediments compared to smaller sized homologues.[16−21] However, soil and sediment properties add to the complexity of sorption processes and make it difficult to predict soil/sediment−water partitioning coefficients (K_D). Soils and sediments are comprised of organic and inorganic matter and positive correlations have most often been reported between organic matter and sorption of anionic PFAS.[17,19]

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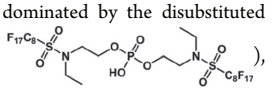
Two groups of PFAA have received the most attention from the scientific community: perfluoroalkyl carboxylic acids (PFCA) and sulfonic acids (PFSA).[22] These PFAA have small pK_a values and are therefore present as anions at environmentally relevant pHs.[22] Long chained PFAA (number of carbon atoms [C] ≥ eight for PFCA, and C ≥ six for PFSA) have higher potentials for bioaccumulation than shorter homologues and have been globally detected in organisms.[23,24] In addition, uptake and metabolization of precursor compounds has been suggested to be a source of PFAA to organisms.[25,26] Historically, large amounts of perfluorooctane sulfonyl fluoride (POSF) has been used as the starting material for the production of the eight-carbon PFSA, perfluorooctanesulfonic acid (PFOS; ) and PFOS precursor compounds including *N*-alkyl substituted perfluorooctane sulphonamides with eight perfluorinated C ( , for simplicity termed preFOS throughout this work), and potential parent compounds: mono-, di-, and trisubstituted phosphate esters of *N*-ethyl perfluorooctane sulfonamido ethanol (SAmPAPs).[27−30] PreFOS and SAmPAPs were used in food contact paper and packaging from the 1970s.[28,29] Commercial SAmPAP formulations were dominated by the disubstituted SAmPAP (SAmPAP diester; ), and the presence of this compound has been investigated in a few previous studies.[29,31,32] PreFOS have a sulfonyl group, the same perfluorinated moiety as PFOS, and have the potential to be degraded to PFOS if the amine group is replaced with a hydroxy group. PFOS was reported to have higher trophic magnification factors (TMF) compared to other long chained PFAA in several studies,[33−35] and transformation of the large amount of preFOS[36] to PFOS has been suggested to be the main mechanism behind this.[33] Some preFOS are neutral at environmentally relevant pH, which combined with their larger size, makes them less water-soluble compared to the anionic PFOS,[37,38] and thus more prone to reside in environmental compartments other than water.

The objective of the present work was to investigate the fate and transport of PFAS, including contribution from transformation of precursor compounds, in both the abiotic and biotic environment close to a point source: lake Tyrifjorden (Norway), downstream of a shutdown factory which produced PFAS coated paper products. A combination of targeted chemical analysis of a limited number of compounds and determination of extractable organic fluorine (EOF) was applied to capture more of the vast number of PFAS. Stable nitrogen and carbon isotope ratios (δ^{15}N and δ^{13}C) were used to assess biota trophic levels and carbon sources in order to investigate transfer and transformation of PFAS through the food chain. Based on concentrations in (abiotic and biotic) field samples, sediment−water partitioning coefficients (K_D), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), and trophic magnification factors (TMF) were calculated for PFSA, PFCA, fluorotelomer sulfonic acids (FTS), and preFOS. This study is the first of its kind to report the fate and transport of a PFAS mixture originating from the paper industry, and where this resulted in a difference in environmental behavior to previously reported studies.

MATERIALS AND METHODS

Case Study Site and Sampled Media. Lake Tyrifjorden (60.03° N, 10.17° E) is a large (138 km^2) and deep (max 288 m) freshwater lake in Norway (more details in the Supporting Informstion (SI)). High levels of PFOS were found in perch livers (*Perca fluviatilis*) sampled in the middle of the lake in 2015 (mean 183 μg kg^{-1}, close to area L3 see SI Figure S1).[39] A shutdown factory which produced disposable paper products (bowls, plates, cups, etc.) from 1964 to 2013, was later identified as the major PFAS source.[40,41] In the present study, lake and river water, pore water, sediments, and aquatic organisms with different diets and trophic levels were sampled. Sampling was performed during spring and summer 2018, with additional sampling in summer 2019, from six sampling areas in the lake itself and from one area in the river directly downstream the factory (factory area). Sampling areas in the lake were chosen with an increasing distance from the river mouth, and thus with an expected decreasing impact of contamination from the river. Lake sampling areas were named L1−L6 and are shown in SI Figure S1.

Sampling. Sampling is described in brief below. Detailed descriptions and quality assurance procedures are provided in the SI.

Abiotic Samples. River and lake water were sampled in triplicate from five areas in the lake (L1, L3, L4, L5, and L6) and from the factory area, shown in SI Table S1. Sediments were sampled from 94 locations in the lake, two locations upstream and nine locations in the river downstream of the factory (shown in SI Figure S3). Sediments for pore water analysis were sampled in triplicate from sampling areas L1, L3, L4, L5, L6, and in the river upstream of the river mouth, shown in SI Figure S4. Lake water, sediment, and pore water were sampled in September 2018. One additional water sample and five sediment samples (from the lake and factory area) were taken in June 2019 and analyzed for SAmPAP diester (which was not analyzed in most samples in 2018, see the SI).

Biota. Fish (perch (*Perca fluviatilis*), pike (*Esox lucius*), whitefish (*Coregonus lavaretus*), roach (*Rutilus rutilus*), trout (*Salmo trutta*), bream (*Abramis brama*), arctic char (*Salvelinus alpinus*)) and crayfish (*Astacus astacus*) were collected in 2018 using nets and traps. Sampled biota varied between areas as shown in SI Table S2. In alignment with the abiotic samples, supplementary analyses were carried out in 2019 to investigate levels of SAmPAP diester in biota from the factory area (2 perch), L1 (2 perch, 2 crayfish), and L3 (2 perch, 2 crayfish), see the SI.

Laboratory Methods. Laboratory methods are described briefly below. Quality assurance, method limit of detections (LOD) and limit of quantifications (LOQ), treatment of sediments for pore water analysis, analysis of total organic carbon (TOC), sediment grain size, and analysis of extractable organic fluorine (EOF) are described in the SI.

The ratio between the stable nitrogen ^{15}N and ^{14}N (δ^{15}N), and carbon ^{13}C and ^{12}C (δ^{13}C) isotopes in muscle tissue were determined for the assessment of trophic level and carbon sources. The δ^{15}N of a consumer is enriched relative to its diet, thus the δ^{15}N can be used to estimate the trophic level of an organism. Trophic fractionation of 3.4 ‰ in lake ecosystems has been reported,[42] thus relative trophic levels were calculated by dividing δ^{15}N by 3.4. δ^{13}C has been used to link increased PFOS concentrations to marine mammals feeding on inshore, benthos linked food webs compared to marine mammals

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Table 1. Mean, Median, And Maximum Concentrations ($\mu g\ kg^{-1}$ d.w.) for PFAS Compounds in the Lake (Areas L1, L2, L3, L4, L5, L6; $n = 94$) and River (Factory Area; $n = 9$) Sediments Collected in 2018 (Only Compounds Detected in at Least One Sample Are Included)[a]

			lake			factory area		
PFAS group	acronym	abbreviation	mean	median	max	mean	median	max
PFCA	perfluorohexanoic acid	PFHxA	0.5 ± 0.1	0.3	4.0	1.0 ± 0.5	0.3	5.0
	perfluoroheptanoic acid	PFHpA	0.3 ± 0.0	0.3	0.3	1.3 ± 0.8	0.3	7.8
	perfluorooctanoic acid	PFOA	0.3 ± 0.0	0.3	0.3	9.3 ± 8.1	0.3	81.6
	perfluorononanoic acid	PFNA	0.2 ± 0.0	0.2	1.4	6.9 ± 6.6	0.2	65.9
	perfluorodecanoic acid	PFDA	1.1 ± 0.2	0.5	5.7	69.4 ± 66.2	0.2	665
	perfluoroundecanoic acid	PFUnDA	0.8 ± 0.1	0.2	4.4	19.9 ± 18.5	0.2	186
	perfluorododecanoic acid	PFDoDA	1.4 ± 0.2	0.6	7.6	21.0 ± 18.3	0.2	184
	perfluorotridecanoic acid	PFTrDA	0.4 ± 0.0	0.2	2.5	3.2 ± 2.4	0.2	24.6
	perfluorotetradecanoic acid	PFTeDA	0.8 ± 0.1	0.2	4.8	23.3 ± 20.1	0.2	203
	perfluoropentadecanoic acid	PFPeDA	0.2 ± 0.0	0.2	0.2	1.5 ± 1.1	0.2	11.1
	perfluorohexadecanoic acid	PFHxDA	0.2 ± 0.0	0.2	0.2	2.8 ± 2.3	0.2	23.7
		∑PFCA	**6.2 ± 0.6**	**3.6**	**25.2**	**160 ± 145**	**3.1**	**1 458**
PFSA	perfluorobutanesulfonic acid	PFBS	0.1 ± 0.0	0.1	0.2	0.1 ± 0.0	0.1	0.1
	perfluorohexanesulfonic acid	PFHxS	0.0 ± 0.0	0.1	0.1	0.3 ± 0.2	0.1	1.5
	perfluoroheptanesulfonic acid	PFHpS	0.0 ± 0.0	0.1	0.1	2.2 ± 2.1	0.1	21.3
	perfluorooctanesulfonic acid[b]	L-PFOS	3.8 ± 0.6	1.2	24.2	179 ± 178	0.4	1 780
	branched PFOS	Br-PFOS	0.2 ± 0.0	0.1	1.1	68.0 ± 67.7	0.1	677
	perfluorodecanesulfonic acid	PFDS	0.0 ± 0.0	0.1	0.1	0.7 ± 0.6	0.1	6.0
	perfluorododecansulfonic acid	PFDoS	0.1 ± 0.0	0.1	0.1	0.2 ± 0.2	0.1	1.9
		∑PFSA	**4.4 ± 0.6**	**1.6**	**25.4**	**250 ± 248**	**1.3**	**2 486**
preFOS	perfluorooctanesulfonamide	FOSA	1.4 ± 0.3	0.5	14.6	13.6 ± 11.0	0.2	112
	methylperfluorooctanesulfonamide	MeFOSA	0.2 ± 0.0	0.2	0.4	0.2 ± 0.0	0.2	0.2
	ethylperfluorooctanesulfonamide	EtFOSA	0.3 ± 0.0	0.2	1.1	6.8 ± 4.9	0.2	49.4
	ethylperfluorooctanesulfonamido ethanol	EtFOSE	7.4 ± 1.6	1.0	72.2	313 ± 243	4.5	2 455
	perfluorooctanesulfonamido acetic acid	FOSAA	0.9 ± 0.1	0.2	8.6	2.7 ± 1.9	0.2	19.2
	methylperfluorooctansulfonamido acetic acid	MeFOSAA	0.2 ± 0.0	0.2	0.4	0.2 ± 0.0	0.2	0.2
	ethylperfluorooctanesulfonamido acetic acid	EtFOSAA	9.4 ± 2.2	0.9	126	258 ± 187	3.9	1 831
		∑preFOS	**19.7 ± 3.7**	**3.2**	**178**	**594 ± 445**	**17.2**	**4 467**
FTS	6:2 fluorotelomer sulfonic acid	6:2 FTS	0.2 ± 0.0	0.2	0.2	0.9 ± 0.6	0.2	6.6
	8:2 fluorotelomer sulfonic acid	8:2 FTS	2.1 ± 0.3	0.6	15.8	253 ± 212	7.5	2 150
	10:2 fluorotelomer sulfonic acid	10:2 FTS	25.2 ± 4.6	2.3	221	472 ± 269	39.7	2 120
	12:2 fluorotelomer sulfonic acid	12:2 FTS	17.2 ± 3.5	2.8	254	370 ± 182	110	1 723
	14:2 fluorotelomer sulfonic acid	14:2 FTS	1.0 ± 0.2	0.2	18.3	106 ± 68.2	18.9	688
		∑FTS	**45.6 ± 8.4**	**6.4**	**509**	**1 201 ± 657**	**176**	**5 540**
∑PFAS 29			**75.9 ± 11.0**	**18.9**	**606**	**317 ± 157**	**43.7**	**1 3951**

[a]Mean concentrations are shown with the standard error of the mean. Concentrations below the LOQ were treated as half the LOQ. [b]Linear Perfluorooctanesulfonic acid (PFOS).

feeding on offshore, pelagic food webs,[43] and a similar approach was used in the present study. The $\delta^{13}C$ is enriched in benthic-littoral food webs compared to pelagic food webs[44] thus, increased (i.e., less negative) $\delta^{13}C$ in organisms can be interpreted as indications of that biota have increased proportions of benthic organisms in their diet (i.e., increased dietary proportions of organisms from food webs with sediment living organisms at the base). A small trophic fractionation of carbon (i.e., organisms have less negative $\delta^{13}C$ compared with their diet) with an average fractionation of 0.39‰ has been reported.[42] Thus, trophic level adjusted $\delta^{13}C$ were calculated by subtracting relative trophic level multiplied by 0.39 from $\delta^{13}C$. Details about trophic level and carbon sources are described in the SI.

Water samples were extracted using solid-phase extraction (SPE). Sediment and biota samples were extracted using acetonitrile and ultrasonication. PFAS were analyzed using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS, see all PFAS and acronyms in SI Tables S3 and S4). Initially, 44 PFAS were quantified using authentic and internal standards, while 19 PFAS were screened for using exact mass and retention time from authentic standards. In addition, peaks for branched PFOS (Br-PFOS) were identified using a standard mixture of Br-PFOS isomers and quantified against the standard for L-PFOS. An additional 28 PFAS were screened for using exact mass and estimated retention time. Three peaks were observed at expected retention times, and they were quantified using the standard for a similar compound. Following this, the detected compounds indicated the presence and thus use of an EtFOSE based PFAS product, which according to the literature may indicate that SAmPAPs were the parent compounds.[45,46]

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Therefore, SAmPAP diester was screened for in one sample taken in 2018 (the sediment sample used for analyses of EOF), however, the analytical range for most 2018 samples (m/z: 150−1100) did not include SAmPAP diester (m/z: 1203). Therefore, biota samples stored from 2018 sampling, and water and sediment samples from 2019 were reanalysed for SAmPAP diester in 2019. Details of the analytical methods and PFAS acronyms are given in the SI.

Statistics and Data Treatment. Means in the present work are arithmetic means, with standard error of the mean (SEM) where appropriate. Relationships between K_D values, fraction of organic carbon (f_{OC}), and particle size distribution were evaluated using stepwise regression. Relationships between relative trophic level or trophic level adjusted $\delta^{13}C$, and PFAS concentrations in biota were evaluated using Spearman rank correlation coefficient (Spearmans rho). Unpaired Wilcoxon Test was used to test differences in trophic level adjusted $\delta^{13}C$ or relative trophic level between pike and perch.

Trophic magnification factors (TMF) were calculated using linear regression of relative trophic level against log-transformed PFAS concentrations, as previously reported in several studies.[10,33,34] Methods for calculating sediment-water partitioning coefficients (K_D values), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), biota trophic level and carbon sources, and fluorine mass balance are shown in the SI along with details for statistical analysis.

RESULTS AND DISCUSSION

PFAS Concentrations in Water. In lake water, PFOS was the only compound detected above the LOQ. Linear (L) PFOS concentrations of 0.15 and 0.18 ng L^{-1} and branched (Br) PFOS concentrations of 0.07 and 0.10 ng L^{-1} were detected (areas L4 and L6, respectively). Samples from areas L1, L3, and L5 were unfortunately lost; however, it is probable that concentrations at these sites would also be low because they all receive the majority of water (and thus PFAS) from the river. The PFOS concentration in river water from the factory area was <LOQ in 2018, while concentrations of 1.5 and 1.9 ng L^{-1} for L and Br-PFOS, respectively, were detected in the supplementary sample of river water from the factory area sampled in 2019. The reason for this difference could be the larger water volumes and river current and in 2019, which may have remobilized contaminants from banks and riverbeds (the river water volume was on average 21 m^3 s^{-1} in August 2018 and 105 m^3 s^{-1} in June 2019, (measuring station Kistefoss, The Norwegian Water Resources and Energy Directorate, personal communications). Increased and different mobilization is also possibly the reason for the difference in Br-PFOS relative to L-PFOS, in the 2019 sample compared to lake water samples from 2018. However, additional samples are needed to confirm this. Concentrations of all PFAS above the LOQ in water samples are listed in SI Table S5. SAmPAP diester was analyzed in the 2019 sample but was not detected. River and lake water concentrations reported in the present study are low and more comparable to pristine lakes than lakes close to PFAS point sources or urban areas (see SI Tables S5 and S6 for a comparison),[9,33,47−49] although it must be kept in mind that such water bodies are highly variable in nature as well as PFAS source contribution.

PFAS Concentrations in Sediment. A large suite of different compounds (29 PFAS and Br-PFOS) was detected in sediments sampled in 2018. PFAS concentrations (dry weight (d.w.)) in river sediments from the factory area varied greatly between samples, however maximum concentrations were high (e.g., max 2455 μg kg^{-1} of ethylperfluorooctanesulfonamido ethanol [EtFOSE]). Except for SAmPAP diester, which was only analyzed for in one sample in 2018, the highest concentration in lake sediments analyzed in 2018 was found for 12:2 FTS at 253.7 μg kg^{-1}. The one sample analyzed for SAmPAP diester in 2018 showed a SAmPAP diester concentration of 850 μg kg^{-1}. The dominant PFAS in sediments were the C9−C14 PFCA, PFOS, four preFOS compounds, and C10−C16 FTS. Mean, median, and maximum concentrations are shown in Table 1. PFAS were relatively evenly distributed in the lake sediments; however, concentrations were highest closest to the river (L1, L2, and L3, see SI Figures S3 and S5−S8) pointing to the fact that the factory is assumed to be the main contamination source.

Supplementary sediment sampling was conducted in 2019 from the factory area (one sample), and the lake (four samples). Results are shown in SI Table S7. Concentrations in the sample from the factory area were low and mostly below the LOQ. The reason for this was likely related to the high water levels and strong current at the time of sampling, which rendered only coarse sediments below a bridge available for sampling. Concentrations in lake sediment samples from 2019 were comparable to samples analyzed in 2018, see SI Table S7 compared to Table 1. SAmPAP diester dominated (70−93% of the total sum detected PFAS in lake sediments; however, concentrations varied significantly (2.1−1 872 μg kg^{-1}). This indicates that a PFAS product dominated by SAmPAP diester was used at the factory, in agreement with the previously reported use of this compound in paper products.[45,46,50] It is known that commercial SAmPAP formulations were dominated by diester,[29] and for this reason this compound was prioritized for analysis. However, the presence of SAmPAP mono- and triester in sediments are expected as well, as has previously been reported.[32] Interestingly, another group of compounds reported in paper products, fluorotelomer alcohol (FTOH) mono- and disubstituted phosphates (diPAP),[50] were analyzed in 2018, but not detected, indicating that these compounds were not used at the factory (SI Table S3).

The sediment concentrations in lake Tyrifjorden were significantly higher than concentrations reported for pristine lakes. For example, sediment concentrations of 0.001 to 0.44 μg kg^{-1} and 0.19 to 2.7 μg kg^{-1} for PFOS and ∑PFAS 19 respectively, were reported in four Canadian arctic lakes not affected by known point sources.[9] Furthermore, mean concentrations in river sediments directly downstream to the factory reported herein were higher than concentrations in Canadian lake sediments downstream of an airport (28−49 μg kg^{-1} for PFOS and 57−64 μg kg^{-1} for ∑PFAS 19).[9] Sediment PFOS concentrations (which dominated) in rivers, lakes, and canals in The Netherlands (0.5−8.7 μg kg^{-1}) were comparable to lake sediment concentrations in the present study.[47] SAmPAP diester concentrations reported here (up to 1 872 μg kg^{-1} in lake sediments) are very high compared to previous reported concentrations: SAmPAP diester and preFOS have previously been reported in freshwater sediments in Taihu Lake, China (max 4.3 μg kg^{-1}),[32] and in marine sediments from an urban area in Canada (max 0.2 μg kg^{-1}).[31] Thus, sediment PFAS concentrations reported here are higher than concentrations in pristine lakes and generally comparable to water bodies close to point sources and/or urban areas.

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Relatively high PFAS concentrations were detected in sediment pore water (SI Table S8). The highest concentration was for PFOA (1246 ng L^{-1}, area L1). Overall, the C5−C10 PFCA and PFOS were most abundant, whereas preFOS and FTS were only detected above the LOQ in a few samples. The PFAS in sediment pore water are those that are readily bioavailable and represent the risk of the PFAS to biota and surrounding environment.[51] The use of passive samplers[52] in sediments can be a useful approach to assess pore water concentrations in future studies. The lower levels of preFOS and FTS compared to the above-mentioned PFAA are likely due to lower solubility of these larger compounds. This is demonstrated by no concentrations of EtFOSE above the LOQ in porewater, a neutral, large compound (compared to, e.g., PFOS). The importance of the high sediment and pore water concentrations will be discussed below in the context of sediment−water partitioning and uptake by biota.

Sediment−Water Partitioning Coefficients (K_D). Sediment-pore water partitioning coefficients (K_D, L kg^{-1}) are shown in Figure 1 for different PFAS across the whole data set. K_D values for all individual samples are listed in SI Table S10. Generally, K_D values increased with increasing number of C atoms, and preFOS and FTS had higher K_D values than PFAA (e.g., median log K_D: PFHxA 0.9, PFOA 1.1, PFDA 1.6, PFOS 1.1, FOSA 3.2, 10:2 FTS 3.6).

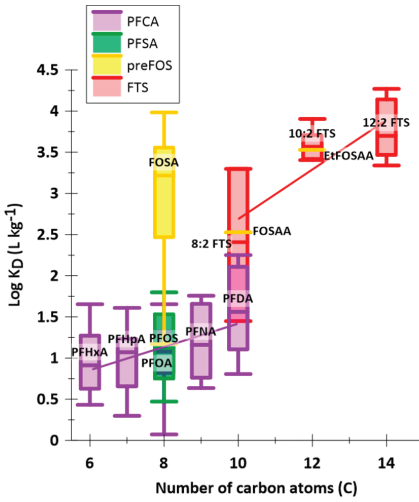

Figure 1. Partitioning coefficients (sediment−pore water, median log K_D values) for different PFAS as a function of number of carbons. Boxes show upper and lower quartiles and whiskers show maximum and minimum values. The purple and red regressions are the relationships between partitioning coefficients and carbon chain length for PFCA log K_D = 0.14C+0.01; R^2:0.17; $p < 0.01$) and FTS (log K_D = 0.30C−0.32; R^2:0.48; $p < 0.01$), respectively. Only compounds for which at least one concentration above the LOQ was detected in both sediments and pore water for at least one replicate are shown. For PFSA, only PFOS showed concentrations above the LOQ in both pore water and sediments in the same sample, and a potential relationship between K_D values and chain length could not be evaluated. Concentrations below the LOQ were treated as half the LOQ. Note that some compounds overlap (PFOS and PFOA, 8:2 FTS and FOSAA, 10:2 FTS and EtFOSAA) and are plotted on top of each other.

The positive association between K_D values and chain length for PFCA and FTS was comparable to values reported elsewhere (see Discussion in the SI).[49] PreFOS have higher K_D values compared to PFOS and PFCA (see Figure 1 and SI Table S10) which is in agreement with previously reported partitioning behavior for EtFOSAA and FOSA compared to PFCA.[53] PreFOS K_D values have also been reported to increase with *N*-alkyl substitution.[31] Indeed, in the present study K_D values follow this trend (FOSAA versus EtFOSAA), and neutral preFOS (i.e., FOSA, EtFOSE) had higher or comparable K_D values than larger acids (EtFOSAA, FOSAA), as expected based on the lower water solubility of neutral compounds. However, these results are based on a few data points (see SI Table S10) and should be treated with care.

As for preFOS, K_D values for long chained FTS were high compared to the shorter PFAA. Based on the K_D values reported herein, long chained PFAA, preFOS, and C > 10 FTS are expected to preferentially partition to the sediment phase, rather than remaining in the water column. This is in agreement with a previous study in which FTS (especially 8:2 FTS) was predominantly found in sediments as compared to other environmental media.[9]

In addition to compound specific properties, K_D values are affected by environmental factors such as sediment characteristics, particularly TOC content.[19] There was no correlation between K_D and sand, silt, or clay content in these sediments or pore waters (Discussion in the SI). A significant relationship between K_D and TOC was found for PFOS ($p = 0.01$, $n = 11$), but no other PFAS in the present study. For a detailed discussion related to this, see the SI.

PFAS Concentrations in Biota. *Fish Liver.* Concentrations in biota varied between tissues and species as summarized in Figure 2. A total of 23 PFAS (+ Br-PFOS) were detected in biota. The dominant PFAS in fish liver were the C10−C13 PFCA and PFOS which were detected in all analyzed samples. The highest concentrations in lake biota were in perch liver ($n = 20$), for example, mean concentrations of PFDoDA: 33.2 $\mu g\ kg^{-1}$; PFTrDA: 22.0 $\mu g\ kg^{-1}$; L-PFOS: 149 $\mu g\ kg^{-1}$; FOSA: 1.3 $\mu g\ kg^{-1}$; and 10:2 FTS: 1.4 $\mu g\ kg^{-1}$. The mean ∑PFAS 23 in perch liver from the lake was 280 $\mu g\ kg^{-1}$, whereas it was 668 $\mu g\ kg^{-1}$ in perch liver from the factory area. PFAS profiles in perch and pike from the factory area were comparable, but PFOS, preFOS, and FTS concentrations were higher, compared to the same biota in the lake, for example, perch liver concentrations of PFDoDA: 42.0 $\mu g\ kg^{-1}$; PFTrDA: 20.0 $\mu g\ kg^{-1}$; L-PFOS 371.5 $\mu g\ kg^{-1}$; FOSA: 44.4 $\mu g\ kg^{-1}$; and 10:2 FTS: 31.3 $\mu g\ kg^{-1}$ (full list for all species is shown in SI Tables S12 and S14). SAmPAP diester was not detected in biota during the supplementary analysis in 2019 (not analyzed for in 2018). In Lake Halmsjön which is significantly impacted with PFAS pollution from firefighting activities at Stockholm airport, ∑PFAS 11 concentrations of 3900 $\mu g\ kg^{-1}$ in perch liver consisting almost entirely PFOS were reported, in contrast to the variety of compounds reported in the present study.[49] It is clear that the PFAS pollution source in the present study directly affects the concentration profile in biota liver and that the PFAS profile is different to biota profiles impacted by previously reported AFFF point sources.

Fish and Crayfish Muscle. PFAS profiles in fish and crayfish muscle were similar to profiles in liver although concentrations

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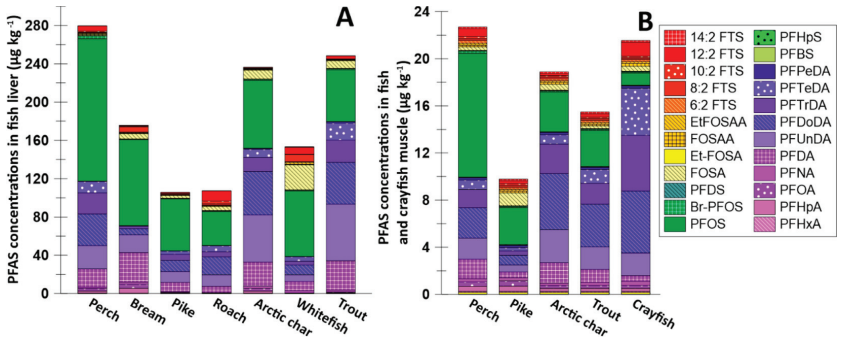

Figure 2. Mean concentrations of detected PFAS (μg kg $^{-1}$ w.w.) in fish liver (A) and fish and crayfish muscle (B) from lake Tyrifjorden (biota from factory area is not included). Only compounds detected above the LOQ in at least one sample replicate are included. Values below the LOQ were treated as half the LOQ.

were lower (Figure 2B). PFOS was the only compound detected above the LOQ in all analyzed muscle samples, and as for liver, the highest concentrations in lake biota were in perch: 10.5 μg kg^{-1}, n = 35. Concentrations in fish muscle from the factory area were higher than concentrations in the lake: perch muscle PFOS concentrations: 25.2 μg kg^{-1}, n = 5 (full list for all species is shown in SI Tables S13 and S14).

PFOS in perch muscle has been reported to decrease with increasing latitude in a study of pristine Swedish lakes.[54] In the two lakes located at comparable latitudes to lake Tyrifjorden, lakes Långtjärn (60°01′N 15°53′E) and Kroktjärn (60°07′N 13°58′E), the ∑PFAS 11 concentrations in perch muscle were approximately 0.6 and 1 μg kg^{-1}.[54] It is clear that lake Tyrifjorden is more heavily contaminated than these Swedish lakes which are not considered to be impacted by a specific PFAS source.

In Lake Halmsjön (PFAS pollution from firefighting activities), ∑PFAS 11 concentrations of 330 μg kg $^{-1}$ in perch muscle were reported and concentrations consisted almost entirely of PFOS.[49] In the Taihu Lake in China (where reported PFAS levels in lake water are high compared to the present study, that is, 13.7 vs 0.18 ng L^{-1}), which is contaminated by wastewater treatment plants (WWTP) and industry, mean PFOS concentrations in fish muscle were between 11.4 and 94.9 μg kg^{-1}, depending on species.[33] Concentrations in lake Tyrifjorden are therefore most similar to those reported from an area with a direct PFAS pollution source.

Pathway from Abiotic to Biota Media and Trophic Transfer. *Bioaccumulation Factors (BAF) and Biota-Sediment Accumulation Factors (BSAF).* BAF for L-PFOS in perch and pike (liver and muscle, the species sampled in the greatest numbers) at stations factory area and L6 are shown in Table 2. These values were calculated for stations where water concentrations were available. Details related to assumptions behind the calculated BAF as well as values for all species and stations can be found in the Methods Section of the SI and Tables S15 and S16). Owing to higher liver concentrations, BAF for liver were higher than for muscle. The highest and lowest BAF_{Liver} for L-PFOS were in perch liver: 5 143 227 (area L5), and in roach liver: 45 283 (area L6), respectively. The highest L-PFOS BAF_{muscle} was 505 582 for perch (area L1) and the lowest was 3114 for crayfish (area L6). The BAF for L-PFOS reported here are higher than reported in previous studies for the same species (Table 2): L-PFOS BAF for perch liver and muscle of 39 000 and 3400, respectively, were calculated for samples taken nearby Stockholm Arlanda airport (AFFF PFAS source),[49] and L-PFOS BAF for whole perch and pike of up to 6300 and 1550 respectively, were reported in samples from Schiphol Amsterdam Airport, again with an AFFF PFAS source.[55] Whole fish concentrations are generally expected to be higher than muscle concentrations,[56] thus the BAF for whole fish is expected to be higher than for muscle. A comparison of the results presented here to previously reported BAF (Table 2), shows that the BAF herein are among the highest ever reported. This may be because the biota are not in equilibrium with the water phase, and that continuous dietary uptake results in relatively high biota concentrations and hence BAF.

The ratios of concentrations in biota (μg kg^{-1} w.w.) to sediment (μg kg^{-1} d.w.), that is, the BSAF for PFAS in liver and muscle are shown in SI Tables S17–S22. The highest BSAF were for L-PFOS in perch liver: 559, 113, 90, and 22 sampled at different areas in the lake (sampling areas L6, L5, L1, and L3 respectively), and PFOS in pike and whitefish liver, 268 and 126 respectively, sampled furthest from the river mouth (sampling area L6). A detailed discussion about BSAF can be found in the SI, however BSAF in the present study vary between areas but are comparable to previously reported BSAF in freshwater environments.[55,57]

The very high BAF in this study compared to previous studies, combined with the BSAF in this study which are comparable to other studies, strengthens the conclusion that uptake routes other than surrounding water and uptake via gills are important in the present study. This suggests that sediments/pore water are an important source of PFAS to the food web.

Correlations with the Benthic Food Web and Uptake from Sediments. Due to the combination of high PFAS concentrations in biota compared to lake water (high BAF) and high concentrations of certain PFAS in lake sediments and pore water (BSAF comparable to elsewhere), correlations between PFAS concentrations and trophic level adjusted muscle $\delta^{13}C$ (as an indicator of dietary sources) were tested. Due to differences in expected contaminant loads between areas, relationships were tested within each area. Significant ($p \leq 0.05$) positive relationships (indicating increased proportions of benthic organisms in the diet, see Materials and

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Table 2. Bioaccumulation Factors (BAF, Water:Biota Tissue) for PFOS in Perch and Pike Sampled at Stations Factory Area and Area L6 in the Present Study Compared to Literature Values[a]

species							
common name	scientific name	marine or freshwater	BAF (L kg^{-1})	water concentration (ng L^{-1})	PFAS source	study type	study
Liver							
perch	*Perca fluviatilis*	freshwater	804 900–>3 714 600	<0.10–0.18	paper industry	field	present study
pike	*Esox lucius*	freshwater	386 000–>484 900	<0.10–0.18	paper industry	field	present study
perch	*Perca fluviatilis*	freshwater	39 000	98	AFFF	field	Ahrens et al. (2015)[49]
common shiner	*Notropus cornutus*	freshwater	6250–124 700	320	AFFF	field	Moody et al. (2002)[58]
mullet	*Mugilidae*	marine	12 400	13	industry/WWTP	field	Yoo et al. (2009)[59]
bluegil	*Lepomismacrochirus*	freshwater	41 600[b]	7	industry/WWTP	field	Taniyasu et al. (2003)[60]
silver perch	*Bidyanus bidyanus*	freshwater	26 000	10	reclaimed water	field	Terechovs et al. (2019)[61]
crucian carp	*Carassius carassius*	freshwater	1500[c]	13–18	industry/WWTP	field	Shi et al. (2018)[62]
chub	*Leuciscus cephalus*	freshwater	4600	27	WWTP	field	Becker et al. (2010)[63]
Muscle							
perch	*Perca fluviatilis*	freshwater	59 200–>251 900	<0.10–0.18	paper industry	field	present study
pike	*Esox lucius*	freshwater	18 700–>57 200	<0.10–0.18	paper industry	field	present study
perch	*Perca fluviatilis*	freshwater	3400	98	AFFF	field	Ahrens et al. (2015)[49]
	Cyprinus carpio	freshwater	10 000	0.03	background	field	Meng et al. (2019)[64]
	Carassius auratus	freshwater	4000	0.03	background	field	Meng et al. (2019)[64]
	Erythroculter dabryi	freshwater	26 670	0.03	background	field	Meng et al. (2019)[64]
	Hypophthalmichthys molitrix	freshwater	8330	0.03	background	field	Meng et al. (2019)[64]
	Siniperca chuatsi	freshwater	65 000	0.03	background	field	Meng et al. (2019)[64]
minnow	*Hemiculter lcucisculus*	freshwater	6092	5.68	industry/WWTP	field	Fang et al. (2014)[33]
silver carp	*Hypophtha lmichthys molitrix*	freshwater	1761	5.68	industry/WWTP	field	Fang et al. (2014)[33]
whitebait	*Reganisalanx brachyrostralis*	freshwater	2835	5.68	industry/WWTP	field	Fang et al. (2014)[33]
crucian	*Carassius cuvieri*	freshwater	15 599	5.68	industry/WWTP	field	Fang et al. (2014)[33]
lake saury	*Coilia mystus*	freshwater	9190	5.68	Industry/WWTP	field	Fang et al. (2014)[33]
carp	*Cyprinus carpio*	freshwater	7623	5.68	Industry/WWTP	field	Fang et al. (2014)[33]
mongolian culter	*Culter mongolicus*	freshwater	15 088	5.68	industry/WWTP	field	Fang et al. (2014)[33]
mud fish	*Oriental weatherfish*	freshwater	10 810	5.68	industry/WWTP	field	Fang et al. (2014)[33]
chinese bitterling	*Rhodeus sinensis Gunther*	freshwater	6444	5.68	industry/WWTP	field	Fang et al. (2014)[33]
gobies	*Ctenogobius giurinus*	freshwater	6144	5.68	Industry/WWTP	field	Fang et al. (2014)[33]
crucian carp	*Carassius auratus*	freshwater	120 000	0.48	industry	field	Wang et al. (2012)[65]
silver perch	*Bidyanus bidyanus*	freshwater	6000	10	reclaimed water	field	Terechovs et al. (2019)[61]
crucian carp	*Carassius carassius*	freshwater	900[c]	13–18	industry/WWTP	field	Shi et al. (2018)[62]
nile tilapia	*Oreochromis niloticus*	freshwater	398	0.073–5.6	Industry/WWTP	field	Ahrens et al. (2016)[66]
	Labeobarbus megastoma	freshwater	5012	0.073–5.6	industry/WWTP	field	Ahrens et al. (2016)[66]
	Labeo- barbus gorguari	freshwater	3981	0.073–5.6	industry/WWTP	field	Ahrens et al. (2016)[66]
	Labeobarbus intermedius	freshwater	794	0.073–5.6	industry/WWTP	field	Ahrens et al. (2016)[66]
eel	*Anguilla anguilla*	freshwater	234–1148	20–490	AFFF	field	Kwadijk et al. (2014)[55]
Whole Fish							
pike	*Esox lucius*	freshwater	1549	340–490	AFFF	field	Kwadijk et al. (2014)[55]
perch	*Perca fluviatilis*	freshwater	2344–6310	20–490	AFFF	field	Kwadijk et al. (2014)[55]
perch	*Perca fluviatilis*	freshwater	6400	98	AFFF	field	Ahrens et al. (2015)[49]
lake trout	*Salvelinus namaycush*	freshwater	12 589	0.2–5.9	background/unknown		Furdui et al. (2007)[67]
	Pseudohemiculter dispar	freshwater	25 670	0.03	background	field	Meng et al. (2019)[64]
sculpin	*Cottus cognatus*	freshwater	234 000	2.20	unknown	field	Houde et al. (2008)[68]
lake trout	*Salvelinus namaycush*	freshwater	34 000	2.20	unknown	field	Houde et al. (2008)[68]
herring	*Clupea harengus membras*	marine	22 000	0.25	background	field	Gebbink et al. (2016)[69]

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Table 2. continued

species							
common name	scientific name	marine or freshwater	BAF (L kg^{-1})	water concentration (ng L^{-1})	PFAS source	study type	study
Whole Fish							
sprat	*Sprattus sprattus*	marine	23 200	0.25	background	field	Gebbink et al. (2016)[69]

[a]Only studies reporting specific species and tissue (liver, muscle, or whole organism) were included. [b]The highest BAF reported in the study. No other species-specific values were reported [c]Value from figure (approximate)

methods and SI) were found (for at least one area) between trophic level adjusted $\delta^{13}C$ and PFAS concentrations in muscle and/or liver for C11−C14 PFCA (PFUnDA, PFDoDA, PFTrDA, PFTeDA), the C10 PFSA (PFDS), two preFOS compounds (FOSA and FOSAA), and the 12−14C FTS (10:2 FTS and 12:2 FTS) (SI Table S25). In areas where the greatest diversity of species was sampled (and the greatest variability in $\delta^{13}C$ was found: muscle samples from areas L3 and L6) significant positive correlations were shown for C11−C14 PFCA, preFOS (FOSAA), and 12:2 FTS. The compounds for which positive correlations with trophic level adjusted $\delta^{13}C$, and thus the benthic food web, were shown are relatively consistent with those compounds that have high K_D values. This suggests that uptake of these compounds is associated with the benthic food web, and thus the sediments are an important PFAS source. Indeed, based on PFAS profiles in Canadian lake food webs, sediments (via the benthic food web) are suggested to be the major source to PFAS in arctic char.[9] Higher PFOS concentrations in river goby (*Gobio gobio*) compared to chub (*Leuciscus cephalus*) have previously been suggested to be due to higher intake of benthic invertebrates living in PFOS contaminated sediments.[63] Similarly, sediments, not water, were suggested to be the major PFAS source to the aquatic food web in Lake Ontario.[34]

Biomagnification. High concentrations in top predator fish feeding on the benthic food web were previously suggested to be due to biomagnification.[34] A similar mechanism could possibly explain the high levels observed in top predatory fish in the present study. Individual relative trophic levels are shown in SI Table S24. In the present study, liver and muscle samples were analyzed in fish and muscle samples were analyzed in crayfish. In order to include both invertebrates (crayfish) and several species of fish in the TMF calculations, TMF are only reported for muscle samples (TMF_{muscle}) from area L3 and L6 (areas were the greatest diversity of species were sampled). The TMF_{Muscle} for L-PFOS was 3.7 and 9.3 at areas L3 and L6, respectively ($p < 0.05$). TMF_{muscle} for PFCA at areas L3 and L6 were below 1 or nonsignificant, except for PFDA at area L6 which had a TMF_{muscle} of 1.8 ($p = 0.01$). TMF_{muscle} for preFOS and FTS were below 1 or nonsignificant ($p > 0.05$). In two freshwater food web studies similar to the present, in Taihu Lake (where PFOS and PFCA were the dominate compounds), TMF for PFOS were reported to be 2.9 and 3.86.[33,70] TMF for PFOS reported in studies of river and estuarine food webs were between 0.94 and 1.5.[71−73] Thus, the TMF for PFOS reported for lake Tyrifjorden were relatively high compared to previous reported values in comparable studies. The low TMF_{muscle} for PFCA are due to relatively high concentrations of these compounds in crayfish which are at a lower trophic level than the investigated fish. High levels in crayfish are likely due to uptake of these compounds (or their precursors) from sediments (pore water and/or benthic organisms) as discussed above.

Franklin[74] reviewed TMF in studies with varying organisms and tissues and argue that the use of different tissues for the different trophic levels (e.g., whole body homogenate versus liver) introduces uncertainties when calculating TMF.[74] Whole body homogenates is recommended, but not always practical.[74] In this study, it was challenging to prepare whole body homogenates (e.g., the scull of large fish and exoskeleton of crayfish). For this reason, muscle samples were used to calculate TMF in the present study. Furthermore, plankton could not be sampled in great enough numbers at the site as has been done in previous studies (e.g., refs 33, 70, 75, and 76). Thus, the results reported here should be interpreted with these factors in mind. One explanation for the high PFOS TMF and relatively large variation between areas in the present study could be related to the role of precursor compounds. Transformation of precursors has been suggested to be one reason for high PFOS TMF[33] and the large variation in TMF values between studies.[74] Therefore, the relatively high TMF for PFOS reported here indicate possible transformation of precursor compounds (released from the factory), and strongly suggest that not all of these compounds were detected by the targeted analysis. However, mechanisms behind the contribution from precursor compounds to TMF values for PFAA are complex and not well understood, and laboratory studies that evaluate biomagnification potential of PFAS are needed.[74]

Precursor Compounds and Biotransformation. EOF was used to investigate to what extent the targeted PFAS analyses could explain the total organic fluorine in sample extracts (assuming that PFAS constitutes a large fraction of the EOF and that inorganic fluoride is not extracted, see the SI).[77−79] Of seven sediment samples analyzed for EOF, only one was above the LOQ (39−133.0 μg F kg^{-1}): a sediment sample from area L1 with 964 μg F kg^{-1}. In fish liver, EOF concentrations varied between 86 μg kg^{-1} (perch from area L6) and 1 348 μg kg^{-1} (perch from area L3). EOF concentrations and the sum of organic fluorine from targeted PFAS analysis (compounds in concentrations above LOQ only) are shown in Figure 3. The sum fluorine from the targeted analysis ($\sum F_{targ}$) as a percent of EOF are shown in SI Figure S10 and Table S28.

$\sum F_{targ}$ accounts for approximately 54% of the EOF in the sediment sample. Previous studies have reported that identified PFAS accounted for between 2 and 44% of the anionic fraction of the extractable organic fluorine in sediments,[80] and less than 8% in water.[77] In the samples in this study, approximately 48% of the EOF in the sediment sample is due to SAmPAP diester. SAmPAP diester has been reported to strongly sorb to sediments,[31] and this can decrease bioavailability[81] and thus dietary absorption efficiency in biota (0.04−2.25% in perch).[82] Nevertheless, given the high sediment concentrations reported here (max: 1872 μg kg^{-1}), uptake of small amounts is likely even though concentrations were below the LOQ in biota (which can occur if degradation rates are much higher than

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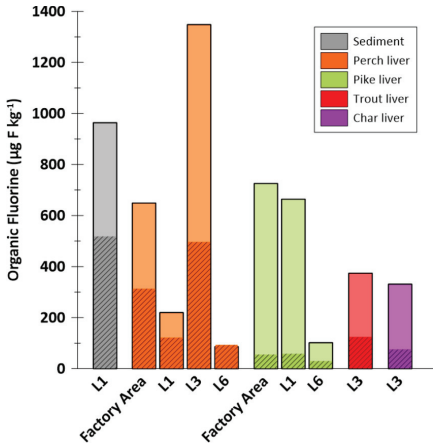

Figure 3. Sum of extractable organic fluorine (EOF, solid bars with black outline, i.e., the complete bar) as well as sum fluorine from detected compounds from targeted analysis (hatched bars) in sediment (d.w.) and in fish livers (w.w.) from areas factory area, L1, L3, and L6 (n = 1).

uptake rates). Perch has previously been reported to biotransform SAmPAP diester to preFOS compounds (EtFOSAA, FOSAA, and FOSA), and PFOS.[82] Contradictory results have previously been reported related to the role of microbial processes on the production of preFOS and PFOS from SAmPAP diester in sediment. Negligible degradation was reported in marine sediments;[81] however, significant degradation was reported in freshwater sediments[32] possibly indicating a difference between the microbial processes in marine and freshwater sediments.[32] In agreement with this, the two 2019 samples with the highest SAmPAP diester concentrations also had high concentrations of the known degradation product, EtFOSAA (SI Table S7). The same applies for the sediment sample analyzed for SAmPAP diester in 2018 (850 μg kg^{-1} and 56.4 μg kg^{-1} SAmPAP diester and EtFOSAA, respectively). Thus, the high SAmPAP diester concentrations in sediments in the present study suggest that there may be significant production of preFOS and PFOS via a similar dissimilatory mechanism.

Intermediates, from bacterial degradation in sediments or biotransformation in higher organisms, and isomers, not targeted by the chemical analysis, as well as SAmPAP mono- and triester might explain some of the unknown EOF. The $\sum F_{targ}$ as a percent of EOF in fish livers varied between species and increased with distance from the factory (highest percentages in area L6), meaning that more of the PFAS present are captured by the target analysis further from the source. The increasing fraction of known PFAS with distance from the factory likely reflects a more complete degradation to terminal end products such as PFSA and PFCA that were targeted as this process progresses with increasing time and in this case, therefore, with distance from the source. The highest percentages of EOF explained by $\sum F_{targ}$ in biota were in perch (37−108%), while the lowest were in pike liver (9−30%). Pike and perch did not differ in trophic level adjusted δ^{13}C and relative trophic levels (p: 0.19−0.90), thus differences in dietary PFAS exposure do not appear to explain the observations. Differences in biotransformation potential is a possible explanation.

In the present study, preFOS compounds have high K_D (e.g., FOSA log K_D: 3.2), are found in high concentrations in sediments (FOSA, EtFOSE, FOSAA, EtFOSAA) and some (FOSA, FOSAA) are positively correlated with δ^{13}C in biota (i.e., increased proportions of benthic organisms in their diet). The relatively low K_D value for PFOS (log K_D: 1.1) and the low water concentrations indicate that PFOS produced from precursors in sediments over time will be dissolved in water, diluted due to the large body of water and removed due to water exchange. The detected concentrations of preFOS and SAmPAP diester in lake Tyrifjorden sediments indicate they are a large potential source for continuous input of PFOS to lake water and the food web. Biotransformation (in sediments) and water exchange and dilution are possible explanations for the relatively low PFOS concentrations reported in lake water compared to sediments. C9−C14 PFCA and long chained FTS dominated sediment concentration profiles, and concentrations in biota were positively correlated to δ^{13}C (C12−C14 PFCA and C12−C14 FTS). High K_D values were calculated for long chained FTS, while lower K_D values were calculated for PFCA. The shorter chain FTS, 6:2 FTS, has previously been reported to degrade to PFCA with a carbon chain length ≤ six.[83] Assuming that the longer FTS, which dominate here, follow the same degradation pattern, they will be transformed to PFCA with chain length shorter, or similar to, the perfluorinated alkyl chain in FTS (C ≤ 14). Thus, in addition to direct exposure to PFCA released from the factory, long chained FTS found in sediments are possibly precursors responsible for the high PFCA concentrations reported for crayfish and fish in the present study (due to biotransformation in crayfish/fish or in organisms which make up their diet). Indeed, transformation of 8:2 and 10:2 FTS (and unknown precursors) has previously been suggested to be a significant contribution to PFCA in an urban river in France,[73] and unknown PFCA precursors have been suggested to be a major exposure pathway to PFCA for fish from the Baltic sea.[69] Indications of significant contributions from PFAA precursors in sediments to PFAA concentrations in biota reported in the present study, and the proposed mechanisms (uptake into benthic organisms and biotransformation as they are transported through the food chain) warrant future laboratory exposure studies, as well as investigations of similar case sites expected to be dominated by PFAA precursor compounds.

Environmental Implications. The low water concentrations in lake Tyrifjorden reflect water exchange and dilution of dissolved compounds. Half-lives of 12 days have been reported for PFOS in blood of rainbow trout (*Oncorhyncus mykiss*) exposed to clean water.[84] It is likely that PFOS, and PFCA of similar chain length or shorter (that are more water-soluble than preFOS and the long FTS compounds), dissolved in lake water or taken up by fish, may be relatively quickly removed from the lake system. It follows therefore that the high biota concentrations reported here are indicative of continuous input to the system, which cannot be explained by active industrial sources in the area. Input from sediments/pore water is a likely explanation.

The overwhelming number of PFAS makes it practically impossible to analyze and track the behavior of each individual compound. However, as illustrated in this study, the complex behavior of PFAA and their precursors can be elucidated to some degree using a combination of targeted analysis of a

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limited number of compounds and nontargeted approaches such as EOF, in combination with the analysis of biota trophic levels and carbon sources. The results illustrate the importance of investigating other matrixes in addition to water, especially in cases where sources are unknown or the PFAS mixture released is not well characterized. PFAA exposure and future exposure potential to biota in the lake would be greatly underestimated if only PFAA concentrations (without precursors) in water and sediments were considered. Due to transformation of larger, less water-soluble, precursor compounds, sediments can be a source to PFAA, some of which are normally associated with uptake from water.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04587.

Detailed site description; details for sampling and sample preparations; laboratory methods, including details for extraction methods and analytical methods (targeted PFAS and extractable organic fluorine); quality assurance procedures; details of statistical methods and data analyses; methods for calculating sediment−water partitioning coefficients (K_D values), bioaccumulation factors (BAF), biota-sediment accumulation factors (BSAF), biota trophic level and carbon sources, and fluorine mass balance; supplementary results and discussion (related to relationships between PFAS carbon chain length and K_D values, and accumulation factors); supplementary tables and supplementary figures (PDF)

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Notes

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Appendix: Paper III

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Supplementary Information

Fluorinated precursor compounds in sediments as a source of Perfluorinated Alkyl Acids (PFAA) to biota

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Site description - Lake Tyrifjorden

Lake Tyrifjorden (60.03° N, 10.17° E) is a freshwater lake in the southern part of Norway (see Figure S1). The surface area of the lake is 138 km^2. The lake is shaped like the letter *H,* where the mid part and the southeast "arm" are deep (60-288 m), while the remaining parts are relatively shallow (mostly less than 40 m), see Figure S2. The average water retention time in the lake is estimated to be 2.6 years, however it is expected to vary in different areas.[1] Area L6 (see Figure S1) is expected to have a reduced water exchange. The main riverine input is the river Storelva which has an average flow of 151 $m^3\ s^{-1}$ (personal communications, The Norwegian Water Resources and Energy Directorate, [data for the measuring stations *Strømstøa* and *Kistefoss* between 01.01.1978 and 31.12.2019]). Thus, due to the size of the lake and the riverine input, there is a large potential for dilution of dissolved compounds. The average precipitation is 1.02 m y^{-1}, the average temperature is 6.2 °C, and the average wind speed is 2.2 m s^{-1}.[2]

Sampling and sample preparation

Six lake sampling areas were selected to represent a gradient of increasing distance, and thus likely decreasing PFAS load from the source area (shown in Figure S1). The areas L1 to L6 are named according to their proximity to the PFAS source areas. L1 is located at the river mouth and was expected to be most influenced by PFAS release. Area L6 is located in a part of the lake which is separated from the rest of the lake by a narrow inlet and is the part of the lake expected to be the least influenced by the contaminant source.

Biota in the lake was sampled between June 7th and October 6th, 2018. Lake water, sediment, and pore water were sampled in the period September 27-31, 2018. Biota, water and sediment in the Factory area (river directly downstream to the factory) were sampled in the period August 21st and 24th, 2018. The total number of samples analysed in 2018 in each area is shown in Table S1 (abiotic samples) and S2 (biotic samples). Sample storage prior to analysis is described in chapter *Quality assurance and sample storage.*

Supplementary sampling of water and sediments was performed in June 2019. The reason for the supplementary sampling campaign was two-fold: 1) that there was a need for a larger water volume to obtain a lower LOQ in the water samples from the factory area, and 2) that the preFOS parent compound SAmPAP diester was detected in a sediment sample from 2018, but an analytical standard was not available at the time. The analytical range for most 2018 samples (m/z: 150-1100) did not

include SAmPAP diester (m/z: 1203). In order to further investigate the presence of SAmPAP diester, biota samples stored from the 2018 campaign were re-analysed for SAmPAP diester.

Lake and river surface water

River and lake surface water was sampled in triplicate from five areas (L1, L3, L4, L5, and L6) each representing the different parts of the lake, and from the factory area, shown in Figure S1. Water samples were collected in HDPE bottles (1 L) which were submerged in the water (approximately 0.5 m below surface). Lake and river water were sampled in September 2018. In 2019, one additional water sample from the factory area was collected following the same method.

Sediments

In 2018, sediments were sampled from the river in two locations upstream the factory and nine locations in the factory area, and in 94 locations scattered across the lake (shown in Figure S3). A small van Veen grab was used to sample the top 10 cm of fine sediment in the river as there was a high proportion of rocks on the river bed. Lake sediments were sampled using a Kajak-Brinkhurst sediment corer from a vessel equipped with a high-resolution sounder. A closing mechanism was triggered on contact with sediments, collecting a core of approximately 30 cm length and 8.5 cm diameter. The top 2 cm were sliced carefully and transferred to a burnt glass jar. At some locations (those with high water content, coarse sediments, or deep water), it was not possible to take a core sample and a van Veen grab was used. The grab was cautiously lowered on to the sediment surface and an undisturbed sample of the top 10 – 15 cm sediment was collected. A steel spoon was used to transfer a sample of the top 0-2 cm into the glass jars. In 2019, sediment samples from the factory area (1 sample), L1 (2 samples), and L3 (2 samples), were collected following the same methods.

Sediments collected for targeted PFAS analyses in pore water and sediment (for calculations of K_D values), analyses of total organic carbon (TOC), and sediment grain size distribution were sampled in triplicate from the same five areas as for water samples (L1, L3, L4, L5, and L6) in the lake and 1 sample location (n=1) in the river (shown in Figure S4).

Biota

Fish (perch [*Perca fluviatilis*], pike [*Esox Lucius*], whitefish [*Coregonus lavaretus*], roach [*Rutilus rutilus*], trout [*Salmo trutta*], bream [*Abramis brama*] and arctic char [*Salvelinus alpinus*] were sampled at the areas: factory area, L1, L2, L3, L5, and L6 using fish nets (35-39 mm mesh size). The nets were stretching from 3 to 15 m below the water surface in the lake, and between 1 and 2.5 m below surface in the shallower river at the factory area. Crayfish (*Astacus astacus*) were sampled using traps placed on the lake bottom substrate (bream from area L6 were used as bait that were contained in a closed bait-bag). Fish were killed by a blow to the head. Sampled biota varied between areas as shown in Table S2

(for biota analysed in 2018). In 2019, supplementary analysis was performed on biota from the factory area (2 perch), L1 (2 perch, 2 Crayfish), and L3 (2 perch, 2 Crayfish).

Laboratory methods

Pore water

Approximately 30-35 g of sediment was centrifuged at 11 000 G for 45 minutes. The pore water (supernatant) and sediments were transferred to different polyethylene test tubes for extraction and analysis.

Total organic carbon content and grain size in sediments

The total organic carbon (TOC) was analysed using thermal oxidation and infrared detection, (LOD of 0.1 %), by ALS Laboratory Group AS according to methods CSN ISO 10694 and CSN EN 13137:2002.

Sediment grain size distribution between fractions (<2 µm, 2-63 µm, and >63 µm) was determined using sieving and laser diffraction (LOD of 0.1% for each fraction). Particles smaller than 2 µm were classified as clay, particles between 2 and 63 µm were classified as silt, and particles above 63 µm were classified as sand.

Extractable organic fluorine

Extractable organic fluorine (EOF) in sediment and fish liver was analysed by Örebro University. A separate portion of the samples were extracted exactly as described for targeted PFAS analysis but PFAS standards were not added to the extract. Therefore, procedural losses could not be accounted for, which introduces a source of error. In a previous study in which biota samples were spiked with NaF and then extracted with acetonitrile (as in the present study), no inorganic fluoride was extracted.[3] Thus it was assumed that extraction of inorganic fluoride was negligible here. An exact volume was obtained by diluting samples with acetonitrile utilizing 10 mL metric flasks.

EOF content was measured using a combustion ion chromatography (CIC) system. The CIC consists of a combustion module (Analytik Jena, Germany), a 920 Absorber Module and a 930 Compact IC Flex ion chromatograph (both from Metrohm, Switzerland). Separation of anions was performed on an ion exchange column (Metrosep A Supp 5 – 150/4.0) using carbonate buffer (64 mmol/L sodium carbonate and 20 mmol/L sodium bicarbonate) as eluent for isocratic elution. In brief, the sample extract (0.1 mL) was injected on to a quartz boat, which was pushed into the furnace by the autosampler. The furnace was kept at 1000-1050 °C for combustion, during which, all organofluorine compounds were converted into hydrogen fluoride (HF). A carrier gas (argon) was constantly pumped through the combustion tube, the gas carries all formed HF into the absorber module where MilliQ water is used to capture the

HF. A 2 mL aliquot of the absorber solution was then injected on a pre-concentration column and then injected on the ion chromatograph. The concentration of F^- ions in the solution was measured using ion chromatography.

Quantification of samples was based on an external calibration curve. For both calibration and samples, the peak area of the preceding combustion blank was subtracted from peak area of the sample to correct for the background contamination.

Fluoride signal was observed in combustion blanks even when no sample was analysed. Prior to sample analysis, multiple combustion blanks were performed until stable fluoride signals were reached; the relative standard deviation of the three most recent combustion blanks was lower than 5 %.

The limit of quantification (LOQ) was determined separately for each sample preparation batch as the procedural blank of the batch plus three times the pooled standard deviation of the procedural blanks. The reported values were not corrected for extraction blanks.

Combustion blanks (CIC analysis cycle without a sample) were made between sample injections to evaluate the presence of carryover between samples and to obtain a reliable estimate of the background fluorine levels. The repeatability of the instrument was tested by triplicate analysis of dilutions made from an anion SRM solution (product code 89886, Sigma-Aldrich). The five dilutions were in the range of 60 ng F g^{-1} to 1200 ng F g^{-1} and the relative standard deviation at all five dilution levels were below 25%. Combustion of 100 ng and 500 ng of SRM 2143 – *p*-Fluorobenzoic (NIST) resulted in recoveries of between 90 - 98%. Combustion of 500 ng of PFOS resulted in recoveries ranging from 89 to 92% and combustion 500 ng of PFOA resulted in 85 to 90% recoveries. Combustions of 100 ng PFOS standard (n=4) before, during and at the end of analysis were found to be 85 ng with a relative standard deviation of 9%.

Biological parameters

Length and weight of fish and crayfish were measured before dissection. The ratio between the stable nitrogen isotopes ^{14}N and ^{15}N ($\delta^{15}N$), and carbon isotopes ^{12}C and ^{13}C ($\delta^{13}C$) in muscle tissue were determined for assessment of trophic level and carbon sources. Stable isotopes were analysed by IFE, Norway (Institute for Energy Technology). Analysis were performed by combustion in an element analyser, reduction of NOx in a Cu-oven, separation of N_2 and CO_2 on a GC-column followed by determination of $\delta^{15}N$ and $\delta^{13}C$ on an Isotope Ratio Mass Spectrometer (IRMS).

Extraction and targeted PFAS analysis

Isotope labelled and native standards were obtained from Wellington, with a few exceptions: 6:2 FTOH, 8:2 FTOH, 10:2 FTOH were obtained from Chiron, while 4:2 F53B, 6:2 F53B, 8:2 F53B, FHxSA and

MeFHxSA were from other research laboratories that the analysing laboratory has project connections with.

For all samples, a mixture of isotope labelled PFAS (MPFAC-MX_C-ES purchased from Wellington Laboratories: M8PFOSA, M2-6:2FTS, M2-8:2FTS, d5-N-MeFOSA-M, d9-N-etFOSE-M, d5-N-EtFOSAA-M, M4-8:2 diPAP) was added as an internal standard (IS) for quantification before extraction. For sediments, approximately 5 grams of wet sediment was weighed and IS was added. The remaining sample was weighed before and after drying to determine the water content, and this was used to calculate the dry weight of the extracted material. Extraction was performed twice using acetonitrile (8+6 mL), ultrasonic bath (30+30 min) and shaking (30+30 min). For biota samples, approximately 2 grams of biota sample was weighed and IS was added. Extraction was carried out twice using acetonitrile (5+4 mL), ultrasonic bath (30+30 min) and shaking (30+30 min). Extracts were concentrated under a nitrogen flow. 500 mL of lake and river water samples, and smaller volumes of pore water were extracted using Waters HLB solid-phase extraction (SPE) columns.

PFAS were analysed using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-qTOF-MS). An Acquity Ultra Performance HPLC system (Waters) was used to inject aliquots of 7 µL extract onto a Waters Acquity BEH C8 reversed phase column (100 x 2.1 mm, 1.8 µm particles. The target compounds were separated at a flow rate of 0.5 mL min^{-1} using acetonitrile (A) and 5.2 mM NH_4OAc in water (B). The following binary gradient was applied: 0-1.5 min, 12% of A; 1.5-11 min, linear change to 99% of A; 11-13 min, 99% of A. The Acquity system was coupled to a Xevo G2-S Q-ToF-HRMS instrument (Waters) using negative ion electrospray ionization (ESI(-)). Mass spectra were registered in full scan mode (mass range m/z of 150-1100 for initial samples, however it was increased to 150-1300 to include SAmPAP diester (m/z: 1203) in later analyses as described below). The following optimized parameters were applied: Capillary voltage, 0.7 kV; desolvation temperature, 500 °C; source temperature, 120 °C; nitrogen desolvation gas flow, 800 L h^{-1}. Quantitative analysis was performed employing extracted mass chromatograms from full scan recording using the m/z (typical mass tolerance of 0.03 µ) for the different analytes.

Initially, 44 PFAS were analysed using authentic and internal standards, while peaks for Br-PFOS were identified using a standard mixture of Br-PFOS isomers and quantified against the standard for L-PFOS. 19 PFAS were screened for using exact mass and retention time from authentic standards. An additional 28 PFAS were screened for using exact mass and estimated retention time (using MassLynx Mass Spectrometry Software). Peaks at expected retention times were observed for three PFAS, and they were quantified using the standard for a similar compound: PFPeDA was quantified using the standard for PFHxDA, and 12:2 FTS and 14:2 FTS were quantified using the standard for 10:2 FTS. All

PFAS and acronyms are shown in Table S3 and Table S4. The detected compounds indicated the presence and thus use of an EtFOSE based PFAS product, which according to the literature could indicate that SAmPAPs were the parent compounds.[4,5] Therefore, SAmPAP diester was screened for using exact mass and estimated retention times in a few samples in 2018 (the sediment samples used for analyses of EOF) and quantified against the standard for PFOS. An authentic standard for SAmPAP diester was later acquired, and biota samples stored from 2018 and water and sediment samples taken in 2019 were reanalysed for SAmPAP diester and the 20 most abundant compounds from the investigation in 2018 (see chapter *Sampling and sample preparation in the SI*). The analytical range for most 2018 samples (m/z: 150-1100) did not include SAmPAP diester (m/z: 1203) and SAmPAP diester could therefore not be looked for in these data. Concentrations determined when using the authentic standard were 17 times higher than when the PFOS standard was used. The difference was due to the ionization efficiency between PFOS and SAmPAP diester which is consistent with a factor of about 17. Following this, the concentration in the sample where PFOS was used as the standard was corrected using a factor of 17. The 45 PFAS (+ Br-PFOS) which were analysed using authentic and internal standards (including SAmPAP diester), the 19 PFAS which were screened for using exact mass and retention time from authentic standards, and the three PFAS that were quantified using the standard for a similar compound are shown in Table S3. The 25 PFAS which were screened for using exact mass and estimated retention times, but not detected are shown in Table S4.

In addition to SAmPAP diester (which was only analysed for in a few samples), 30 compounds and Br-PFOS were detected and quantified. The quantified compounds included 12 perfluorocarboxylic acids (PFCA): perfluoro-n-pentanoic acid (PFPA); perfluoro-n-hexanoic acid (PFHxA); perfluoro-n-heptanoic acid (PFHpA); perfluoro-n-octanoic acid (PFOA); perfluoro-n-nonanoic acid (PFNA); perfluoro-n-decanoic acid (PFDA); perfluoro-n-undecanoic acid (PFUnDA); perfluoro-n-dodecanoic acid (PFDoDA); perfluoro-n-tridecanoic acid (PFTrDA); perfluoro-n-tetradecanoic acid (PFTeDA); perfluoro-n-pentadecanoic acid (PFPeDA); perfluoro-n-hexadecanoic acid (PFHxDA), 6 perfluorosulfonic acids (PFSA): perfluoro-1-butanesulfonate (PFBS); perfluoro-1-hexanesulfonate (PFHxS); perfluoro-1-heptanesulfonate (PFHpS); linear and branched perfluoro-1-octanesulfonate (PFOS); perfluoro-1-decanesulfonate (PFDS); perfluoro-1-dodecansulfonate (PFDoS); 7 preFOS compounds: perfluoro-1-octanesulfonamide (FOSA); N-methylperfluoro-1-octanesulfonamide (MeFOSA); N-ethylperfluoro-1-octanesulfonamide (EtFOSA); 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (et-PFOSE); perfluoro-1-octansulfonamidoacetic acid (FOSAA); 2-(N-methylperfluoro-1-octansulfonamido)acetic acid (me-FOSAA); 2-(N-ethylperfluoro-1-octansulfonamido)acetic acid (EtFOSAA), and 5 fluorotelomer sulfonates (FTS): 6:2 FTS; 8:2 FTS; 10:2 FTS; 12:2 FTS; 14:2 FTS.

Quality assurance and sample storage

Lab blanks were run following the same procedures as for field samples. Blank samples were used for each batch of samples analysed (20-25 samples). Each batch contained only samples of the same media, and samples for standard addition. Concentrations in the blank samples were low (<0.5 ng g^{-1} or ng L^{-1}) and consistent regardless of the use of different equipment, indicating little cross contamination. Blank values were subtracted from results when calculating concentrations in samples. No significant carry-over was detected between samples, even when sample concentrations were extremely high (e.g. for SAmPAP diester). The autosampler was set up with a stainless-steel needle and a washing program using MeOH/Isopropyl alcohol (IPA) as a strong washing solution. Instruments were cleaned daily, and blank samples were run before and after each analysis batch (typically 20-30 samples). A random sample was selected from each matrix for duplicate analysis to control for repeatability. Recoveries of QA samples (matrix matched standard addition samples) in the present work were satisfactory (within the range of 70-110%). Recoveries and LOQ for individual PFAS are reported in Table S3. LOQ were between 0.1-0.5 ng g^{-1} or ng L^{-1} except for the sulfonamido/fluorotelomer alcohols, where the LOQ were higher, i.e. 2 ng g^{-1}. LOQ for PFAS screened for using exact mass and retention times from authentic standards were assumed based on closely related analogues.

As the whole lake is polluted by PFAS (see Figure S3), the use of a reference site in the lake system was not possible. When carrying out the field sampling, field blanks were included. These consisted of blank passive samplers which were exposed to the air while the sampling took place and then analysed using the same method as the sediment samples. In this way, the blanks were able to determine whether there was any contribution of ambient PFAS sources to the sampled media while the field campaign was being carried out. There were no detected PFAS in the field blank passive samplers. To avoid contamination, water samples were sampled while the vessel moved slowly forward in order to collect water that had not been in contact with the boat (to avoid contamination from the boat itself). The bottles for the water samples were rinsed with lake water from the sampling area before taking the sample. Water samples were stored in clean and closed HDPE bottles. Sediment samples were kept in clean and closed burnt glass jars. Abiotic samples were kept in an insulated box and brought to the laboratory within 24 hours of sampling. For biota samples, whole organisms were carefully wrapped in three layers of clean aluminium foil and put in a clean plastic bag (polyethylene bags for food storage), before being frozen at - 20 °C. Frozen biota samples were sent to the laboratory (in a sealed, insulated box) for further sample treatment and analysis. Dissections were performed in the laboratory to avoid contamination during sampling and transport. Clean nitrile gloves were used during sampling.

Outdoor clothes that could contain PFAS in the fabric and equipment with Teflon surfaces were avoided.

Statistics and data analysis

The data is presented as means along with standard error of the mean (SEM). Concentrations below the LOQ were assigned values of half the LOQ unless otherwise stated.

Owing to the fact that 2019 samples were from another field season (water and sediments), and were analysed for a limited number of compounds (SAmPAP diester + 20 PFAS), they were not included in statistical analysis or in the calculation of K_D, BAF, BSAF, and TMF.

Sediment-water partitioning coefficients (K_D values)

Sediment-water partitioning coefficients (K_D values, L kg^{-1}) were calculated for pore water and sediments, as follows:

$$K_d = \frac{C_S}{C_{PW}} \qquad \text{(eq I.)}$$

Where C_S is the sediment concentration (µg kg^{-1} d.w.) and C_{PW} is the pore water concentration (µg L^{-1}). K_D values were calculated from sediment and pore water (extracted from the same sediments) specific for the sample location.

Bioaccumulation factor and biota-sediment accumulation factor

Area specific BAF (L kg^{-1}) for L-PFOS (PFOS (linear and branched) was the only compound detected in lake water) were calculated for each species (liver and/or muscle) using the average water concentration in areas where results were available (factory area and L6). BAF_{Liver} and BAF_{Muscle} denotes BAF for liver and muscle tissue, respectively. In areas where no water concentrations were available (L1, L2, L3, and L5), the water concentrations based on average sediment concentrations and the relationship between sediments and lake water at area L4 were used (concentrations in area L4 was preferred over L6 because L6 is located in a part of the lake which is separated from the rest of the lake by a narrow inlet. No biota was sampled in L4). Because the L-PFOS concentration in river water from the factory area was below the LOQ, the actual limit (0.10 ng L^{-1}) was used to calculate minimum BAF.

Bioaccumulation factors (BAFs, L kg^{-1}) were calculated for the different biota tissues, shown in equation II:

$$BAF = \frac{C_B}{C_W} \quad \text{(eq II.)}$$

Where C_B is the individual concentration in biota (liver or muscle, µg kg^{-1} w.w.) and C_W is the area specific average concentration in lake or river water (µg L^{-1}). BAF were only calculated for PFOS because this was the only compound detected in lake water.

Water concentrations used for calculations of BAF in areas where no measured water concentrations were available (L1, L2, L3, L5) were calculated based on the relationship between average sediment concentrations and average water concentrations in area L4 and the average sediment concentration in the area of interest, as shown in equation III.

$$C_{W,x} = \frac{C_{S,x}}{C_{S,L4}/C_{W,L4}} \quad \text{(eq III.)}$$

Where $C_{W,\,x}$ is the water concentration in the area of interest (ng L^{-1}), $C_{S,\,x}$ is the average sediment concentration at the area of interest (µg kg^{-1}), $C_{S,\,L4}$ is the average sediment concentration at area L4 (µg kg^{-1}), and $C_{W,\,L4}$ is the average water concentration at area L4 (ng L^{-1}).

Biota-sediment accumulation factors (BSAFs, kg kg^{-1}) were calculated for the different tissues, shown in equation IV:

$$BSAF = \frac{C_B}{C_S} \quad \text{(eq IV.)}$$

Where C_B is the individual concentration in biota (liver or muscle, µg kg^{-1} w.w.) and C_S is the area specific average concentration in sediment (µg kg^{-1} d.w.).

Trophic level and carbon sources

The $\delta^{15}N$ of a consumer is enriched relative to its diet, thus the $\delta^{15}N$ can be used to estimate the trophic level of an organism. Trophic fractionation of $\delta^{15}N$ in lake ecosystems is reported to be 3.4 ‰,[6] thus relative trophic levels were calculated by dividing $\delta^{15}N$ by 3.4. Trophic levels in the present study were not adjusted to an organism with a known trophic level, therefore the levels are reported as *relative trophic levels* (differences in trophic position between organisms are correct, however the number does not indicate the number of trophic levels above the primary producer in the food web). Individual $\delta^{15}N$ and relative trophic levels are shown in Table S24. Trophic magnification factors (TMF) were calculated by a linear regression of relative trophic level against log-transformed (natural logarithm) PFAS concentrations, a method previously reported in several studies.[7–9]

The use of $\delta^{13}C$ for evaluating the ultimate sources of carbon (i.e. dominating primary producers in the food web) has been described by Post.[6] Briefly, the $\delta^{13}C$ in lake food webs tends to be enriched in benthic-littoral parts of food webs.[10] Thus, an increased (i.e. less negative) $\delta^{13}C$ is associated with increased proportions of benthic organisms as food sources. A small trophic fractionation of carbon (i.e. organisms have less negative $\delta^{13}C$ compared with their diet) was reported with an average

fractionation of 0.39 ‰.[6] Thus, trophic level adjusted $\delta^{13}C$ were calculated by subtracting relative trophic level multiplied with 0.39 from $\delta^{13}C$. Individual $\delta^{13}C$ and trophic level adjusted $\delta^{13}C$ are shown in Table S24.

Fluorine mass balance

Concentrations of targeted PFAS were converted into fluorine concentrations using equation V:

$$C_F = n_F \frac{MW_F}{MW_{PFAS}} C_{PFAS} \qquad \text{(eq V.)}$$

Where C_F is the fluorine concentration (μg kg^{-1}), n_F is the number of fluorine atoms in the specific PFAS, MW_F is the molecular weight of fluorine (g mol^{-1}), MW_{PFAS} is the molecular weight of the specific PFAS (g mol^{-1}), and C_{PFAS} is the detected concentration of the specific PFAS (μg kg^{-1}).

Statistics

Statistical analysis was carried out using R version 3.4.2. (R Core Team; Vienna, Austria),[11] Packages olsrr[12] and agricolae[13].

Potential relationships between K_D values, fraction organic carbon (f_{OC}), and particle size distribution were evaluated using stepwise regression by entering and removing predictors based on p values to build linear regression models (functions: lm, and ols_step_both_p).

PFAS concentrations in biota were not normally distributed according to the Shapiro-Wilk w-test (function: shapiro.test) and shape of data histograms. In general, there were relatively high amounts of individuals with either high or low PFAS concentrations, causing the dataset to be skewed towards the sides, especially at areas close to the source (see example of histograms for L-PFOS in Figure S9). Therefore, potential positive relationships between relative trophic level or trophic level adjusted $\delta^{13}C$, and concentrations of the different PFAS in biota were evaluated using the non-parametric correlation test, Spearman rank correlation coefficient (Spearmans rho). Trophic level adjusted $\delta^{13}C$ were chosen based on the discussion above. However, unadjusted $\delta^{13}C$ were also tested (not shown) and the only differences in statistically significant correlations were for PFUnDA at the factory area and PFUnDA and PFTeDA at area L6 (significant correlations were found for trophic level adjusted $\delta^{13}C$ but not for unadjusted).

The non-parametric unpaired Wilcoxon Test/Mann–Whitney U test (function: wilcox.test) was used to test potential differences in trophic level adjusted $\delta^{13}C$ or relative trophic level between pike and perch at the different sampling areas.

Supplementary Results and Discussion

Relationships between carbon chain length and K_D values

Linear regression was used to evaluate relationships between carbon chain length and K_D values for PFCA and FTS (the two groups for which K_D values could be calculated for several homologues). For each CF_2 moiety, the K_D increased by approximately 0.14 log units for PFCA and approximately 0.30 log units for FTS (shown as lines in Figure 1 in the main paper). This is in agreement with a previous reported K_D increase of an average of 0.2 log units for each additional PFCA CF_2 moiety in sediments from Stockholm Arlanda Airport.[14] The log K_D values found here for L-PFOS (1.13 ±0.15) were comparable to the log K_D for PFOA (1.08 ±0.14). The PFCA, PFOA, and the PFSA, L-PFOS, have the same number of C in their chains, however L-PFOS has 1 more CF_2 moiety in the carbon backbone. The average log K_D for PFNA, which as L-PFOS has 7 CF_2 moieties, was comparable to (1.16 ±0.13) K_D for L-PFOS. In contrast, PFSA have previously been reported to have 0.23 log units stronger sorption compared to equal chain length (same number of CF_2 moieties) PFCA.[15]

Sediment characteristics

The mineral fraction of soils and sediments, i.e. the sand, silt, and clay content, differs in particle size, and the smaller colloidal clay particles are primarily composed of silicates and iron and aluminium oxides, and thus carrying positive and/or negative charges.[16] Charged particles in soils and sediments can affect the sorption of ionic PFAS, and electrostatic interactions are reported to be a major component affecting PFAS sorption at environmentally relevant pH.[17]

Compound specific K_D values differed between areas. To investigate the reason for this, possible contributions from different sediment properties were explored. To this end, K_D was plotted against: sediment particle size distribution and TOC (from the same samples as used to calculate K_D values) using stepwise regression (as described in chapter *Statistics and data analysis*, sediment characteristics are summarized in Table S9). K_D values and possible predictors from all samples in Table S10 were included, and samples were not differentiated by area.

No statistically significant relationships were found between K_D values and sand, silt or clay content in sediment or pore water ($p>0.05$), and they were therefore not included in the model. A significant positive linear relationship was found between K_D values and f_{OC} for L-PFOS ($p=0.01$), where the slope of the curve was 1965 kg^{-1} and the intercept was 2.4 L kg^{-1}. Thus, a simple linear regression was used and L-PFOS K_D values were expressed as shown in equation VI:

$$K_d\ PFOS = 1965\ L\ kg^{-1} \times f_{OC} + 2.4\ L\ kg^{-1} \qquad \text{(eq VI.)}$$

The R^2 for the correlation was 0.59, thus the model (the single parameter regression) and hence the varying f_{OC} explains about 60% of the observed variation in L-PFOS K_D values.

Similarly, Milinovic et al. found the f_{OC} to be the factor best correlated with K_D for L-PFOS, PFOA, and PFBS.[18] In that study sorption of PFAS to soil was described by equation VII which includes a contribution from hydrophobic interactions with organic carbon and sorption to the mineral phases.[18]

$$K_d = K_{OC} \times f_{OC} + K_{d,MINERAL} \qquad \text{(eq VII.)}$$

Where K_{OC} (L kg^{-1}) is the organic carbon-water partitioning coefficient, f_{OC} is the fraction organic carbon expressed as fraction organic carbon in dry matter sediments (g TOC per g sediment), and $K_{D,MINERAL}$ (L kg^{-1}) is the sorption to the soil mineral fraction.

In the present study a K_{OC} value for L-PFOS was deduced from the regression used to build the model in equation VI (1965 L kg^{-1}), corresponding to a log K_{OC} of 3.3. The $K_{D,MINERAL}$ contribution to the K_D is the intercept, corresponding to a log $K_{D,MINERAL}$ of 0.4. Thus, for environmental conditions and sediments similar to those in the present study, the K_D for L-PFOS if no organic carbon is present would correspond to a log K_D of 0.4.

No statistically significant relationships were found between f_{OC} and K_D values for other compounds ($p>0.05$), although K_D values generally increased with increasing f_{OC}. One of the limitations with using such a method based on the data here is that there was only a very narrow range of TOC content (0.26-4.50%) and relatively low PFAS concentrations (e.g. sediment concentrations of <10 µg kg^{-1}for L-PFOS <15 µg kg^{-1} for PFOA). Previous studies have used much wider TOC ranges which makes it easier to decipher relationships. For example, a TOC range of 0.56 to 9.66% was used in previously reported experimental investigation of PFAS sorption to freshwater sediments.[15] Much higher concentrations, up to >10 000 µg kg^{-1} for L-PFOS and > 2 500 µg kg^{-1} for PFOA were used in a study with soils with TOC contents of 0.2 to 39%.[18] These studies reported positive relationships between PFAS and TOC content. Based on the previously reported correlations between different PFAS concentrations and TOC content,[15,18] K_{OC} values (L kg^{-1}) were calculated for the PFAS here as shown in Table S11, although statistically significant relationships between f_{OC} and PFAS other than L-PFOS were not found. Log K_{OC} values for PFOA (2.2) and PFNA (2.8) were both lower than for L-PFOS, in agreement with the previous reported difference in K_{OC} values for PFSA and PFCA with the same C chain length.[15] Thus, although few statistically significant correlations could be found in the present study PFAS generally appear to be sorbed more strongly to lake sediments with higher TOC content.

Biota-sediment accumulation factors (BSAF)

The ratios of concentrations in biota (µg kg^{-1}) to sediment (µg kg^{-1}), i.e. the BSAF for PFAS in liver and muscle are shown in Table S17-S22. The highest BSAF were for L-PFOS in perch liver from sampling areas L6, L5 and L1 (559, 113, and 90) and L-PFOS in pike and whitefish liver from area L6 (268 and

126). Apart from L-PFOS, the highest BFSAF were for the C10-C13 PFCA in perch livers from area L6 (PFDA: 81, PFUnDA: 52, PFDoDA: 47, PFTrDA: 37) and pike (PFDA: 53, PFUnDA: 36, PFDoDA: 26, PFTrDA: 29).

A conversion equation for muscle to whole perch (equation VIII)[19] was used to calculate BSAF for whole perch in the present study. Calculated BSAF for L-PFOS in whole perch were 0.4, 31.0, 3.8, 12.8, and 88.5 at sampling areas factory area, L1, L3, L5, and L6, respectively. Log BSAF for L-PFOS have been reported to be 1.69-1.81 in perch (whole) and 1.73 in pike (whole),[20] which corresponds to approximately 49-65 in perch and 54 in pike. However, that study used wet weight concentrations for sediment.[20] Assuming 50% water content, sediment dry weight BSAF from that study would be approximately 30 in whole perch or pike which is comparable to calculated BSAF in whole fish from the two areas with the highest values in the present study (L5 and L6). Thus, the BSAF for L-PFOS in the present study varies between areas but are comparable to, although somewhat lower than, previously reported BSAF.

$$C_{Whole\ fish} = 2.8459 \times C_{Muscle} - 0.4636 \qquad \text{(eq VIII.)}$$

Where $C_{Whole\ fish}$ is the concentration in whole perch (μg kg^{-1}), and C_{Muscle} is the concentration in perch muscle (μg kg^{-1}).

Organic carbon normalized BSAF ($BSAF_{oc}$) were calculated for pike and perch and are shown in table Table S23. Log $BSAF_{OC}$ for C6-15 PFCAs were between -1.5 and -0.4 in liver and between -2.0 and -0.6 in muscle, while Log $BSAF_{OC}$ for L-PFOS were between -0.5 and -0.1 in liver and between -1.7 and -1.0 in muscle, across both species and all areas. Labadie et al.[21] reported log $BSAF_{OC}$ for PFCA and PFSA in different tissues of European chub (*Leuciscus cephalus*), including liver and muscle. Log $BSAF_{OC}$ for C7-13 PFCA were reported to be between -0.9 and 0.4 in liver and between -1.3 and -0.3 in muscle, while $BSAF_{OC}$ for L-PFOS were reported to be 0.6 in liver and -0.3 in muscle. Thus, as for BSAF, previous reported $BSAF_{OC}$ were comparable to, although slightly higher than in the present study.

Supplementary tables

Table S1. Number of abiotic samples analysed in 2018 at sampling areas L1 – L6.

Sample type	Factory area	River downstream sources	L1	L2	L3	L4	L5	L6
Sediment	9		14	15	21	12	7	25
Pore water and sediment		1	1 [b]	3		3	3	[b]
Sediment core			1			1		
Surface water	1		[a]		[a]	3	[a]	3

[a] Samples were lost during transport to the laboratory
[b] Water samples could not be analysed due to high levels of organic material

Table S2. Number of biota samples analysed in 2018 at sampling areas L1 – L6 (liver and muscle). Number of muscle samples in brackets.

Species	Factory area	L1	L2	L3	L4	L5	L6
Perch (*Perca fluviatilis*)	5 (5)	5 (10)		5 (10)		5 (5)	5 (10)
Pike (*Esox lucius*)	4 (4)	2 (2)		3 (3)			5 (5)
Whitefish (*Coregonus lavaretus*)		3 [a]	2 [a]	3 [a]		3 [a]	1 [a]
Roach (*Rutilus rutilus*)		1 [a]		3 [a]		3 [a]	1 [a]
Trout (*Salmo trutta*)			5 (5)	1 (1)			
Bream (*Abramis brama*)							2
Arctic char (*Salvelinus alpinus*)				1 (1)			
Crayfish (*Astacus astacus*)				(10)			(10)

[a] 4-5 individual livers were combined to make each sample

Table S3. 45 PFAS quantified using authentic and internal standards (+ Br PFOS), 19 PFAS screened for using exact mass and retention time from authentic standards, and three PFAS which were detected using exact mass and estimated retention time and quantified using the standard for a similar compound. Rows with PFAS that were detected in this work are filled with grey.

PFAS group	Acronym	Name	CAS	LOQ			Recovery [a]	
				Water (ng L^{-1})	Sediment (µg kg^{-1})	Biota (µg kg^{-1})	Mean (%)	St.dev
PFCA	PFBA	Perfluoro-n-butanoic acid	375-22-4	0,5	1,0	1,0	96.9	14.3
	PFPA	Perfluoro-n-pentanoic acid	2706-90-3	0.5	0.5	0.5	103.1	5.8
	PFHxA	Perfluoro-n-hexanoic acid	307-24-4	0.5	0.5	0.5	101.6	3.0
	PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.5	0.5	0.5	103.4	3.4
	PFOA	Perfluoro-n-octanoic acid	335-67-1	0.5	0.5	0.5	97.4	3.7
	PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.4	0.4	0.4	100.6	3.9
	PFDA	Perfluoro-n-decanoic acid	335-76-2	0.4	0.4	0.4	102.4	3.2
	PFUnDA	Perfluoro-n-undecanoic acid	2058-94-8	0.4	0.4	0.4	98.3	1.4
	PFDoDA	Perfluoro-n-dodecanoic acid	307-55-1	0.4	0.4	0.4	97.0	2.3
	PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	0.4	0.4	0.4	94.9	2.0
	PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	0.4	0.4	0.4	95.9	3.1
	PFPeDA [b, c]	Perfluoro-n-pentadecanoic acid			0.4	0.4		
	PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5		0.4	0.4	82.4	5.3
	PFODA	Perfluoro-n-octadecanoic acid	16517-11-6		0.4	0.4	69.8	4.4
PFSA	PFPrS [d]	Perfluoro-1-propanesulfonate		0.2	0.2	0.2		
	PFBS	Perfluoro-1-butanesulfonate	59933-66-3	0.1	0.1	0.1	96.1	2.0
	PFPeS	Perfluoro-1-pentanesulfonate	22767-49-3	0.1	0.1	0.1	95.1	4.8
	PFHxS	Perfluoro-1-hexanesulfonate	355-46-4	0.1	0.1	0.1	94.3	3.2
	PFHpS	Perfluoro-1-heptanesulfonate	22767-50-6	0.1	0.1	0.1	93.1	1.7
	PFOS	Perfluoro-1-octanesulfonate	4021-47-0	0.1	0.1	0.1	98.5	3.2
	PFNS	Perfluoro-1-nonanesulfonate	98789-57-2	0.1	0.1	0.1	94.2	2.3
	PFDS	Perfluoro-1-decanesulfonate	335-77-3	0.1	0.1	0.1	81.7	2.1
	PFDoDS	Perfluoro-1-dodecansulfonate	79730-39-5		0.2	0.2	74.4	3.5
	ipPFNS [d]	Perfluoro-7-methyloctanesulfonate		0.2	0.2	0.2		
	Br-PFOS [e]	PFOS branched isomers		0.2	0.2	0.2		
PreFOS	FOSA	Perfluoro-1-octanesulfonamide	754-91-6	0.1	0.1	0.1	98.3	4.9
	MeFOSA	N-methylPerfluoro-1-octanesulfonamide	31506-32-8	0.2	0.2	0.2	78.3	5.7
	EtFOSA	N-ethylPerfluoro-1-octanesulfonamide	4151-50-2	0.2	0.2	0.2	91.0	3.4
	MeFOSE	2-(N-methylPerfluoro-1-octanesulfonamido)-ethanol	24448-09-7	2	2	2	78.5	6.1
	EtFOSE	2-(N-ethylPerfluoro-1-octanesulfonamido)-ethanol	1691-99-2	2	2	2	90.9	3.8
	FOSAA	Perfluoro-1-octansulfonamidoacetic acid	2806-24-8	0.3	0.3	0.3	89.8	3.9
	MeFOSAA	2-(N-methylPerfluoro-1-octansulfonamido)acetic acid	2355-31-9	0.3	0.3	0.3	90.8	3.5
	EtFOSAA	2-(N-ethylPerfluoro-1-octansulfonamido)acetic acid	2991-50-6	0.3	0.3	0.3	97.9	3.3
FTS	4:2 FTS	1H,2H-Perfluorohexan sulfonate (4:2)	757124-72-4	0.3	0.3	0.3	95.7	3.7
	6:2FTS	1H,2H-Perfluorooctane sulfonate (6:2)	27619-97-2	0.3	0.3	0.3	93.0	3.6
	8:2 FTS	1H,2H-Perfluorodecan sulfonate (8:2)	39108-34-4	0.3	0.3	0.3	99.8	2.1
	10:2 FTS	1H,2H-Perfluorododecan sulfonate (10:2)	120226-60-0	0.3	0.3	0.3	86.5	2.5
	12:2 FTS [b, f]	1H,2H-Perfluorotetradecan sulfonate (12:2)		0.3	0.3	0.3		

	14:2 FTS[b, f]	1H,2H-Perfluorohexadecan sulfonate (14:2)		0.3	0.3	0.3		
	8-ClPFOS	8Cl-Perfluoro-1-octanesulfonate		0.2	0.2	0.2	94.5	4.6
	8:2 F53B	C_{10} H F_{16} Cl O_4 S		0.3	0.3	0.3	98.2	4.6
	6:2 F53B	C_8 H F_{16} Cl O_4 S	73606-19-6	0.3	0.3	0.3	93.5	3.6
	4:2 F53B	C_6 H F_{12} Cl O_4 S		0.3	0.3	0.3	96.4	1.8
	PFBPA	Perfluoro butylphosphonic acid	52299-24-8	0.5	0.5	0.5	97.0	4.3
	PFHxPA	Perfluoro hexyl phosphonic acid	40143-76-8	0.5	0.5	0.5	93.4	4.1
	PFPOA[d]	Perfluoro octyl phosphonic acid	40143-78-0	0.5	0.5	0.5		
	PFDPA[d]	Perfluoro decyl phosphonic acid	52299-26-0	0.5	0.5	0.5		
	6:2 PAP[d]	1H,1H,2H,2H-Perfluorooctyl phosphate	57678-01-0	0.5	0.5	0.5		
	8:2 PAP[d]	1H,1H,2H,2H-Perfluorodecyl phosphate	57678-03-2	0.5	0.5	0.5		
	6:2 diPAP	Bis (1H,1H,2H,2H-Perfluorooctyl phosphate)	57677-95-9	0.5	0.5	0.5	101.6	3.0
	8:2 diPAP	Bis (1H,1H,2H,2H-Perfluorodecyl phosphate)	678-41-1	0.5	0.5	0.5	109.7	6.0
	6:2/8:2 diPAP	Comb of 6:2 and 8:2 Perfluoroalkyl phoshate	943913-15-3	0.5	0.5	0.5	103.3	3.0
	10:2 diPAP[d]	Bis (1H,1H,2H,2H-Perfluorododecyl phosphate)	1895-26-7	0.5	0.5	0.5		
Other	6:2 FTOH[d]	2-Perfluorohexyl ethanol	647-42-7		2	2		
	8:2 FTOH[d]	2-Perfluorooctyl ethanol	678-39-7		2	2		
	10:2 FTOH[d]	2-Perfluorododecyl ethanol	865-86-1		2	2		
	6:2 FTCA[d]	2-Perfluorohexyl ethanoic acid (6:2 FTA)	53826-12-3	2	2	2		
	8:2 FTCA[d]	2-Perfluorooctyl ethanoic acid (8:2 FTA)	53826-12-3	2	2	2		
	10:2 FTCA[d]	2-Perfluorodecyl ethanoic acid (10:2 FTA)	53826-13-4	2	2	2		
	6:2 FTUCA[d]	2H-Perfluoro-2-octenoic acid (6:2 FTUA)	70887-88-6	2	2	2		
	8:2 FTUCA[d]	2H-Perfluoro-2-decenoic acid (8:2 FTUA)	70887-84-2	2	2	2		
	10:2 FTUCA[d]	2H-Perfluoro-2-dodecenoic acid (10:2 FTUA)	70887-94-4	2	2	2		
	PFHxSA[d]	Perfluoro-1-hexansulfonamide	41997-13-1	0.5	0.5	0.5		
	MeFHxSA	Perfluoro-1-hexansulfonamide	68259-15-4	0.5	0.5	0.5	93.4	6.8
	Gen X[d]	Perfluoro(2-methyl-3-oxahexanoate)	62037-80-3	0.5	0.5	0.5		
	ADONA[d]	Dodecafluoro-3H-4,8-dioxanonanoat	958445-44-8	0.5	0.5	0.5		
	PFECHS	Perfluoroethylcyclohexanesulfonate	67584-42-3	0.5	0.5	0.5	95.2	3.1
	SAmPAP diester[g]	bis[2-[N-ethyl(heptadecafluorooctane)-sulphonylamino]ethyl] phosphate	30381-98-7	0.5	0.5	0.5	77.4	12.9

[a] Recoveries shown in the table were calculated based on spiking of sediment samples, n=5.
[b] Standard was not available, detected using exact mass and estimated retention time.
[c] Quantified using the standard for PFHxDA.
[d] Screened for using exact mass and retention time from an authentic standard. Approximate LOQ based on the LOQ for a closely related analogue.
[e] Quantified using the standard for L-PFOS.
[f] Quantified using the standard for 10:2 FTS.
[g] Detected using exact mass and estimated retention time in the sediment sample used for ToF MS analysis in 2018. A standard was acquired for 2019 samples, see materials and methods.

441 Table S4. 25 PFAS screened for using exact mass and estimated retention time, but not detected

Acronym	Name	CAS
PFHpDA	Perfluoro-n-heptadecanoic acid	
PFUnDS	Perfluoro-1-undecansulfonate	
PFTrDS	Perfluoro-1-tridecansulfonate	
PFTeDS	Perfluoro-1-tetradecansulfonate	
6:2 53B	C8 H F17O4 S	754925-54-7
12:2 FTOH	2-Perfluorododecyl ethanol	39239-77-5
PFBSA	Perfluoro-1-butansulfonamide	30334-69-1
PFPeSA	Perfluoro-1-pentansulfonamide	82765-76-2
PFHpSA	Perfluoro-1-heptansulfonamide	82765-77-3
MeFBSA	Perfluoro-1-butansulfonamide	68298-12-4
MeFPeSA	Perfluoro-1-pentansulfonamide	68298-13-5
MeFHpSA	Perfluoro-1-heptansulfonamide	68259-14-3
EtFBSA	Perfluoro-1-butansulfonamide	40630-67-9
EtFPeSA	Perfluoro-1-pentansulfonamide	162682-16-8
EtFHpSA	Perfluoro-1-heptansulfonamide	68957-62-0
MeFBSE	2-(N-mehylperfluoro-1-butansulfonamido)-ethanol	34454-97-2
MeFPeSE	2-(N-methylperfluoro-1-pentansulfonamido)-ethanol	68555-74-8
MeFHxSE	2-(N-methylperfluoro-1-hexansulfonamido)-ethanol	68555-75-9
MeFHpSE	2-(N-methylperfluoro-1-heptansulfonamido)-ethanol	68555-76-0
EtFBSE	2-(N-ethylperfluoro-1-butansulfonamido)-ethanol	34449-89-3
EtFPeSE	2-(N-ethylperfluoro-1-pentansulfonamido)-ethanol	68555-72-6
EtFHxSE	2-(N-ethylperfluoro-1-hexansulfonamido)-ethanol	34455-03-3
EtFHpSE	2-(N-ethylperfluoro-1-heptansulfonamido)-ethanol	68755-73-7
EtFHxSA	Perfluoro-1-hexansulfonamide	87988-56-5
FOSE	Perfluoro-1-octanesulfonamido-ethanol	10116-92-4

Table S5. Concentrations in surface water at the different sampling areas. Average ± the standard error of mean (SEM) for samples in triplicate.

Sampling area	PFAS compounds (ng L^{-1})						
	PFPA	PFHxA	PFHpA	PFOA	PFNA	L-PFOS	Br-PFOS
Factory Area 2018	0.5	1.3	3.2	3.5	0.4	<0.1	<0.1
Factory Area 2019	[a]	[a]	[a]	[a]	[a]	1.5	1.9
L4	<0.5	<0.5	<0.5	<0.5	<0.4	0.15 ±0.003	0.07 ±0.003
L6	<0.5	<0.5	<0.5	<0.5	<0.4	0.18 ±0.009	0.10 ±0.009

[a] Not analysed

Table S6. L-PFOS water concentrations in selected studies.

ng L-PFOS L^{-1}	Case study site	PFAS source or pristine	Study
0.02-0.09	Four arctic lakes, Canada	Pristine	Lescord et al. (2015)[22]
4.7-32	Rivers lakes and canals, The Netherlands	Urban areas	Kwadijk et al. (2010)[23]
max 22	Surface and drinking waters, Germany	Waste materials	Skutlarek et al. (2006)[24]
13.7	Taihu Lake, China	WWTP and industry	Fang et al. (2014)[7]
59-137	Lake Halmsjön, Sweden	AFFF	Ahrens et al. (2015)[14]
26-41	Two arctic lakes, Canada	AFFF	Lescord et al. (2015)[22]

WWTP = wastewater treatment plants
AFFF = aqueous film-forming foams

Table S7. Sediment concentrations (µg kg^{-1}) in supplementary samples from 2019.

PFAS compound	Factory area	Sampling area L1		Sampling area L3	
		Sample 1	Sample 2	Sample 1	Sample 2
PFDA	<0.4	<0.4	<0.4	<0.4	<0.4
PFUnDA	<0.4	<0.4	<0.4	<0.4	<0.4
PFDoDA	<0.4	<0.4	<0.4	<0.4	<0.4
PFTrDA	<0.4	<0.4	<0.4	<0.4	<0.4
PFTeDA	<0.4	<0.4	<0.4	<0.4	<0.4
L-PFOS	0.1	0.3	0.5	0.9	1.7
Br-PFOS	<0.1	<0.1	<0.1	<0.1	<0.1
FOSA	<0.1	0.2	1.8	<0.1	<0.1
MeFOSA	<0.3	<0.3	<0.3	<0.3	<0.3
EtFOSA	<0.3	<0.3	0.8	<0.3	<0.3
MeFOSE	<1.0	<1.0	<1.0	<1.0	<1.0
EtFOSE	<1.0	1.1	41	<1.0	<1.0
FOSAA	<0.3	<0.3	1.4	<0.3	<0.3
MeFOSAA	<0.3	<0.3	0.6	<0.3	<0.3
EtFOSAA	<0.3	1.8	65.8	<0.3	<0.3
6:2 FTS	<0.3	<0.3	<0.3	<0.3	<0.3
8:2 FTS	<0.3	<0.3	0.9	<0.3	<0.3
10:2 FTS	<0.3	1.6	9.8	<0.3	1.1
12:2 FTS	<0.3	3.5	9.1	<0.3	1.6
14:2 FTS	<0.3	1.5	3.7	<0.3	0.7
SAmPAP diester	0.7	75.6	1872	2.1	16.1

Table S8. Concentrations (ng L^{-1}) in pore water at the different sampling areas. Mean ± the standard error of mean (SEM) for samples in triplicate.

PFAS compound	Sampling area				
	River	L1	L3	L4	L5
PFPA	9.9 ±2.9	112.2 ±0.1	14.3 ±3.8	43.4 ±9.3	60.0 ±17.8
PFHxA	17.7 ±6.6	146.3 ±17.0	32.1 ±5.7	85.5 ±18.6	65.1 ±15.7
PFHpA	34.3 ±11.3	356.2 ±39.4	80.6 ±7.2	260.9 ±48.3	104.9 ±13.9
PFOA	53.4 ±9.5	1245.9 ±64.4	122.3 ±12.2	262.3 ±51.5	298.9 ±70.7
PFNA	4.1 ±0.4	18.2 ±1.3	10.2 ±1.7	44.4 ±9.4	32.8 ±6.9
PFDA	2.2 ±0.6	29.3 ±2.5	2.9 ±0.7	14.9 ±4.4	22.4 ±4.6
PFBS	0.3 ±0.1	0.4 ±0.3	0.5 ±0.1	1.0 ±0.2	2.0 ±0.4
PFHxS	0.2 [a]	8.4 ±5.2	1.3 ±0.2	3.8 ±0.5	0.3 ±0.1
PFHpS	<0.1 [a]	1.0 ±0.5	1.0 ±0.1	3.8 ±1.2	0.1 ±0.0
L-PFOS	6.4 ±1.1	61.1 ±19.0	135.7 ±19.7	392.3 ±52.9	65.0 ±10.2
Br-PFOS	2.4 ±0.3	12.3 ±3.5	24.9 ±1.9	85.6 ±4.8	6.8 ±0.4
FOSA	0.2 [a]	4.8 ±0.6	<0.1	0.7[a]	3.4[a]
FOSAA	<0.3 [a]	13.6 ±5.2	<0.3	<0.3	<0.3
EtFOSAA	<0.3 [a]	47.8 ±1.4	<0.3	<0.3	<0.3
8:2 FTS	<0.3 [a]	16.6 ±1.4	<0.3	5.3[a]	<0.3
10:2 FTS	<0.3 [a]	8.5 ±2.8	<0.3	1.1[a]	<0.3
12:2 FTS	<0.3 [a]	5.3 ±0.5	<0.3	<0.3	<0.3

[a] Only one concentration above LOQ

Table S9. Sediment particle size distribution and total organic carbon content determined after extraction of pore water.

Sediment characteristics		Sample station										
		River	L1	L3-1	L3-2	L3-3	L4-1	L4-2	L4-3	L5-1	L5-2	L5-3
Sand (>63 µm)	(%)	99.8	47.6	84.5	20.1	75.8	22.4	8.4	4.4	96.9	92.0	86.1
Silt (63-2 µm)	(%)	0.2	52.0	15.4	79.2	24.1	76.6	75.4	77.0	3.0	8.0	13.8
Clay (<2 µm)	(%)	0.1	0.3	0.1	0.6	0.1	1.0	16.1	18.5	0.1	0.1	0.1
TOC [a]	(%)	0.4	4.5	1.0	3.7	1.4	3.9	0.4	0.4	0.3	0.5	0.9

[a] TOC denotes percent organic carbon (dry weight)

Table S10. Partitioning coefficients (K_D values, L kg^{-1}) for individual compounds in the different stations measured in pore water and sediments.

PFAS	Sample station										
	River	L1	L3-1	L3-2	L3-3	L4-1	L4-2	L4-3	L5-1	L5-2	L5-3
PFPA	35.5 [a]	2.2 [a]	22.9 [a]	11.5 [a]	24.7 [a]	4.0 [a]	7.7 [a]	7.0 [a]	8.0 [a]	4.4 [a]	2.7 [a]
PFHxA	22.6 [a]	8.2	45.1	17.8	9.7 [a]	18.7	4.2 [a]	6.9	6.6 [a]	3.9 [a]	2.7 [a]
PFHpA	28.8	9.6	40.7	17.2	12.5	14.7	6.3	4.5	11.8	2.3 [a]	2.0 [a]
PFOA	21.1	12.0	45.2	22.7	14.8	15.9	7.8	6.6	6.8	2.0	1.2
PFNA	54.3 [a]	57.2	28.3 [a]	45.5	15.4 [a]	14.5	5.8 [a]	5.7 [a]	8.4 [a]	7.1 [a]	4.3 [a]
PFDA	129 [a]	178	116 [a]	132	73.0 [a]	36.5	20.9 [a]	17.3 [a]	12.8 [a]	9.9 [a]	6.4 [a]
PFUnDA	[c]	4125	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
PFDoDA	[c]	6226	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
PFTeDA	[c]	4022	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
PFBS	138 [a]	359 [a]	142 [a]	106 [a]	93.3 [a]	33.9 [a]	72.2 [a]	53.4 [a]	17.7 [a]	32.5 [a]	30.3 [a]
PFHxS	277 [a]	15.7 [a]	56.3 [a]	36.2 [a]	33.1 [a]	15.2 [a]	10.3 [a]	15.9 [a]	166 [a]	400 [a]	123 [a]
PFHpS	[c]	100 [a]	66.7 [a]	49.2 [a]	39.9 [a]	20.0 [a]	8.2 [a]	17.9 [a]	427 [a]	347 [a]	[c]
L-PFOS	10.4	141.1	55.6	62.8	34.0	25.6	8.1	17.3	5.6	3.9	3.0
FOSA	281 [a]	295	[c]	9629 [b]	3595 [b]	1166	2332 [b]	2899 [b]	[c]	[c]	14.8 [a]
EtFOSE	[c]	7326 [b]	[c]	2331 [b]	888 [b]	1333 [b]	[c]	[c]	[c]	[c]	[c]
FOSAA	[c]	336	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
EtFOSAA	[c]	3373	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
8:2 FTS	[c]	256	[c]	1988 [b]	[c]	28.1 [a]	[c]	[c]	[c]	[c]	[c]
10:2 FTS	[c]	3368	[c]	8026 [b]	2538 [b]	2617	4047 [b]	5114 [b]	[c]	[c]	[c]
12:2 FTS	[c]	6646	[c]	13861 [b]	2937 [b]	18608 [b]	4999 [b]	4024 [b]	[c]	[c]	2187 [b]
14:2 FTS	[c]	15491 [b]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]

[a] Concentration below LOQ in sediment
[b] Concentration below LOQ in pore water
[c] Concentrations below LOQ in both sediment and pore water

Table S11. K_{OC} values (L kg^{-1}) from linear regression for PFAS detected in both pore water and sediments. Data are shown with the standard deviation.

PFAS group	Compound	K_{OC} (L kg^{-1})	
PFCA	PFHxA	86	±257
	PFHpA	23	±245
	PFOA	142	±254
	PFNA	683	±359
	PFDA	2 206	±1048
PFSA	L-PFOS [a]	1 965	±548
preFOS	FOSA	42 454	±71 198
FTS [b]	12:2 FTS	249 882	±109 655

[a] A statistically significant relationship between K_D and OC was found for L-PFOS only.
[b] K_{OC} regression values for 8:2 FTS and 10:2 FTS were negative and not included.

Table S12. Lake biota mean liver concentrations (μg kg^{-1} wet weight) ± the standard error of mean (SEM) for the different species. 22 PFAS + Br-PFOS were detected above the LOQ in liver of lake biota. Number of individuals sampled varied between the different species (Perch: 20, Bream: 2, Pike: 10, Roach: 8, Arctic char: 1, Whitefish: 12, Trout:6). Empty cells indicate that no concentrations were above the LOQ.

	Perch	Bream	Pike	Roach	Arctic Char	Whitefish	Trout
PFHxA	0.5 ±0.2						0.3 [b]
PFHpA	2.2 ±0.9	5.3 [b]			2.4		0.6 [b]
PFOA	2.6 ±1.0	4.3 [b]	0.6 ±0.3		2.7		0.9 ±0.5
PFNA	1.4 ±0.4	2.0 [b]	1.0 ±0.4	0.2 ±0.02	2.4	2.1 ±0.8	1.8 ±0.3
PFDA	19.2 ±4.4	30.9 ±5.5	9.6 ±1.8	6.6 ±1.8	25.2	9.9 ±2.8	30.6 ±7.9
PFUnDA	24.2 ±7.8	18.6 ±3.4	11.3 ±3.3	11.9 ±3.6	49.3	6.8 ±1.8	59.0 ±18.1
PFDoDA	33.2 ±13.5	6.5 ±0.8	11.6 ±3.1	18.9 ±6.1	45.3	10.4 ±3.2	43.7 ±9.2
PFTrDA	22.0 ±10.6	2.6 ±0.1	6.3 ±1.7	5.4 ±1.2	14.6	3.9 ±0.9	23.2 ±4.6
PFTeDA	11.7 ±5.3		3.4 ±1.1	6.2 ±1.7	8.6	4.7 ±1.0	17.7 ±5.5
PFPeDA	0.4 ±0.1		0.2 [b]		1.1		1.6 ±0.4
PFBS						0.1 [b]	
PFHpS	0.1 ±0.02		0.1 [b]				0.1 [b]
PFOS	148.6 ±23.4	90.0 ±7.0	54.2 ±8.3	35.4 ±7.4	71.1	68.5 ±15.4	54.2 ±14.8
Br-PFOS	3.1 ±0.5	0.5 ±0.5	0.6 ±0.1	0.8 ±0.2	0.9	0.9 ±0.2	1.0 ±0.1
PFDS	0.1 ±0.1		0.1 [b]	0.3 ±0.1	0.3	0.1 ±0.04	0.4 ±0.1
FOSA	1.3 ±0.5	5.7 ±3.2	2.9 ±1.0	4.1 ±1.2	9.3	26.2 ±6.8	8.1 ±1.6
FOSAA	0.2 [b]	0.4 ±0.1		0.7 ±0.2	0.8	0.5 ±0.2	0.6 ±0.1
EtFOSAA	1.1 ±0.3	0.7 ±0.3	0.2 ±0.02	0.2 ±0.03	0.3	2.0 ±0.6	0.3 ±0.03
6:2 FTS	0.5 ±0.1			0.2 [b]	0.5	0.5 ±0.2	0.5 [b]
8:2 FTS	0.4 ±0.1	5.7 ±3.2	0.9 ±0.3	1.5 ±1.3		7.3 ±4.7	
10:2 FTS	1.4 ±0.3	0.7 ±0.1	0.4 ±0.1	3.1 ±0.9	0.2	0.5 ±0.1	0.3 ±0.1
12:2 FTS	5.2 ±1.2	0.8 ±0.1	1.1 ±0.4	10.4 ±2.9	0.7	7.3 ±2.0	3.0 ±1.1
14:2 FTS	0.3 ±0.05			0.2 ±0.05		0.4 ±0.1	0.2 [b]

[a] 182.3 μg L-PFOS kg^{-1} in perch liver from the lake have been reported in another study investigating lake Tyrifjorden.[25]

[b] Only one individual showed a concentration above the LOQ

Table S13. Lake biota mean muscle concentrations (µg kg^{-1} wet weight) ± the standard error of mean (SEM) for the different species. 15 PFAS + Br-PFOS were detected above the LOQ in muscle of lake biota. Number of individuals sampled varied between the different species (Perch: 35, Pike: 10, Crayfish: 20, Arctic char: 1, Trout:6). Empty cells indicate that no concentrations were above the LOQ.

	Perch		Pike		Crayfish		Arctic Char	Trout	
PFHpA	3.4	±0.9	2.3	[a]					
PFOA	1.9	±0.4	1.2	±0.2					
PFNA	0.6	±0.1	0.5	±0.05	0.6	±0.1		0.5	[a]
PFDA	1.7	±0.3	0.6	±0.03	0.6	±0.1	1.7	1.3	±0.3
PFUnDA	1.8	±0.4	0.6	±0.1	1.9	±0.2	2.8	2.2	±0.6
PFDoDA	2.9	±1.1	1.1	±0.3	5.3	±1.4	4.8	4.3	±1.3
PFTrDA	1.9	±0.8	0.8	±0.2	4.7	±1.1	2.5	2.1	±0.7
PFTeDA	1.2	±0.5	0.4	±0.1	4.0	±0.9	0.8	1.6	±0.5
PFOS	10.5	±1.3	3.2	±0.4	1.0	±0.2	3.4	3.1	±0.9
Br-PFOS	0.3	±0.1							
FOSA	0.5	±0.1	1.1	±0.4	0.7	±0.2	0.5	0.3	±0.04
FOSAA					0.4	±0.1			
EtFOSAA	0.6	±0.1							
6:2 FTS	0.8	±0.2							
10:2 FTS	0.4	±0.04	0.4	[a]					
12:2 FTS	1.1	±0.2	0.7	±0.1	2.2	±0.2		0.9	[a]

[a] Only one individual showed a concentration above the LOQ

Table S14. Mean concentrations in liver and muscle (µg kg^{-1} wet weight) ± the standard error of mean (SEM) for different species from the river in the Factory Area. 14 PFAS + Br-PFOS were detected above the LOQ in muscle and 20 PFAS + Br-PFOS were detected above the LOQ in liver of biota from the Factory area. Number of individuals sampled varied between the different species (Perch: 5, Pike: 4). Empty cells indicate that no concentrations were above the LOQ.

	Perch liver		Pike liver		Perch muscle		Pike muscle	
PFHxA	0.8	±0.2	0.8	±0.3				
PFHpA					0.7	±0.2		
PFOA					0.9	±0.6		
PFNA			0.4		0.3	[b]		
PFDA	25.4	±4.2	4.3	±1.0	2.0	±0.4	0.6	±0.3
PFUnDA	14.3	±2.9	2.9	±1.0	1.2	±0.2	0.4	±0.1
PFDoDA	42.0	±13.9	2.8	±1.6	2.9	±0.7	0.6	±0.1
PFTrDA	20.0	±3.9	4.9	±1.8	1.0	±0.1	0.2	±0.03
PFTeDA	18.7	±8.5	2.7	±0.4	1.2	±0.4		
PFPeDA	0.6	±0.1						
PFHpS	0.7	±0.3						
PFOS	371.5	±74.3	48.5	±12.8	25.2	±6.0	5.7	±2.8
Br-PFOS	36.6	±13.7	1.5	±0.6	1.6	±0.4	0.1	
FOSA	44.4	±37.8	98.4	±33.9	5.9	±4.5	16.1	±4.8
EtFOSA			0.5	[b]				
FOSAA	0.4	±0.1	0.2	[b]				
EtFOSAA	27.6	±13.2	3.7	±1.1	2.0	±0.9	0.4	±0.04
6:2 FTS	0.3	[b]						
8:2 FTS	7.0	±1.9	1.1	±0.3	0.4	±0.1	0.2	±0.1
10:2 FTS	31.3	±4.0	4.1	±1.0	1.9	±0.2	0.3	±0.1
12:2 FTS	24.3	±8.4	3.7	±0.7	0.8	±0.2		
14:2 FTS	0.5	±0.2						

[a] 25.5 µg L-PFOS kg^{-1} in perch liver upstream the factory, and 836.5 µg L-PFOS kg^{-1} downstream to the factory have been reported in another study investigating lake Tyrifjorden.[25]

[b] Only one individual showed a concentration above the LOQ

Table S15. Mean L-PFOS bioaccumulation factors (BAF, L kg^{-1}) for fish liver at the different sampling areas. Data are shown with the standard error of the mean (SEM) for 2-5 replicates.

Sampling area	Perch	Pike	Whitefish	Roach	Char	Trout
Factory area [a]	>3 714 600 ±743 371	>484 900 ±127 926	n.a.	n.a.	n.a.	n.a.
L1 [b]	4 090 371 ±707 799	2 102 859 ±780 808	2 062 931 ±510 187	n.a.	n.a.	n.a.
L2 [b]	n.a.	n.a.	265 739 ±14 327	n.a.	n.a.	413 721 ±129 140
L3 [b]	1 025 110 ±465 710	194 055 ±58 955	794 815 ±163 856	283 235 ±77 687	388 492	553 127
L5 [b]	5 143 227 ±1 122 317	n.a.	1 683 054 ±325 749	923 730 ±132 640	n.a.	n.a.
L6	804 906 ±53 021	386 038 ±66 744	181 132	45 283	n.a.	n.a.

n.a.: not available because species was not sampled in this area.
BAF without SEM are based on n=1 (roach and whitefish livers were analysed as homogenized samples of 5 individuals)
[a] The L-PFOS concentration in the river at the factory area was below the LOQ (0.10 ng L^{-1}). The LOQ was used for calculation of BAFs, thus these BAFs represents minimum values.
[b] Water concentrations were calculated using the relationship between sediments and surface water at sampling area L4 in combination with sediment concentrations at the different areas (Water samples from areas L1, L3, and L5 were lost).

Table S16. Mean L-PFOS bioaccumulation factors (BAF, L kg^{-1}) for fish and crayfish muscle at the different sampling areas. Data are shown with the standard error of the mean (SEM) for 2-10 replicates.

Sampling area	Perch	Pike	Char	Trout	Crayfish
Factory area [a]	>251 947 ±59 786	>57 206 ±28 498	n.a.	n.a.	n.a.
L1 [b]	505 582 ±125 750	108 212 ±36 786	n.a.	n.a.	n.a.
L2 [b]	n.a.		n.a.	20 500 ±7 306	n.a.
L3 [b]	62 315 ±17 404	18 441 ±7 886	31 252	41 325	8 451 ±1 288
L5 [b]	210 943 ±38 439	n.a.	n.a.	n.a.	n.a.
L6	59 151 ±7 430	18 741 ±1 591	n.a.	n.a.	3 114 ±418

n.a.: not available because species was not sampled in this area.
BAF without SEM are based on n=1
[a] The L-PFOS concentration in the river at the factory area was below the LOQ (0.10 ng L^{-1}). The LOQ was used for calculation of BAFs, thus these BAFs represents minimum values.
[b] Water concentrations were calculated using the relationship between sediments and surface water at area L4 in combination with sediment concentrations at the different areas (Water samples from areas L1, L3, and L5 were lost).

Table S17. Biota-sediment accumulation factors for liver ($BSAF_{Liver}$) for perfluoroalkyl carboxylates (PFCA) at the different sampling areas. Data are shown as means with the standard error of the mean (SEM).

Species	Area	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFPeDA
Perch	Factory area	1.2 ±0.0				0.4 ±0.1	0.7 ±0.1	2.0 ±0.7	6.3 ±1.2	0.8 ±0.4	0.5 ±0.1
	L1					17.6 ±7.3	39.8 ±15.4	23.2 ±7.8	51.6 ±18.6	10.1 ±3.0	4.9 ±0.6
	L3	2.3 ±1.1	28.2 ±10.7	29.1 ±12.0	17.9 ±6.1	11.8 ±6.9	28.9 ±17.9	30.9 ±20.6	117.8 ±90.8	40.5 ±30.7	7.3 ±1.3
	L5			17.3 ±0.8	6.2 ±1.7	49.4 ±8.3	52.4 ±15.5	34.6 ±8.1	48.3 ±13.0	23.1 ±3.2	
	L6		20.8	15.6	6.5	80.9 ±3.9	51.6 ±1.7	47.1 ±5.4	37.2 ±3.4	8.7 ±0.9	
Pike	Factory area	1.3 ±0.1			0.1	0.1 ±0.0	0.2 ±0.0	0.3 ±0.1	1.6 ±0.6	0.1 ±0.0	
	L1	0.1				15.3 ±8.5	55.2 ±36.3	20.3 ±10.7	23.3 ±14.4	8.2 ±4.8	
	L3			11.0	3.1 ±0.8	2.6 ±0.2	5.4 ±0.7	4.6 ±0.5	11.3 ±6.1	6.4 ±1.0	
	L6				15.8 ±2.8	52.8 ±16.1	36.2 ±14.6	25.8 ±10.2	29.0 ±14.4	5.5 ±2.3	
Whitefish	L1					6.8 ±1.4	8.3 ±1.6	6.5 ±1.5	10.6 ±2.0	5.9 ±1.4	
	L2				5.0 ±1.2	4.1 ±2.9	1.7 ±0.7	0.8 ±0.6	1.5 ±0.5	1.5 ±1.3	
	L3				32.2 ±10.8	9.0 ±2.1	9.4 ±2.0	10.4 ±2.7	17.9 ±4.3	11.5 ±2.7	
	L5				15.2 ±7.3	24.1 ±10.0	13.5 ±3.1	11.8 ±2.0	13.7 ±1.8	14.5 ±2.8	
	L6					20.2	17.3	8.8	4.4		
Roach	L1					8.4	20.5	11.9	10.1	4.7	
	L3				1.4 ±0.6	4.1 ±1.8	12.5 ±4.9	12.7 ±5.4	17.3 ±6.2	13.9 ±5.3	
	L5					10.4 ±1.4	14.1 ±2.3	18.6 ±5.4	15.7 ±2.1	12.6 ±2.6	
	L6					19.7	31.7	27.0	20.9		
Char	L3		9.6	10.8	12.1	10.2	30.4	18.0	31.5	12.7	5.5
Trout	L2			6.7	7.8 ±1.4	14.8 ±4.8	30.2 ±11.9	11.7 ±2.9	24.5 ±6.1	6.9 ±2.7	8.3 ±2.1
	L3	1.0	10.0	11.6	15.1	14.1	55.9	27.6	58.0	31.2	14.5

Blank cells denote missing values due to concentrations below LOQ in biota and/or in sediments

Table S18. Biota-sediment accumulation factors for liver ($BSAF_{Liver}$) for perfluoroalkyl sulfonates (PFSA) and PFOS precursor compounds (preFOS) at the different sampling areas. Data are shown as means with the standard error of the mean (SEM).

Species	Area	PFHpS	L-PFOS	Br-PFOS	PFDS	PFOSA	EtFOSA	FOSAA	EtFOSAA
Perch	Factory area	0.3 ±0.1	2.1 ±0.4	0.5 ±0.2		3.3 ±2.8		0.3 ±0.0	0.1 ±0.3
	L1	4.2 ±0.6	89.5 ±15.5	57.0 ±13.7		2.2 ±0.9		0.3	0.1 ±0.1
	L3	4.8 ±0.4	22.4 ±10.2	9.3 ±2.2	14.0 ±10.3	1.0 ±0.6			0.3 ±0.0
	L5		112.5 ±24.6	11.8 ±2.6		1.0 ±0.6			0.5 ±0.0
	L6		559.1 ±36.8	19.2 ±2.4		4.1 ±1.2			0.9 ±0.2
Pike	Factory area		0.3 ±0.1	0.02 ±0.01		7.2 ±2.5	0.2	0.1	0.0 ±0.0
	L1		30.7 ±18.2	15.0 ±1.9		8.4 ±3.8			0.0 ±0.0
	L3		4.2 ±1.3	1.5 ±0.3		0.6 ±0.3			0.2 ±0.0
	L6		268.2 ±46.4	5.8 ±1.4		33.1 ±4.5			0.8 ±0.0
Whitefish	L1		41.1 ±7.6	13.8 ±1.7		64.8 ±9.0		0.3	0.1 ±0.0
	L2		6.3 ±0.5	2.0 ±0.1		1.2 ±0.2			0.0 ±0.0
	L3		17.4 ±3.6	3.5 ±1.0	9.0	16.7 ±3.2		2.8 ±1.1	1.1 ±0.3
	L5		36.8 ±7.1	1.6 ±0.4	4.4	11.3 ±1.6		1.1	0.3 ±0.1
	L6		125.8	5.2	6.2	70.7			0.7 ±0.0
Roach	L1		26.2	1.9		10.0		0.6	0.0 ±0.0
	L3		6.2 ±1.7	1.7 ±0.8	16.8	1.6 ±1.0		3.7 ±0.9	0.1 ±0.0
	L5		20.2 ±2.9	3.3 ±0.7	6.9 ±0.8	5.5 ±1.4		0.8 ±0.1	0.1 ±0.0
	L6		31.5	2.4	14.2	5.3			±0.0
Char	L3		8.5	2.3	5.6	3.1		1.7	0.2 ±0.0
Trout	L2		9.1 ±2.8	3.3 ±0.5	10.0 ±3.7	3.1 ±0.7		0.2 ±0.0	0.0 ±0.0
	L3	3.4	12.1	3.2	10.0	4.0		1.7	0.2 ±0.0

Blank cells denote missing values due to concentrations below LOQ in biota and/or in sediments

Table S19. Biota-sediment accumulation factors for liver ($BSAF_{Liver}$) for fluorotelomer sulfonates (FTS) at the different sampling areas. Data are shown as means with the standard error of the mean (SEM).

Species	Area	6:2 FTS	8:2 FTS	10:2 FTS	12:2 FTS	14:2 FTS
Perch	Factory area	1.0	0.0 ±0.0	0.1 ±0.0	0.1 ±0.0	0.0 ±0.0
	L1	4.0	0.5 ±0.2	0.1 ±0.0	0.7 ±0.2	1.0 ±0.2
	L3	8.0 ±1.8		0.0 ±0.0	0.4 ±0.2	
	L5	5.1		0.1 ±0.0	1.2 ±0.2	0.9
	L6		0.6 ±0.2	1.1 ±0.2	2.0 ±0.2	
Pike	Factory area		0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	
	L1		0.0 ±0.0	0.0 ±0.0	0.1 ±0.1	
	L3			0.0	0.1 ±0.0	
	L6		5.8 ±0.8	1.7 ±1.1	1.6 ±0.4	
Whitefish	L1			0.0 ±0.0	0.3 ±0.1	
	L2	2.7		0.0	0.2 ±0.2	
	L3		16.0 ±3.2	0.0 ±0.0	1.0 ±0.5	2.9
	L5	11.5 ±2.7		0.1 ±0.0	2.2 ±0.5	2.1 ±0.5
	L6		12.4	0.4	3.7	
Roach	L1			0.1	0.3	
	L3	2.7	4.2	0.2 ±0.1	1.3 ±0.5	1.0
	L5			0.3 ±0.1	2.1 ±0.6	1.0
	L6		0.9	3.9	4.6	
Char	L3	3.3		0.0	0.1	
Trout	L2			0.0 ±0.0	0.1 ±0.0	0.1
	L3	14.0		0.0	0.2	

Blank cells denote missing values due to concentrations below LOQ in biota and/or in sediments

Table S20. Biota-sediment accumulation factors for muscle ($BSAF_{Muscle}$) for perfluoroalkyl carboxylates (PFCA) at the different sampling areas. Data are shown as means with the standard error of the mean (SEM).

Species	Area	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
Perch	Factory area	0.7 ±0.2	0.2 ±0.1	0.1	0.0 ±0.0	0.1 ±0.0	0.1 ±0.0	0.3 ±0.0	0.1 ±0.0
	L1	17.0	10.6	3.0	2.4 ±0.8	4.5 ±1.2	2.1 ±0.6	3.6 ±0.7	0.9 ±0.2
	L3	10.1	6.0	2.9 ±0.3	1.2 ±0.4	2.1 ±0.8	2.3 ±1.2	7.9 ±4.6	2.9 ±1.6
	L5				2.4 ±0.4	2.5 ±0.8	2.4 ±1.1	4.1 ±1.6	1.4 ±0.4
	L6		6.1		5.6 ±0.4	4.2 ±0.4	2.7 ±0.3	2.6 ±0.2	
Pike	Factory area				0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	
	L1				1.1 ±0.1	3.1 ±0.7	1.9 ±0.8	3.8 ±0.7	0.7 ±0.3
	L3				0.2	0.4 ±0.0	0.4 ±0.0		0.6
	L6	9.2	4.7 ±0.6	2.5 ±0.2	2.8 ±0.2	2.5 ±0.2	2.6 ±0.0	2.1	
Crayfish	L3			2.9 ±0.3	0.3 0.0	1.4 ±0.2	3.5 ±0.9	15.1 ±3.9	10.4 ±1.8
	L6			3.2 ±0.5	2.7 0.3	7.9 ±1.2	8.6 ±2.0	12.4 ±2.3	5.0 ±0.7
Char	L3				0.7	1.7	1.9	5.4	1.2
Trout	L2				0.6 ±0.1	1.2 ±0.4	1.2 ±0.4	1.8 ±0.8	0.7 ±0.3
	L3			2.6	0.8	2.0	2.6	8.1	2.5

Blank cells denote missing values due to concentrations below LOQ in biota and/or in sediments

Table S21. Biota-sediment accumulation factors for muscle ($BSAF_{Muscle}$, kg kg^{-1}) for perfluoroalkyl sulfonates (PFSA) and PFOS precursor compounds (preFOS) at the different sampling areas. Data are shown as means with the standard error of the mean (SEM).

Species	Area	L-PFOS	PFOSA	FOSAA	EtFOSAA
Perch	Factory area	0.1 ±0.0	0.4 ±0.3		0.0 ±0.0
	L1	11.1 ±2.8	0.7 ±0.2		0.0 ±0.0
	L3	1.4 ±0.4	0.2 ±0.1		
	L5	4.6 ±0.8			
	L6	41.1 ±5.2			
Pike	Factory area	0.0 ±0.0	1.2 ±0.4		0.0 ±0.0
	L1	2.4 ±0.8	5.0 ±0.7		
	L3	0.4 ±0.2	0.2 ±0.1		
	L6	13.0 ±1.1	8.1 ±1.0		
Crayfish	L3	0.2 ±0.0	0.3 ±0.1	0.8 ±0.1	
	L6	2.2 ±0.3	2.6		
Char	L3	0.4	0.2		
Trout	L2	0.6 ±0.2	0.1 ±0.0		
	L3	0.5	0.1		

Blank cells denote missing values due to concentrations below LOQ in biota and/or in sediments

Table S22. Biota-sediment accumulation factors for muscle ($BSAF_{Muscle}$) for fluorotelomer sulfonates (FTS) at the different sampling areas. Data are shown as means with the standard error of the mean (SEM).

Species	Areas	6:2 FTS	8:2 FTS	10:2 FTS	12:2 FTS
Perch	Factory area		0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
	L1			0.0	0.1 ±0.0
	L3	5.2 ±1.1		0.0 ±0.0	0.1 ±0.0
	L5				0.2 ±0.0
	L6				
Pike	Factory area		0.0 ±0.0	0.0 ±0.0	
	L1				
	L3				0.1 ±0.0
	L6			1.6	
Crayfish	L3				0.2 ±0.0
	L6				
Char	L3				
Trout	L2				0.0
	L3				

Blank cells denote missing values due to concentrations below LOQ in biota and/or in sediments

Table S23. Sediment organic carbon (OC) normalized log biota-sediment accumulation factors (Log $BSAF_{oc}$) for L-PFOS in perch and pike liver and muscle. Values are given as average ± standard error of mean (SEM)

PFAS	Perch liver	Perch muscle	Pike liver	Pike muscle
PFPA	n.a.	n.a.	n.a.	n.a.
PFHxA	-1.5 ±0.1	n.a.	-1.5 ±0.0	n.a.
PFHpA	-0.4 ±0.1	-1.3 ±0.4	n.a.	-0.6 [a]
PFOA	-0.5 ±0.1	-1.4 ±0.5	-0.7 ±0.0	-0.9 ±0.1
PFNA	-1.0 ±0.2	-1.4 ±0.3	-1.1 ±0.3	-1.2 ±0.0
PFDA	-0.7 ±0.2	-1.6 ±0.1	-1.1 ±0.4	-2.0 ±0.4
PFUnDA	-0.5 ±0.2	-1.4 ±0.1	-0.7 ±0.3	-1.7 ±0.3
PFDoDA	-0.5 ±0.1	-1.6 ±0.1	-0.7 ±0.2	-2.0 ±0.3
PFTrDA	-0.2 ±0.1	-1.3 ±0.1	-0.7 ±0.2	-1.7 ±0.5
PFTeDA	-0.8 ±0.1	-1.9 ±0.1	-1.3 ±0.3	-1.6 ±0.2
PFPeDA	-1.3 ±0.2	n.a.	-0.8	n.a.
PFHxDA	n.a.	n.a.	n.a.	n.a.
PFBS	n.a.	n.a.	n.a.	n.a.
PFPeS	n.a.	n.a.	n.a.	n.a.
PFHxS	n.a.	n.a.	n.a.	n.a.
PFHpS	-1.4 ±0.2	n.a.	-0.6 n.a.	n.a.
L-PFOS	-0.1 ±0.2	-1.0 ±0.2	-0.5 ±0.4	-1.7 ±0.3
Br-PFOS	-0.8 ±0.2		-1.6 ±0.3	
PFNS	n.a.	n.a.	n.a.	n.a.
PFDS	-0.8 ±0.3	n.a.	-0.5 [a]	n.a.
PFDoS	n.a.	n.a.	n.a.	n.a.
FOSA	-1.7 ±0.2	-2.3 ±0.2	-0.8 ±0.2	-1.3 ±0.2
MeFOSA	n.a.	n.a.	n.a.	n.a.
EtFOSA	n.a.	n.a.	-2.3	n.a.
MeFOSE	n.a.	n.a.	n.a.	n.a.
EtFOSE	n.a.	n.a.	n.a.	n.a.
FOSAA	-2.1 ±0.1	n.a.	-2.5	n.a.
MeFOSAA	n.a.	n.a.	n.a.	n.a.
EtFOSAA	-2.5 ±0.1	-3.7 ±0.2	-3.1 ±0.3	-4.5 ±0.1
4:2 FTS	n.a.	n.a.	n.a.	n.a.
6:2 FTS	-1.0 ±0.1	-1.0 ±0.1	n.a.	n.a.
8:2 FTS	-2.3 ±0.2	-4.2 ±0.0	-2.3 ±0.5	-4.9 ±0.2
10:2 FTS	-2.6 ±0.1	-3.7 ±0.1	-2.7 ±0.3	-4.0 ±0.9
12:2 FTS	-2.1 ±0.1	-3.1 ±0.1	-2.4 ±0.3	-3.0 ±0.1
14:2 FTS	-2.1 ±0.4	n.a.	n.a.	n.a.

n.a. = not available because analyte was not detected in biota

[a] n=1, SEM could not be calculated

Table S24. Individual $\delta^{13}C$, $\delta^{15}N$, relative trophic levels, and trophic level adjusted $\delta^{13}C$.

Area	Species	Sample name	$\delta^{13}C$	$\delta^{15}N$	Relative trophic level	Trophic level adjusted $\delta^{13}C$
Factory area	Perch	VU-A-1	-25.96	10.11	2.97	-27.12
	Perch	VU-A-2	-26.64	11.13	3.27	-27.91
	Perch	VU-A-3	-25.62	10.29	3.03	-26.80
	Perch	VU-A-4	-25.68	10.94	3.22	-26.93
	Perch	VU-A-5	-25.99	10.91	3.21	-27.24
	Pike	VU-G-1	-26.54	10.64	3.13	-27.76
	Pike	VU-G-2	-27.59	10.86	3.19	-28.84
	Pike	VU-G-3	-25.66	11.93	3.51	-27.02
	Pike	VU-G-4	-27.42	10.81	3.18	-28.66
L1	Perch	NF-A-1	-26.84	11.00	3.24	-28.10
	Perch	NF-A-2	-29.58	9.30	2.74	-30.65
	Perch	NF-A-3	-27.97	12.07	3.55	-29.36
	Perch	NF-A-4	-25.35	10.51	3.09	-26.55
	Perch	NF-A-5	-26.88	8.09	2.38	-27.81
	Pike	NF-G-1	-26.21	11.35	3.34	-27.51
	Pike	NF-G-2	-25.67	11.67	3.43	-27.00
	Roach	NF-M-1	-22.36	11.52	3.39	-23.69
	Whitefish	NF-S-1	-26.15	8.32	2.45	-27.11
	Whitefish	NF-S-11	-26.49	12.23	3.60	-27.89
	Whitefish	NF-S-6	-24.93	10.73	3.16	-26.16
L3	Perch	SØ-A-1	-20.11	13.03	3.83	-21.60
	Perch	SØ-A-2	-24.35	10.93	3.21	-25.61
	Perch	SØ-A-3	-19.83	12.23	3.60	-21.23
	Perch	SØ-A-4	-23.61	11.93	3.51	-24.97
	Perch	SØ-A-5	-26.07	12.63	3.71	-27.52
	Pike	SØ-G-1	-24.55	12.34	3.63	-25.96
	Pike	SØ-G-2	-25.94	11.57	3.40	-27.27
	Pike	SØ-G-3	-23.84	12.90	3.79	-25.32
	Crayfish	SØ-KP-1	-18.40	10.24	3.01	-19.57
	Crayfish	SØ-KP-2	-19.39	9.89	2.91	-20.52
	Crayfish	SØ-KP-3	-17.13	9.83	2.89	-18.26
	Crayfish	SØ-KP-4	-17.64	10.20	3.00	-18.81
	Crayfish	SØ-KP-5	-19.48	9.96	2.93	-20.62
	Roach	SØ-M-11	-21.86	12.55	3.69	-23.30
	Roach	SØ-M-6	-20.85	10.85	3.19	-22.09
	Arctic char	SØ-R-1	-27.83	14.76	4.34	-29.52
	Whitefish	SØ-S-1	-19.82	12.60	3.71	-21.26
	Whitefish	SØ-S-10	-25.37	12.94	3.81	-26.86
	Whitefish	SØ-S-6	-23.95	13.62	4.01	-25.51
	Trout	SØ-Ø-1	-26.13	12.92	3.80	-27.61
L5	Perch	VI-A-1	-22.93	11.18	3.29	-24.22
	Perch	VI-A-2	-26.90	11.84	3.48	-28.26
	Perch	VI-A-3	-23.59	11.72	3.45	-24.93

	Perch	VI-A-4	-23.07	12.31	3.62	-24.48
	Perch	VI-A-5	-22.67	11.83	3.48	-24.02
	Roach	VI-M-1	-16.98	10.72	3.15	-18.21
	Roach	VI-M-11	-21.15	11.02	3.24	-22.42
	Roach	VI-M-6	-19.77	10.72	3.15	-21.00
	Whitefish	VI-S-1	-24.21	10.40	3.06	-25.40
	Whitefish	VI-S-11	-21.39	11.61	3.41	-22.72
	Whitefish	VI-S-6	-23.24	11.52	3.39	-24.56
L6	Perch	SF-A-1	-24.77	16.48	4.85	-26.66
	Perch	SF-A-2	-24.35	16.65	4.90	-26.26
	Perch	SF-A-3	-23.31	16.24	4.78	-25.17
	Perch	SF-A-4	-24.06	16.39	4.82	-25.94
	Perch	SF-A-5	-24.15	16.45	4.84	-26.04
	Perch	SF-A-6	-24.80	16.68	4.91	-26.72
	Perch	SF-A-7	-24.04	16.76	4.93	-25.97
	Perch	SF-A-8	-23.82	16.28	4.79	-25.69
	Perch	SF-A-9	-24.17	14.75	4.34	-25.86
	Perch	SF-A-10	-23.59	16.77	4.93	-25.51
	Bream	SF-B-1	-24.73	15.21	4.47	-26.47
	Bream	SF-B-2	-23.96	14.70	4.32	-25.65
	Crayfish	SF-KP-1	-22.46	12.15	3.57	-23.85
	Crayfish	SF-KP-2	-24.22	12.75	3.75	-25.68
	Crayfish	SF-KP-3	-23.76	13.26	3.90	-25.28
	Crayfish	SF-KP-4	-24.10	13.86	4.08	-25.69
	Crayfish	SF-KP-5	-22.20	12.88	3.79	-23.68
	Pike	SF-G-1	-24.77	16.76	4.93	-26.70
	Pike	SF-G-2	-23.50	16.15	4.75	-25.35
	Pike	SF-G-3	-23.03	16.26	4.78	-24.89
	Pike	SF-G-4	-24.73	16.92	4.98	-26.67
	Pike	SF-G-5	-24.56	16.66	4.90	-26.47
	Roach	SF-M-1	-24.67	15.14	4.45	-26.41
	Whitefish	SF-S-1	-26.82	15.14	4.45	-28.55

Table S25. Probability values (p values) and Spearman correlation coefficients (rho) for significant positive correlations between trophic level adjusted $\delta^{13}C$ and PFAS concentrations in biota (L=liver, M= muscle). Only compounds showing significant correlations are shown. Columns for areas and tissues which have the greatest diversity of species are filled with yellow.

		L1				L3				L5				L6			
		p		rho		p		rho		p		rho		p		rho	
		L	M	L	M	L	M	L	M	L	M	L	M	L	M	L	M
PFCA	PFUnDA	-	-	-	-	-	-	-	-	-	-	-	-	-	0.03	-	0.44
	PFDoDA	-	-	-	-	-	0.05	-	0.45	-	-	-	-	0.03	-	0.51	-
	PFTrDA	-	-	-	-	-	0.05	-	0.45	-	-	-	-	-	0.00	-	0.61
	PFTeDA	-	-	-	-	-	0.00	-	0.67	-	-	-	-	-	0.01	-	0.56
PFSA	PFDS	-	-	-	-	-	-	-	-	0.01	-	0.68	-	-	-	-	-
preFOS	FOSA	0.04	0.02	0.56	0.82	-	-	-	-	-	-	-	-	-	-	-	-
	FOSAA	-	-	-	-	-	0.05	-	0.45	-	-	-	-	-	-	-	-
FTS	10:2 FTS	-	-	-	-	0.00	-	0.67	-	-	-	-	-	-	-	-	-
	12:2 FTS	-	-	-	-	0.01	0.00	0.58	0.78	-	-	-	-	-	-	-	-

(-) denotes non-significant correlations.

Table S26. Trophic magnification factors (TMF) probability values (p values) for different PFAS showing significant relationships (p≤0.05) between concentrations in muscle tissue and relative trophic levels. Only compounds showing significant correlations are shown.

		L3		L6	
		TMF	p	TMF	p
PFCA	PFOA	-	-	-	-
	PFNA	-	-	-	-
	PFDA	-	-	1.8	0.01
	PFUnDA	-	-	0.5	0.00
	PFDoDA	-	-	0.3	0.00
	PFTrDA	-	-	0.1	0.00
	PFTeDA	0.2	0.05	0.2	0.00
PFSA	L-PFOS	3.7	0.04	9.3	0.01
	Br-PFOS	-	-	-	-
	PFDS	-		-	-
preFOS	FOSAA	0.5	0.00	-	-
FTS	12:2 FTS	0.1	0.01	-	-

(-) denotes non-significant correlations.

443 Table S27. The highest trophic magnification factors (TMF) in the review by Franklin[26]

PFAS	PFAS source	Sample types	Highest TMF	Study
PFOA	WWTP/Background	Marine food web	13	Houde et al.(2006)[27]
PFNA	Background	Arctic marine food web	7.03	Kelly et al.(2009)[28]
PFDA	Background	Arctic marine food web	19.8	Tomy et al.(2009)[29]
PFUnDA	Background	Arctic marine food web	13.7	Tomy et al.(2009)[29]
PFDoDA	Background	Terrestrial food web	5.2	Müller et al.(2011)[30]
PFTrDA	Background	Terrestrial food web	4.2	Müller et al.(2011)[30]
PFTeDA	Unknown	Lake food web	-	Martin et al.(2004)[8]
L-PFOS	Background	Arctic marine food web	19.6	Tomy et al.(2009)[29]
FOSA	WWTP/Background	Marine food web	5.9	Houde et al.(2006)[27]

444 (-) denotes non-significant correlation to trophic level.
445 n.a. = only 1 significant value, thus SEM could not be calculated

Table S28. The sum fluorine from the targeted analysis (ΣF_{targ}) as a percent of extractable organic fluorine (EOF), n=1.

sampling area	Sample type	EOF (µg F kg^{-1})	ΣF_{targ} (µg F kg^{-1})	ΣF_{targ} /EOF (%)
L1	Sediments	963.7	518.4	53.8
Factory area	Perch liver	648.9	313.1	48.3
L1	Perch liver	219.5	121.8	55.5
L3	Perch liver	1347.9	496.1	36.8
L6	Perch liver	85.8	93.0	108
Factory area	Pike liver	725.5	55.5	7.6
L1	Pike liver	664.1	58.4	8.8
L6	Pike liver	101.5	29.9	29.5
L3	Trout liver	373.9	124.3	33.2
L3	Char liver	330.9	75.3	22.8

Supplementary figures

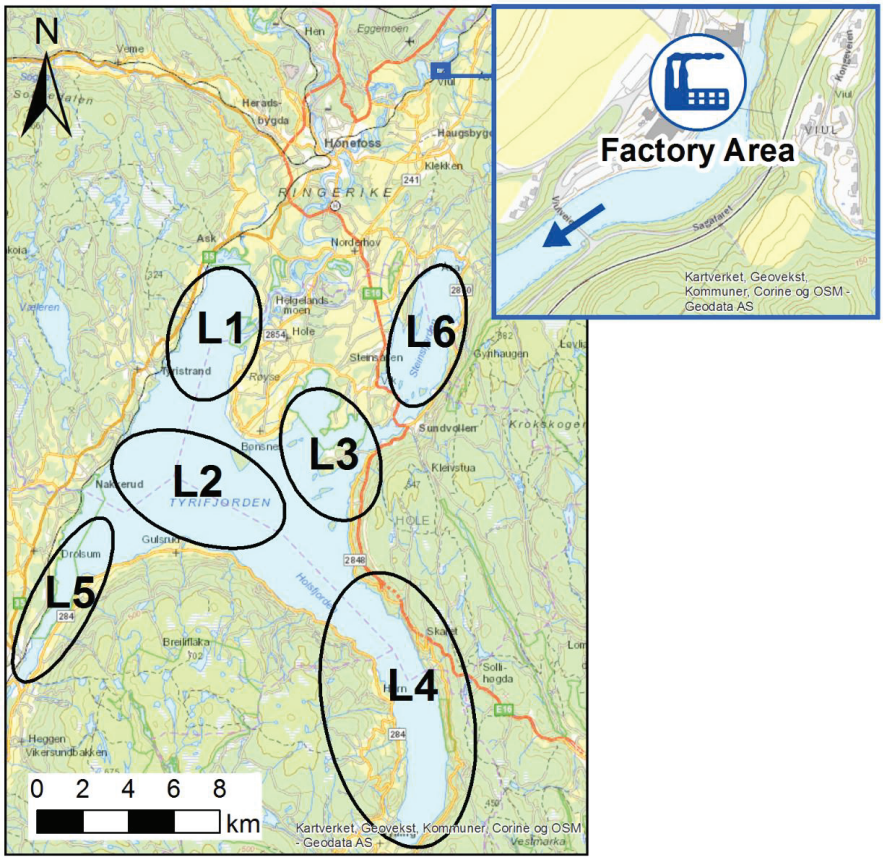

Figure S1. Lake Tyrifjorden and the rivers upstream, and location of the source area (factory area) and lake sampling areas L1-L6. Lake sampling areas L1 and L6 represents areas closest to and least impacted by the river, respectively.

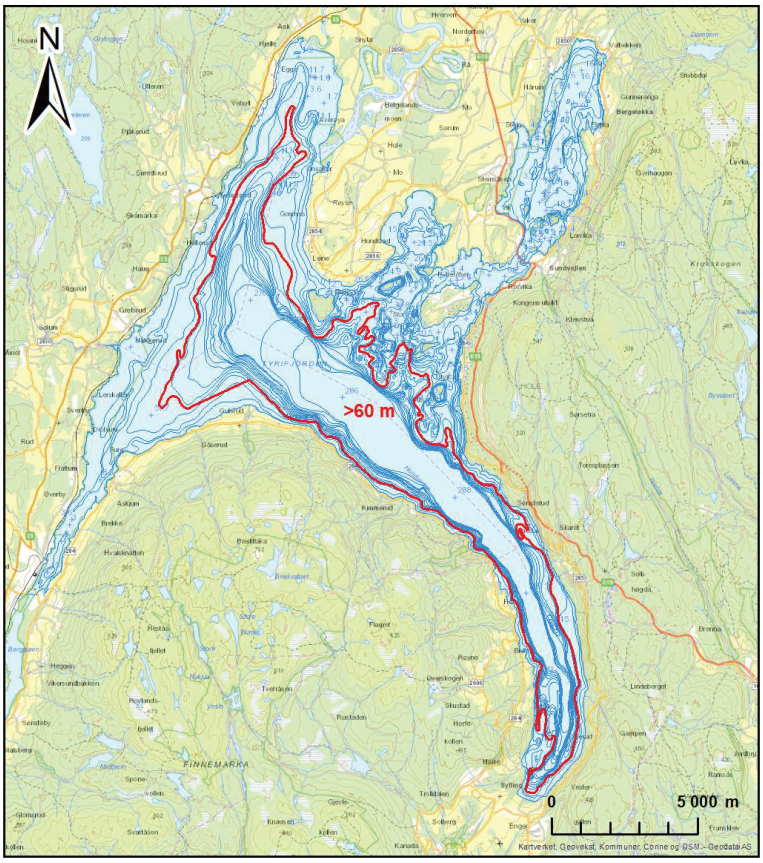

Figure S2. Map showing the depth of different areas of lake Tyrifjorden. Area deeper than 60 m is outlined in red.

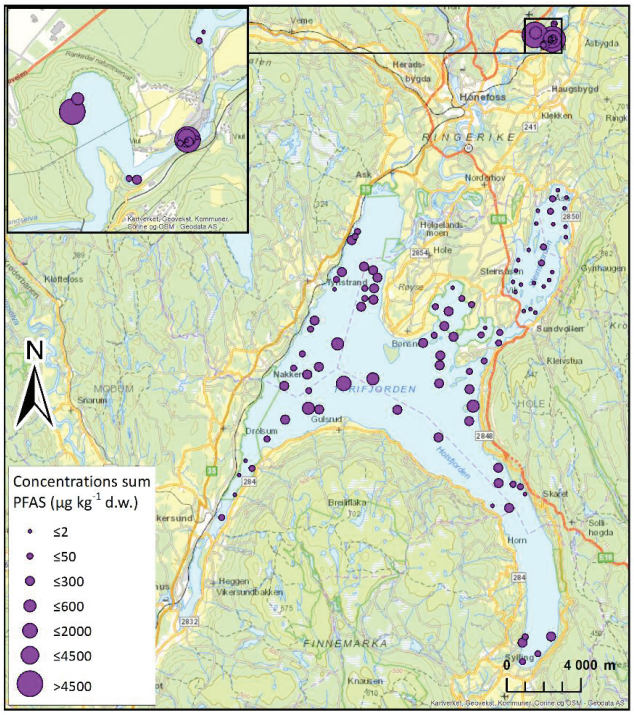

Figure S3. Sediment sampling areas and corresponding sum concentrations of detected PFAS (Σ_{29} PFAS)

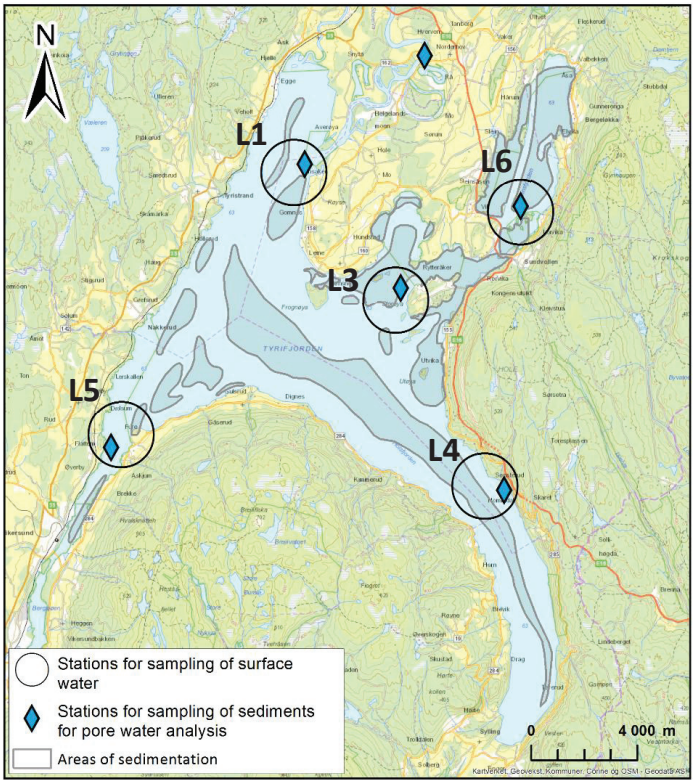

Figure S4. Sampling sites for lake surface water and sediments used for pore water analysis.

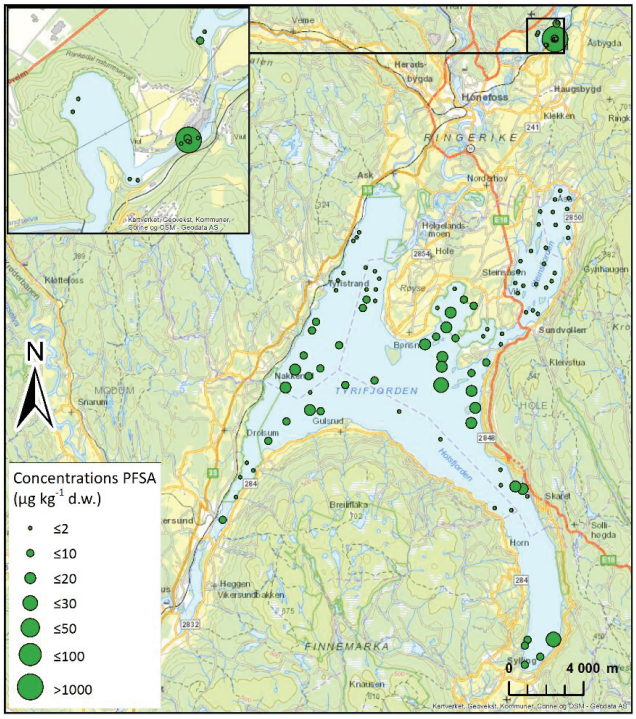

Figure S5. Sediment sampling areas and corresponding PFSA concentrations.

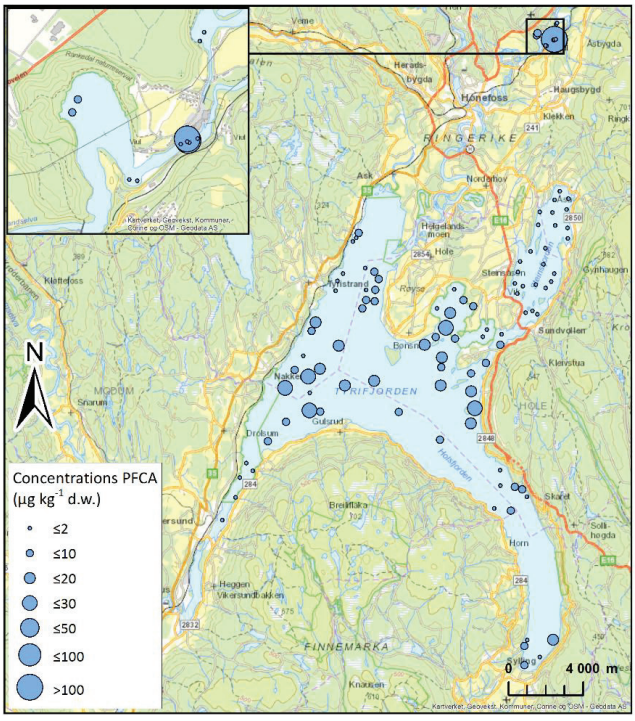

Figure S6. Sediment sampling areas and corresponding PFCA concentrations

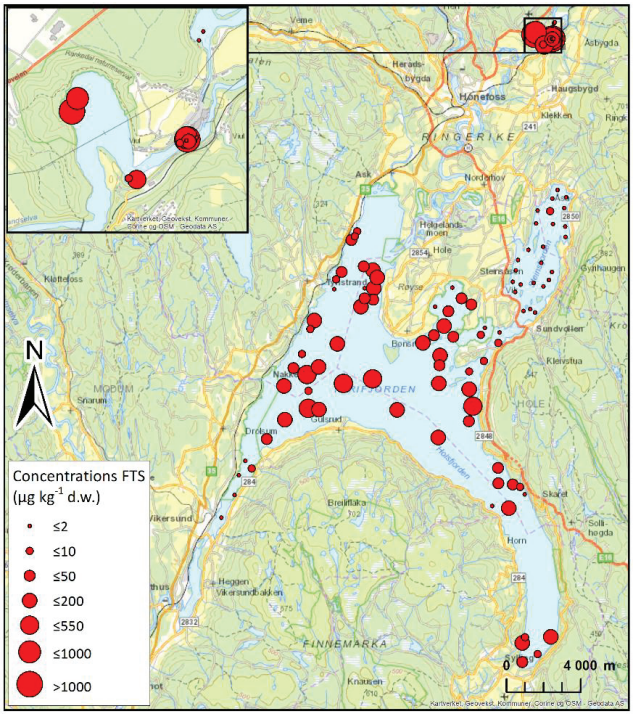

Figure S7. Sediment sampling areas and corresponding FTS concentrations.

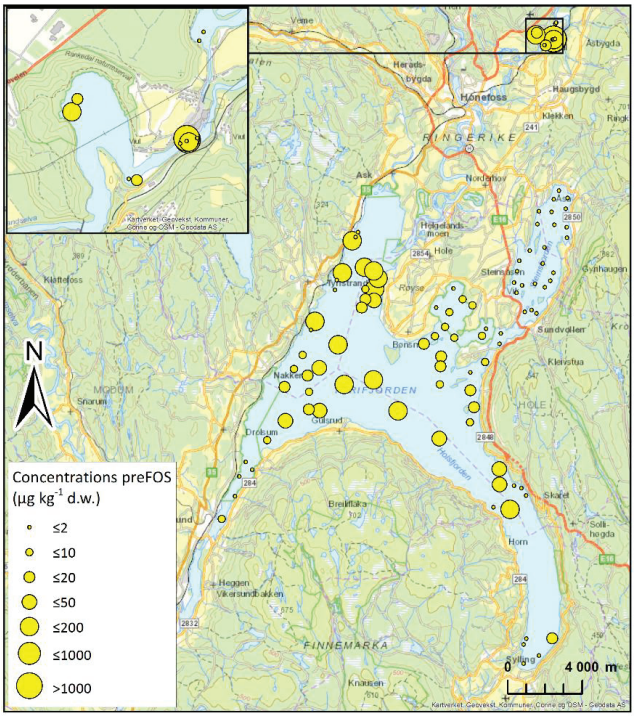

Figure S8. Sediment sampling areas and corresponding preFOS concentrations.

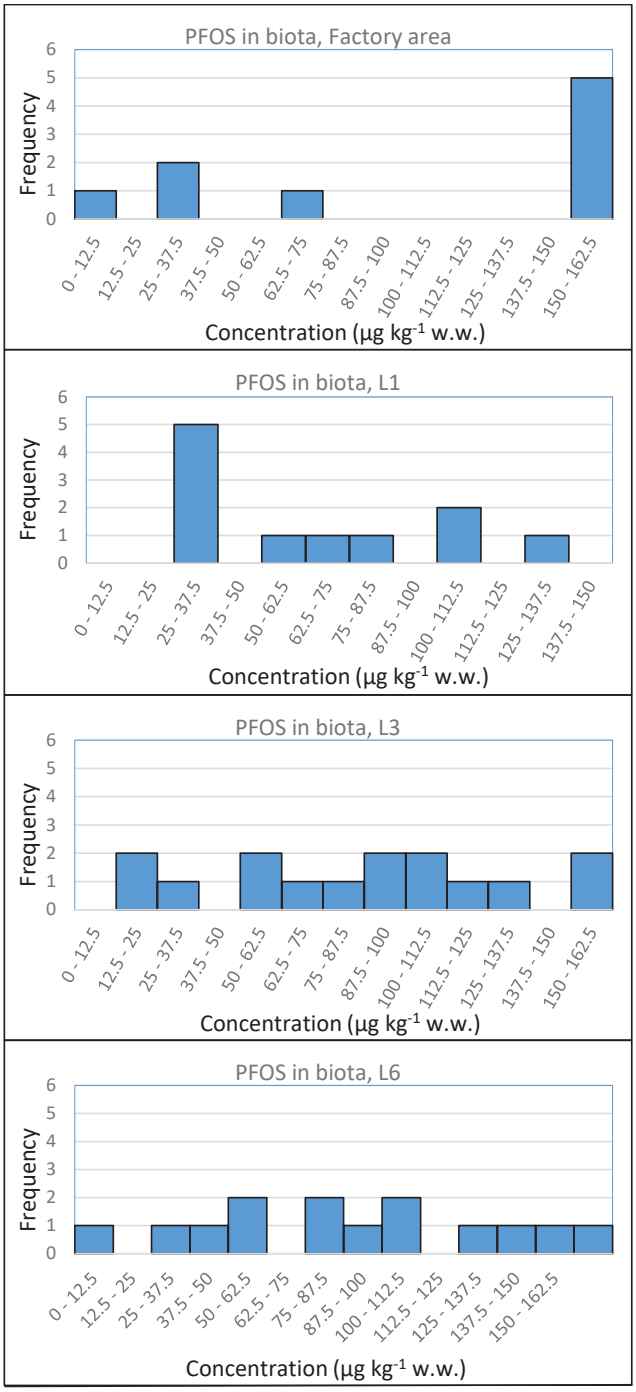

Figure S9. Histograms showing the concentration distribution for L-PFOS in biota at sampling areas Factory area (top) L1, L3 and L6 (bottom), respectively.

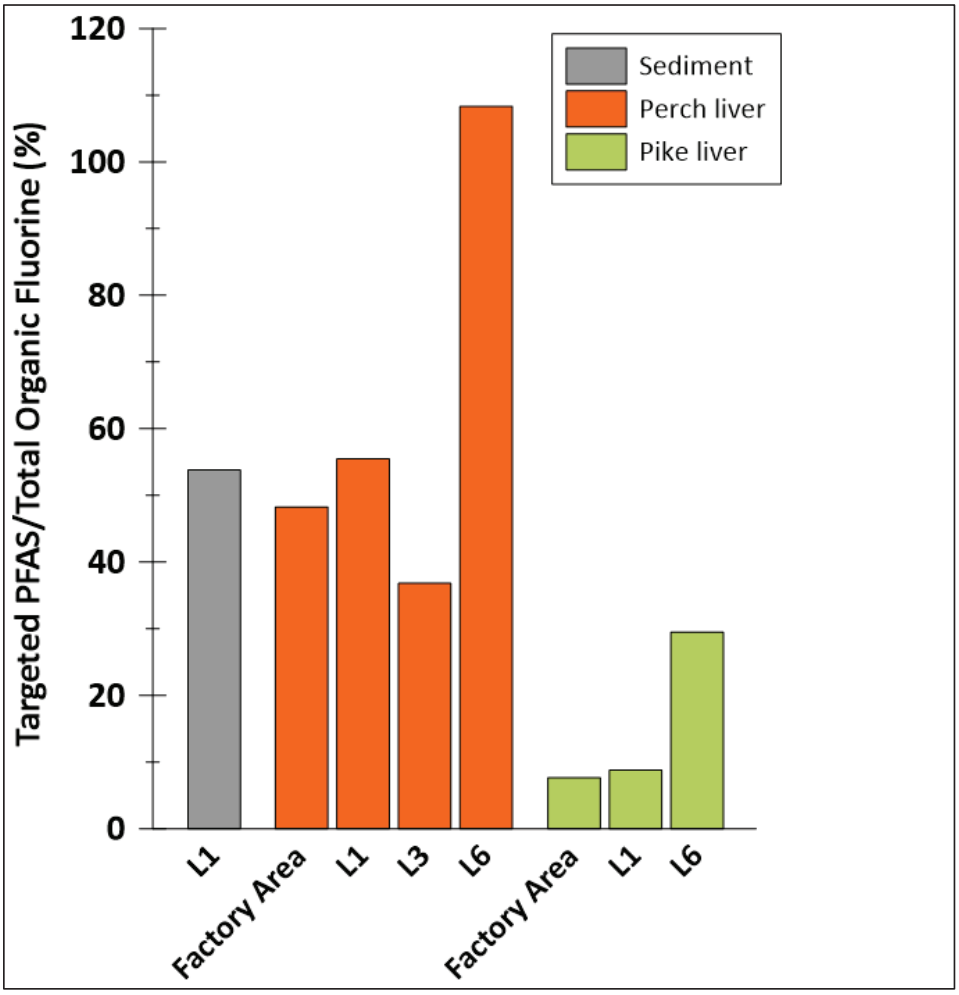

Figure S10. Sum organic fluorine in the targeted PFAS as a percentage of fluorine determined in the extractable organic fluorine (EOF) analysis (n=1).

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Paper IV

Bioaccumulation of Fluorotelomer Sulfonates and Perfluoroalkyl Acids in Marine Organisms Living in Aqueous Film-Forming Foam Impacted Waters

The marine environment at Bodø airport. Photo: Håkon Austad Langberg

Appendix: Paper IV

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Bioaccumulation of Fluorotelomer Sulfonates and Perfluoroalkyl Acids in Marine Organisms Living in Aqueous Film-Forming Foam Impacted Waters

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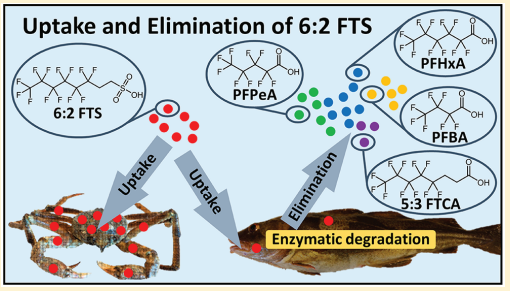
Supporting Information

ABSTRACT: The use of aqueous film-forming foams (AFFFs) has resulted in hot spots polluted with poly- and perfluorinated alkyl substances (PFASs). The phase out of long-chained perfluoroalkyl acids (PFAAs) from AFFFs resulted in the necessity for alternatives, and short-chained PFAAs and fluorotelomer-based surfactants have been used. Here, the distribution of PFAS contamination in the marine environment surrounding a military site in Norway was investigated. Up to 30 PFASs were analyzed in storm, leachate, and fjord water; marine sediments; marine invertebrates (snails, green shore crab, great spider crab, and edible crab); and teleost fish (Atlantic cod, European place, and Lemon sole). Perfluorooctanesulfonic acid (PFOS) was the most abundantly detected PFAS. Differences in PFAS accumulation levels were observed among species, likely reflecting different exposure routes among trophic levels and different capabilities for depuration and/or enzymatic degradation. In agreement with previous literature, almost no 6:2 fluorotelomer sulfonate (6:2 FTS) was detected in teleost fish. However, this study is one of the first to report considerable concentrations of 6:2 FTS in marine invertebrates, suggesting bioaccumulation. Biota monitoring and risk assessments of sites contaminated with fluorotelomer sulfonates (FTSs) and related compounds should not be limited to fish, but should also include invertebrates.



INTRODUCTION

The use of aqueous film-forming foams (AFFFs) at firefighting training areas, airports, military sites, and fire stations has resulted in hot spots of poly- and perfluorinated alkyl substance (PFAS)-polluted soil, sediment, and water.[1−3] PFASs have been shown to exert toxic effects on ecosystems and human health,[4,5] and since the early 2000s, perfluorooctanesulfonic acid (PFOS) and related long-chained perfluoroalkyl acids (PFAAs) (defined here as perfluoroalkyl carboxylic acids [PFCAs] with number of carbon atoms [C] ≥ 8, and perfluoroalkyl sulfonic acids [PFSAs] with C ≥ 6), have been phased out in AFFFs. This has resulted in the need for alternatives, and short-chained PFAAs and fluorotelomer-based surfactants (6:2 fluorotelomer sulfonate [6:2 FTS] and fluorinated telomer products with 6:2 configuration) have been used as replacements in AFFF.[6−10]

The physiochemical properties of PFASs suggest that water, and water-living organisms, are important environmental compartments for PFAS partitioning.[11] Different toxicokinetics have been reported for different organisms and PFAS groups, and elimination rates for PFAAs show large species- and gender-dependent variations.[12] As an example, the serum half-life of PFOS was 1 to 2 months in rodents but several years in humans.[12] Long-chained PFAAs have been reported to accumulate in a wide range of fish species; however, half-lives are generally shorter (days)[13] than those for rodents and humans. PFSAs have been shown to have longer half-lives than PFCAs of the same chain length.[11,13,14] Half-lives of 4.5 days for perfluorooctanoic acid (PFOA) and 12 days for PFOS have been reported in blood of rainbow trout (*Oncorhyncus mykiss*).[13] 6:2 FTS has been shown to be effectively eliminated in teleost fish[15] and has, on the basis of fish bioaccumulation data, been considered as unlikely to bioaccumulate in aquatic systems.[9]

The environmental quality standard for PFOS in the European Water Framework Directive (9.1 $\mu g\ kg^{-1}$) refers to fish,[16] and biota monitoring at PFAS hot spots has thus

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Appendix: Paper IV

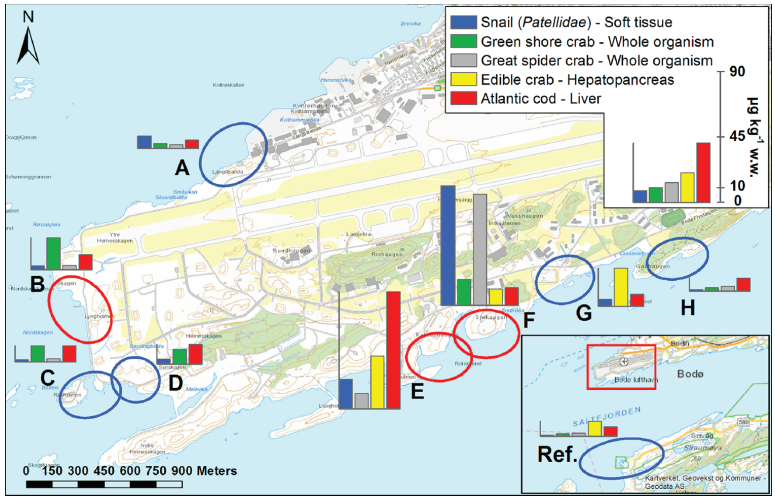

Figure 1. Geographical location of the sampling stations around the Air Station (stations A–H) and the reference station (ref.) on the other side of the fjord. Stations A, C, D, G, and H are located near discharge points for stormwater not associated with any particular PFAS source (blue circles). Stations B, E, and F are point sources for PFAS-contaminated leachate and stormwater (red circles). Bar charts show the average concentrations of Σ_{22} PFASs in biotic tissue at each sampling station. The numerical values are given in Table S7. Not all species were caught at all sampling stations.

focused on fish.[17−20] Less is known about PFASs in invertebrates. PFAAs have been detected in insect larvae, bivalves, zooplankton, and larger crustaceans such as prawns and crabs.[21−28] Depuration of long-chained PFAAs is reported for some crustaceans. The half-lives of PFOS and perfluorohexanesulfonic acid (PFHxS) in school prawn (*Metapenaeus macleayi*) were 159 and 6 h, respectively,[29] demonstrating the effect of chain length. Half-lives in mud crab (*Scylla serrata*) in the same study were considerably longer at 998 h for PFOS and 190 h for PFHxS,[29] illustrating species-dependent depuration rates. Therefore, with the exception of a few species, PFAS behavior in invertebrates is largely unexplored. A wider understanding related to PFAS accumulation, elimination, and toxicity in aquatic invertebrates is needed to identify possible implications for risk assessments of PFAS contamination in aquatic ecosystems.

In the present study, the accumulation of PFASs (arising from the use of AFFFs) in the marine food chain was investigated. The objective was to evaluate potential species-specific differences in PFAS accumulation. The military site at Bodø Airport, Bodø Air Station, was chosen as the case study site. PFAS profiles and concentrations in invertebrates (marine snails and crabs), representing less mobile organisms living close to point sources of AFFF-polluted stormwater, were compared to mobile teleost fish. PFAS profiles and concentrations in stormwater, leachate water, fjord water (seawater), and marine sediments were used to evaluate PFAS distribution in the abiotic environment. To the best of our knowledge this is the first study to evaluate the accumulation of long-chained PFAAs and replacement products in invertebrates living close to an AFFF pollution hot spot.

MATERIALS AND METHODS

Case Study Site. Bodø Air Station (67.26° N, 14.36° E) is a military airbase located on a peninsula in the Norwegian Arctic. It experiences strong winds and tidal currents resulting in strong water circulation and thus, dilution of contaminants. In the period 2013−2017 (the time frame of this study and the two preceding years), the average wind speed was 6.5 m s^{-1},[30] and the average tidal range was 1.9 m.[31] The Air Station shares facilities with the civil airport in Bodø (Bodø Airport). Little is known about the first use of AFFFs at the site, but it has probably been used since the mid-1960s. The use of PFOS-based AFFFs was phased out in Norway in 2007 (as an early adoption of EU regulations).[32] As a result, firefighting foam containing fluorotelomer-based surfactants (6:2 FTS and/or related products) was used at the Air Station from 2007. According to the Norwegian Defense Estates Agency (personal communication, C.E. Amundsen, June 2016), the process of phasing out PFAS-based foam started in 2012 and was completed at airport firefighting training areas in 2015.

Eight sampling stations around the Air Station were selected to capture the main outlets of PFASs in stormwater and soil leachate (Figure 1). A reference station was located on the other side of the fjord, about 5 kilometers (km) from the Air Station. Stations A, C, D, G, and H are located near discharge points for stormwater not associated with any particular PFAS source. These areas were assumed to represent nominal levels of PFAS discharge from the Air Station. Station B is close to the outlet of PFAS-contaminated stormwater from a fire station. Sampling stations E and F are situated in an area extensively used for firefighting training. Station E is at an outlet of stormwater assumed to have high concentrations of AFFF-related PFAS compounds. Station F is an area where AFFF-contaminated water leaches from the soil at the firefighting training area. There are no known sources of PFAS contamination in proximity to the reference station.

Leachate and Stormwater. Storm water was sampled in several campaigns during 2015−2016. At station F, which has been used for firefighting training, soil leachate water entering the fjord was sampled at the same time as stormwater. No soil leachate water was observed at other stations. Sampling was

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performed for stormwater (3−5 times) and soil leachate water (twice) to capture concentration spikes (see details in Table S1 in the Supporting Information). Unfiltered samples were collected by submerging a 0.5 L high-density polyethylene bottle in the water source. Samples were kept cool and dark and sent for chemical analysis within 48 h of sampling. Water flow rates (L s^{-1}) were estimated at the time of sampling (March and May) by measuring the cross section and velocity of the water. The water amount from each station per year (L $year^{-1}$) was calculated as described in eq I. The average PFAS concentrations (ng L^{-1}) were multiplied by the amount of water from each station per year (L $year^{-1}$) to estimate the amount of PFASs released to the sea (g $year^{-1}$), eq II.

Amount of water per year:

$$Q_a = v \cdot t \quad \text{(I)}$$

where Q_a is the annual discharge volume (L $year^{-1}$), v the flow rate (L s^{-1}), and t the time (s $year^{-1}$).

Amount of PFASs released per year:

$$m_{PFAS} = Q_a \cdot C_{PFAS} \quad \text{(II)}$$

where m_{PFAS} is the amount of PFASs released to the sea per year (g $year^{-1}$), Q_a the annual discharge volume (L $year^{-1}$), and C_{PFAS} the PFAS concentration (ng L^{-1}).

Marine Abiotic Environment. Sediments were sampled in May 2017 at all stations, except for station G where the sea floor consisted of rocks. Water depths varied between 1 and 5 m depending on the station (details provided in the Supporting Information). A mixed sample of fine-grained sediments was collected from a radius of 20 m from the emission point. Sediments were collected by pushing a plexiglas tube (7.5 cm diameter) into the sea floor to a depth of approximately 10 cm.

Passive samplers (deployed at the same time as sediment sampling) were used to measure concentrations in the fjord water (seawater) at all stations. The passive sampler, the SorbiCell (described elsewhere[33]), is a flow-through sampler, based on sorption and sampler volume, with an entrance filter, two zones with adsorbent material, and a tracer salt for the calculation of the water volume that has passed the sorbent (details are provided in the Supporting Information). Passive samplers were deployed in the fjord, as close as possible to the emission point, 0.5 m below the water surface. Passive samplers were collected 3 weeks after deployment, and the cartridges were kept cool and dark until analysis.

Marine Biota. Biota were sampled at the same time as sediments and the deployment of passive samplers. Marine invertebrates, snails (*Patellidae*); two species of small crabs, green shore crab (*Carcinus maenas*) and great spider crab (*Hyas araneus*); the larger edible crab (*Cancer pagurus*); teleost fish, Atlantic cod (*Gadus morhua*); and two species of flatfish, European place (*Pleuronectes platessa*) and Lemon sole (*Microstomus kitt*), were sampled. Species available for sampling varied among stations (Table S2).

Snails were collected by hand from rocks in the intertidal zone as close to the emission source as possible. At the reference station, snails were collected over a length of approximately 100 m along the shore in the intertidal zone. Small crabs were collected by hand from a radius of 20 m from the emission point at water depths between 1 and 5 m depending on the station (details in the Supporting Information), using waders in the intertidal zone and in shallow water and by divers in deeper water. Edible crab and fish were sampled using commercial fish traps placed on the sea floor, approximately 200 m from shore at water depths between 5 and 30 m depending on the station (as it was not possible to catch fish within 20 m from the emission points, details in the Supporting Information). Raw shrimp and mackerel were used as bait (in a closed bait-bag). Fish were killed with a blow to the head, and crabs were killed by spiking the crab from the underside. The weight (g) and length (cm) of the fish (fork-length) and edible crabs (carapace width) and sex of all three crab species were recorded (Table S3). For safety reasons and in order to avoid cross contamination, clean nitrile coated gloves were used during sampling of large crabs and fish. Clean nitrile gloves were used during sampling of other matrixes and during handling of all samples. Equipment was washed and dried, and nitrile gloves were changed between samples. Crabs and fish were wrapped in clean aluminum foil (whole organisms to avoid risk of contamination). All biotic samples were frozen at −20 °C before they were sent for dissection and chemical analysis.

Sample Preparation and Analysis. Analyses were performed by Eurofins Environment Testing Norway AS according to DIN EN ISO/IEC 17025:2005. A total of 30 PFAS compounds were analyzed; however, the number of analyzed compounds varied among the different sampled media (see Table S4).

PFAS concentrations in sediments were quantified using method DIN 38414-S14. Total organic carbon (TOC) in sediments was calculated using a loss on ignition method. Water was analyzed for PFASs following method DIN 38407-F42. The SorbiCell sorbent material was extracted using methanol. Extraction of biotic tissue was performed by freeze-drying the sample, adding internal standards before extraction with methanol in an ultrasonic bath, and solvent cleanup. Extracts were analyzed using high-performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS). Clean sand was used as a blank sample for biota and sediments. Distilled water was used as a blank sample for water samples. Sediment, biota, and water blank concentrations were acceptable according to the accredited lab procedures. For passive samplers, sorbent material from the same batch as used in the samplers was used as a blank. Extractions were carried out for both adsorbent zones to check whether the sorption capacity had been exceeded. To validate the actual volume the Sorbicell samples, the depletion of the tracer salt in the sampler and the field volume (water which has passed through the sampler during deployment) was monitored. PFAS was not detected in passive sampler blanks. However, PFBA was detected in both adsorbent zones for all samplers, which may indicate that the sorption capacity was exceeded for this compound. Thus, although peaks were seen for PFBA, they were not quantified. Samples from the reference site were used as a control as they had close to background PFAS concentrations. See the Supporting Information for details about extraction, analysis, and limits of quantification (LOQ).

Snails (soft tissue) were analyzed as one pooled and thoroughly mixed sample ($n > 30$) from each sampling station. One pooled and mixed sample of whole organisms ($1 \leq n \leq 11$) was made for each of the two species of small crabs per station. Hepatopancreas in edible crab was analyzed individually. Fish livers were weighed and analyzed individually (Table S3). The stomach contents of the fish were removed

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Table 1. Calculated Amount of PFASs (g year^{-1}) and Relative Frequency of Dominant PFAS (%) Following Storm Water, in Each Sampling Station (at the Air Station)

station	A	B	C	D	E/F[a]	G	H
PFAS loads released to the sea per year (g year^{-1})	66	182	0	94	1552[b]	16	161
relative frequency of dominant PFAS compounds (%)[c]	**PFPeA:** 28–35 **PFHxA:** 0–14 **PFHxS:** 0–24 **PFOS:** 48–55	**6:2 FTS** 0–36 **PFPeA:** 22–45 **PFHxA:** 10–12 **PFHxS:** 5–25 **PFOS:** 15–100	**PFPeA:** 29- 40 **PFHxA:** 13–14 **PFHxS:** 0–16 **PFOS:** 24–60	**PFPeA:** 13–26 **PFHxA:** 6–13 **PFHxS:** 9–15 **PFOS:** 33–57	**6:2 FTS:** 7–27 **PFPeA:** 17–25 **PFHxA:** 5–11 **PFHxS:** 3–10 **PFOS:** 35–48	**6:2 FTS:** 0–38 **PFPeA:** 36–45 **PFHxA:** 0–20 **PFOS:** 26–35	**6:2 FTS:** 9–16 **PFPeA:** 27–41 **PFHxA:** 10–16 **PFHxS:** 5–16 **PFOS:** 10–23

[a]Stations E and F are in close proximity to each other and were treated as one station. [b]In addition to runoff with stormwater, leachate from PFAS contaminated soil is expected to result in an additional 340 g of 6:2 FTS and 128 g of PFOS being released to the fjord from station E/F. [c]Sampling was performed in several rounds; thus, the PFAS profiles are given as ranges.

before the remaining tissue was homogenized and analyzed individually.

Data Handling and Statistical Analysis. Statistical analyses were carried out using R, version 3.4.2[34] (packages: vegan,[35] agricolae,[36] factoextra,[37] and FactoMineR[38]). Concentrations in biota are given on wet weight basis (w.w.). Errors (±) in the present work are reported as standard error of the mean (SEM). Concentrations below the LOQ were assigned values of half the LOQ. Details about the statistical analysis are given in the Supporting Information.

Concentrations in whole fish (μg kg^{-1}) were calculated using whole fish weight (kg), liver weight (kg), and concentrations in liver and remaining tissue (μg kg^{-1}). In Atlantic cod, the ratio between PFOS concentrations in liver and in remaining tissue was estimated, and possible relationships between Fulton's condition factor (weight to length ratio, K) or liver somatic index (LSI), and PFAS burdens in liver (sum $[\Sigma]_{22}$ PFAS) were investigated (equations are given in the Supporting Information).

RESULTS AND DISCUSSION

Leachate and Stormwater. Overall, the most dominant compounds in stormwater were 6:2 FTS, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), PFHxS, and PFOS detected at maximum concentrations of 921, 738, 194, 142, and 1010 ng L^{-1}, respectively. The calculated amount of Σ_{19} PFASs released to the fjord at each station (g year^{-1}) and the site-specific levels of dominating compounds, given as percentages (%) of the Σ_{19} PFASs, are listed in Table 1 (see Figure S1 for PFAS amounts in stormwater and concentrations in biota at the different stations). As stations E and F are in close proximity to each other (approximately 150 m), and as it was not possible to distinguish between PFAS loads, they were treated as one station. PFAS profiles in stormwater were similar at all stations; however, PFAS concentrations and loads varied. The highest loads were estimated at the stations associated with PFAS sources: stations B and E/F (182 and 1552 g Σ_{19} PFAS year^{-1}, respectively). PFOS was generally detected in the highest proportions of total PFAS (10–100%), followed by PFPeA (13–45%). PFHxS and PFHxA were detected at approximately comparable concentrations (0–25% and 0–20%, respectively). The level of 6:2 FTS (0–38%) showed large variability among the stations. 6:2 FTS constituted a relatively large proportion of the total PFAS at stations B (0–36%), E/F (7–27%), G (0–38%), and H (9–16%), while it was not detected at stations A, C, and D.

Soil leachate water was sampled only at station F. The leachate water was dominated by 6:2 FTS and PFOS (average of 89 μg L^{-1} 6:2 FTS and 33 μg L^{-1} PFOS), and the yearly contributions to the fjord were estimated to be 340 and 128 g, respectively. Station F has been extensively used for firefighting training, thus PFAS loads from soil leachate at all other sites are expected to be smaller. However, the nominal level of PFAS contamination observed all over the Air Station suggests some runoff from PFAS contaminated soil at all locations.

The reported levels herein are similar to levels reported in the groundwater at another Norwegian airport.[39] Previous studies have reported highly variable concentrations of PFAS in water from areas where AFFF has been used. At a closed military airfield in Sweden (used from 1946 to 1994), PFHxS and PFOS dominated surface water samples (lakes and ponds) (the highest concentrations were 25 ng L^{-1} and 45 ng L^{-1}), while PFHxA and PFOA were detected in significantly lower concentrations (max 4 and 9 ng L^{-1}).[17] Analysis of PFPeA and fluorotelomers were not included in that study. Surface water from a military airport in France was dominated by 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) (max 426 ng L^{-1}) with lower levels of PFHxA (max 19 ng L^{-1}) and other PFCAs, while PFSA concentrations were below the LOQ.[40] At two fire training areas at U.S. military bases in operation from 1942 to 1990 and 1950 to 1993, respectively, both fluorotelomers, PFCA, and PFSA were detected in high concentrations in groundwater. 6:2 FTS was detected at maximum concentrations of 220 000 and 37 000 ng L^{-1}, and maximum concentrations of PFPeA were 120 000 and 35 000 ng L^{-1}. Concentrations of PFHxA (max 350 000 and 99 000 ng L^{-1}) and PFHxS (max 360 000 and 170 000 ng L^{-1}) were comparable to, or higher than, PFOS concentrations (max 78 000 and 65 000 ng L^{-1}).[41] Concentrations in the latter study are much higher than concentrations found in our study; however, several of the most dominant compounds are also the ones that dominate in our study. The large differences in PFAS composition among locations could be due to differences in the historical use of AFFFs. For example, PFCAs were not detected in AFFF formulations used by the U.S. military from 1988 to 2001.[7] However, PFCAs were used worldwide in AFFF formulations from approximately 1965 to 1975.[42] In addition, the use of fluorotelomer-based AFFFs has been linked to significant in situ production of PFCAs,[2] and 6:2 FTS is known to degrade to PFCA (≤7 C),[43−45] with PFHxA being one of the major degradation products.[43] Thus, the relatively high levels of PFHxA reported in our study (up to 20% of the total PFAS, and a max concentration of 194 ng L^{-1}) may indicate that older AFFF formulations (based on PFCA) have

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been used at Bodø Air Station. However, PFHxA levels at the Air Station may also be due to degradation of newer, fluorotelomer-based AFFF (fluorinated telomer products with 6:2 configuration such as 6:2 FTS and/or 6:2 FTAB).

Marine Abiotic Environment. PFBA was detected in all passive samplers, but it was not quantified as discussed above. No other PFASs were detected in the samplers. Thus, total fjord water PFAS concentrations were considered below the limit of detection (0.5−3 ng L^{-1}) at all sites. A previous study at Oslo Airport (OSL) demonstrated the SorbiCell to be suitable for monitoring PFAS in ground and surface water (reported concentrations of Σ_{16} PFAS between 113 and 6744 ng L^{-1}) (manuscript in preparation). All PFAS concentrations in sediments were close to or below the LOQ. Only sediments from sites B and D contained concentrations of PFAS above the LOQ (0.10−0.20 μg kg^{-1}). PFPeA (0.26 μg kg^{-1}) and PFOS (0.32 μg kg^{-1}) were detected at sampling station B, and PFOS (0.29 μg kg^{-1}) was detected at station D. The TOC content in sediments was low and in the range of 0.4−1.6%. PFAS concentrations in soil and sediments have previously been shown to be correlated with organic carbon content; however, these were in cases where significantly higher carbon contents have been reported than in the present study.[46,47] The low PFAS concentrations in seawater indicate that dissolved PFASs released to the fjord system are relatively efficiently diluted and removed from water surrounding the airport. On the basis of Endo et al.,[48] we do not consider salting out to have an important influence on neutral PFAS partitioning; however, for anionic PFASs (i.e., the compounds analyzed here), sorption to cationic salts and suspended solids can play a role in overall sorption processes.[49] In addition, sorption of PFAA onto clay has previously been shown to increase with salinity.[50] Therefore, because of the higher salt-content in seawater compared to leachate and stormwater, distribution coefficients (K_d) for the analyzed PFAS are expected to be higher in the marine environment compared to leachate and stormwater. The amount of, and PFAS sorption to, suspended solids was not investigated in the present study. However, a fraction of the suspended solids are deposited on the sea floor with time; thus, sediment concentrations are expected to be affected by sorption to suspended solids. The low PFAS concentrations in sediments observed here indicate that salting out and sorption to suspended solids are not the main mechanisms for PFAS removal from the water surrounding the airport. It is possible that PFAS accumulation at the marine boundary layer for sea spray aerosol formation contributes to losses from the seawater to the atmosphere.[51] Thus, the low concentrations of PFASs in the marine abiotic environment at the Air Station are likely due to the local geographical characteristics which, because of strong winds and currents, favor sea spray formation, water circulation, and dilution of contaminants.

Marine Biota. Normalization for dry weight and lipid or protein content was not carried out; thus, potential differences in PFAS concentrations caused by differences in affinity among tissues could not be evaluated. Nevertheless, the dominant PFAS in all samples, both at the Air Station and the reference station, was PFOS. This is in agreement with the reported concentrations in leachate and stormwater herein, with previous studies that have shown PFOS to dominate soil samples from Norwegian airports,[52,53] and studies that have shown PFOS and other long-chained PFAAs have high bioaccumulation potential in aquatic organisms.[13−15,21,29,54,55] PFAS concentrations were higher at the airport compared to the reference station, and concentrations were generally highest at the source areas (stations B, E, and F), shown in Figure 1. PFAS concentrations in biotic samples are given in Table S7.

Fish PFAS Burdens and Biological Parameters. A (weak) negative relationship was found between the LSI and Σ_{22} PFAS in Atlantic cod liver ($p < 0.01$, figure S2). This is in agreement with previously reported negative correlations for Atlantic cod in Norwegian fjords and harbors,[56] and for the freshwater and diadromous species fathead minnow (*Pimephales promelas*) and rainbow trout exposed to PFOS.[57] Nevertheless, liver enlargement is reported in the freshwater species blacknose dace (*Rhinichthys atratulus*) and common shiner (*Luxilus cornutus*) living in an AFFF-contaminated area.[20] The relationship between PFAS exposure and LSI in fish should be investigated in future studies, including potential differences between freshwater and marine species. No relationships were found between length, weight, or Fulton's condition factor K and PFAS levels ($p > 0.05$). This is in accordance with previous studies reporting no relationships between PFAS levels and length, weight, or age in Lake Ontario Lake Trout[58] or in perch from Swedish lakes.[59] Nevertheless, a positive relationship was reported for PFOS concentrations and fork-length (but not body weight) of polar cod in the Barents Sea.[60]

Invertebrate PFAS Burdens and Biological Parameters. A relationship between size and PFAS levels in hepatopancreas in edible crabs was not found ($p > 0.05$). There is a general lack of studies investigating the relationship between invertebrate size or sex and PFAS levels. However, the lack of relationships reported herein is in accordance with a study investigating mud crabs,[29] where no relationships between size and PFAS levels were observed (nor any differences between sex). Potential relationships should be investigated further in future studies.

Biota PFOS Concentrations. At the Air Station, no significant differences in fish liver PFOS concentrations were observed among sampling stations (A−H) ($p > 0.05$). A previous study investigating the spatial PFOS distribution in fish and invertebrate species from source areas (approximately 5 km between sampling stations) found a clear relationship with distance for one site, while the opposite was shown for another,[23] possibly reflecting fish migration.

Tracking and recapturing experiments with coastal Atlantic cod have shown that average core areas for populations are about 8 km^2[61] (movement between a few hundred meters to a few km were reported for study periods up to 20 months[62,63]). The distance between stations A and H is 6 km, and the average distance between stations is 750 m. Thus, in the present study, some migration between sampling stations was expected. PFOS concentrations in Atlantic cod caught at the Air Station (stations A−H), both liver and whole fish (including liver), were significantly higher than in individuals from the reference station on the other side of the fjord, about 5 km from the Air Station ($p_{liver} = 0.01$, $p_{whole} = 0.03$), as shown in Figure 2. PFOS concentrations in Atlantic cod liver were 6.48 ± 2.6 μg kg^{-1} at the Air Station and 1.63 ± 0.26 μg kg^{-1} at the reference station. PFOS concentrations in whole fish were 1.98 ± 0.74 μg kg^{-1} at the Air Station and 0.60 ± 0.09 μg kg^{-1} at the reference station. In comparison, an average PFOS liver concentration of 3.1 μg kg^{-1} was reported for Atlantic cod in the northern parts of Norway.[56] Thus, even though some migration can be expected, cod caught near the Air Station showed higher concentrations compared to cod from the

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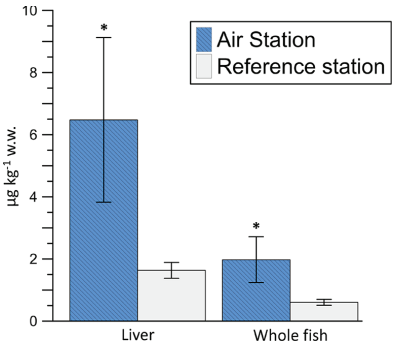

Figure 2. PFOS concentrations in Atlantic cod (μg kg^{-1} in liver, and in whole fish including the liver) caught near the Air Station (stations A–H; n_{liver} = 26, $n_{whole\ fish}$ = 24) and at the reference station (n = 6). Concentrations are given as average ± standard error of mean (SEM). An asterisk (*) denotes concentrations significantly different from reference station (Unpaired Wilcoxon Test, $p < 0.05$).

reference station, as well as cod from other parts of northern Norway.

The average ratio between PFOS concentrations in liver and in whole fish (including liver) for Atlantic cod was 3.5 ± 0.4 and did not differ significantly between the Air station and the reference station (Figure S3, $p > 0.05$) (ratios for all PFAS compounds detected in both liver and in remaining fish are shown in Table S5). PFOS ratios were relatively consistent, and no trends with size or contamination level in Atlantic cod were observed. However, some individuals caught in stations not associated with any particular PFAS source (A, C, and D) had much higher ratios (>5). Based on tissue-specific elimination rates, ratios between liver and other tissues (e.g., muscle, carcass, or remaining whole fish homogenates) might be an expression of the exposure history of individual fish. The validity of this observation should be explored in future studies. Falk et al.[55] reported that the ratio between concentrations in different tissues of rainbow trout was relatively constant when the fish were exposed to contaminated water. Following exposure, the ratio of liver versus other tissues (especially muscle and carcass) increased owing to the longer half-life of PFAS in the liver. PFOS was estimated to have a half-life of 8.4 days in muscle, whereas the half-life in the liver was estimated to be 20.4 days. Therefore, in cases where high ratios were observed, it may indicate that the particular individuals were previously exposed in one more contaminated location, before moving to the less contaminated location.

PFOS concentrations in snails from the Air Station were 3.86 ± 0.36 μg kg^{-1}, and the highest detected concentration was 14.30 μg kg^{-1} (station E). For the small crab species, green shore crab and great spider crab, PFOS concentrations were 5.50 ± 0.80 and 3.92 ± 0.79 μg kg^{-1}, respectively. The highest detected concentrations were 13.60 μg kg^{-1} (station B) and 16.20 μg kg^{-1} (station F), respectively. Concentrations in hepatopancreas of edible crab were 6.15 ± 0.90 μg kg^{-1}, and the highest detected concentration was 17.00 μg kg^{-1} (station

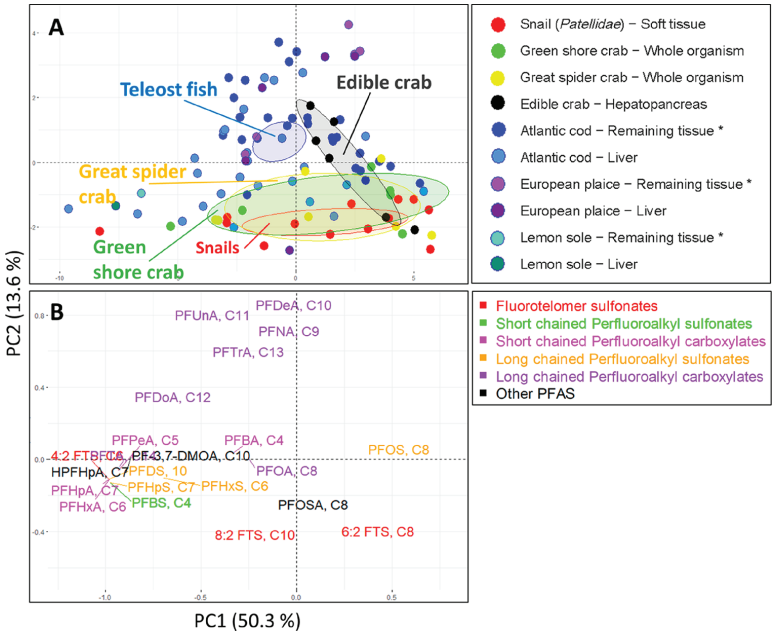

Figure 3. Principal component analysis (PCA) based on proportional levels (% Σ_{22} PFAS) in samples of biotic tissue. PC1 and PC2 explain 63.9% of the variance. (A, score plot) Biotic samples are plotted according to their PFAS profile. *Analysis on fish remaining tissue is performed on homogenized whole fish after removal of liver and gut content. (B, loading plot) PFAS compounds are plotted according to their distribution in biotic samples. Ellipses show 99% confidence intervals for the respective groups. Concentrations below the detection limit (LOQ) are treated as half the LOQ.

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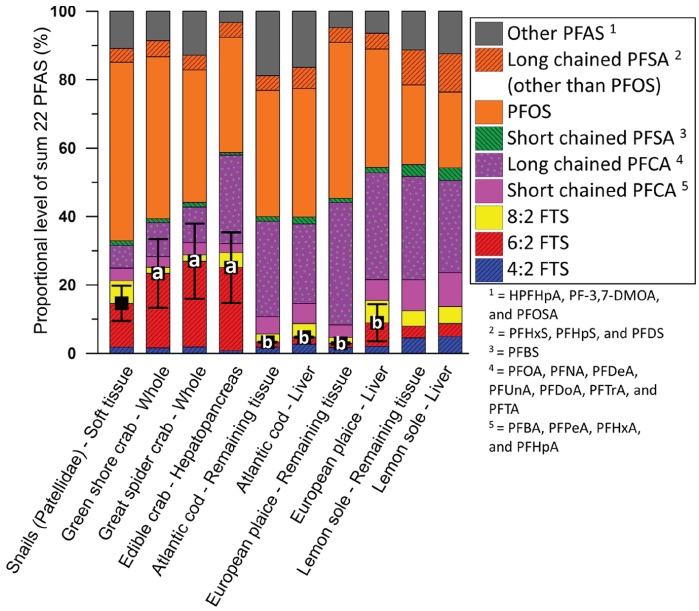

Figure 4. PFAS profiles in different biota tissues (stations A–H). Profiles are given as relative concentrations (of Σ_{22} PFAS). Error bars show ±standard error of mean (SEM) for 6:2 FTS (not shown for Lemon sole where $n = 1$). Different letters denote significant differences in 6:2 FTS proportion (Kruskal–Wallis and Bonferroni correction, $p < 0.05$). Concentrations below the LOQ are treated as half the LOQ.

G). PFOS concentrations in snails, green shore crab, and great spider crab at the reference station were 0.08, 0.40, and 0.34 μg kg^{-1}, respectively. Hepatopancreas in the two individuals of edible crab from the reference station contained PFOS concentrations of 4.38 and 5.91 μg kg^{-1}. Stations that had the largest PFAS loads from storm and leachate water (B, E, and F) also had the highest concentrations in invertebrates. In school prawn (meat) and mud crab (claw meat) living in PFAS-contaminated source areas, PFOS concentrations of 5.60–15.00 and 3.70–39.00 μg kg^{-1}, respectively, have been observed depending on location.[29] PFOS concentrations of 38–82 μg kg^{-1} dry weight were observed in swimming crab from an industrial area in China.[26] Although these organisms and tissues are different from those in our study, they represent invertebrate species in source areas showing levels comparable to those at the Air Station (sampling stations A–H). PFOS levels in invertebrate organisms (bivalve, lugworm, crab), including hepatopancreas in a small crab species, from the coast of Japan (no known local PFAS sources) were not reported above the LOQ (0.3 μg kg^{-1}).[64] This is consistent with the low levels reported in small crabs from the reference station in our study.

Biota PFAS Distribution. Principal component analysis (PCA) was carried out using relative PFAS concentrations (expressed as % of the Σ_{22} PFAS in biota from the Air Station) in order to determine how PFAS profiles varied (Figure 3). Average PFAS profiles in biota are shown in a stacked bar chart in Figure 4 and listed in Table S6. The score plot (Figure 3A) shows individual biotic samples plotted according to their PFAS profile. Biotic samples did not group according to sampling stations (and as such this is not shown in the manuscript), indicating that PFAS profiles in biota were similar among the different stations. The loading plot (Figure 3B) shows PFAS compounds plotted according to their distribution in biota. Principal component 1 (PC1, x-axis) explained 50% of the variance in the data set and is dominated by 6:2 FTS and PFOS on the right. PC2 (y-axis) explained 14% of the variance. The most important compounds in PC2 are long-chained PFCA in the upper part of the plot and fluorotelomer sulfonates (FTS) in the lower part of the plot. Profiles in fish consisted of a higher proportion of long-chained PFCA and almost no FTS and grouped in the upper part of the plot. The Σ of long-chained PFCA (PFOA, perfluorononanoic acid [PFNA], perfluorodecanoic acid [PFDeA], perfluoroundecanoic acid [PFUnA], perfluorododecanoic acid [PFDoA], perfluorotridecanoic acid [PFTrA], and perfluorotetradecanoic acid [PFTA]) were on average 24.6 and 29.1% of Σ_{22} PFAS in fish liver and remaining tissue. Snails and small crabs (green shore crab and great spider crab) grouped in the lower part of the plot, dominated by FTS. On average, the Σ of long-chained PFCA made up 8.4% of the total detected PFAS in whole body snails and small crabs. Hepatopancreas in edible crab is seen in both parts of the plot, reflecting that the tissue contains significant portions of both FTS and long-chained PFCA (also shown in Figure 4). The latter made up 25.8% of Σ_{22} PFAS. The multivariate PERMANOVA analysis followed by Bonferroni correction showed significant differences in PFAS profiles ($p < 0.05$) among Atlantic cod, both liver and remaining tissue, and the invertebrate organisms (snail, green shore crab, great spider crab, and hepatopancreas in edible crab). No other significant differences were found. The observed higher proportion of long-chained PFCAs in fish is likely due to their higher potential for biomagnification as reported in studies showing concentrations of PFCAs with 8–

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14 C increasing with trophic level.[28,65,66] The same reasoning likely applies to the higher proportion of long-chained PFCA in hepatopancreas in the large crab species (edible crab), compared to smaller crabs (green shore crab and great spider crab) and snails.

6:2 FTS Accumulation. The most noticeable difference between PFAS profiles in fish and invertebrate species was the proportion of 6:2 FTS. Figure 4 shows the proportion 6:2 FTS (as a percentage) of Σ_{22} PFAS. A statistically significant lower percentage 6:2 FTS were observed in Atlantic cod and European plaice (both liver and remaining tissue), compared to all three crab species ($p < 0.05$). The highest concentrations of 6:2 FTS in invertebrates were 56.3 μg kg^{-1} in snails, 12.3 μg kg^{-1} in green shore crab, and 56.8 μg kg^{-1} in great spider crab caught at sampling station F and 26.4 μg kg^{-1} in the hepatopancreas of edible crab caught at sampling station E (the two stations in the area used for firefighting). In contrast, 6:2 FTS was detected in only 3 of 39 fish, and the highest level was 3.25 μg kg^{-1} in the liver of a European plaice caught at station A. These results indicate significant differences in PFAS accumulation in marine invertebrates compared to teleost fish, and this is one of the first studies to show this.

Biotransformation of fluorotelomer-based compounds has been reviewed by Butt et al.,[67] and the review shows that few biotransformation studies have included fish. Studies on rainbow trout have found that tissue concentrations of 6:2 FTS increase at the beginning of an exposure period (first days or few weeks). However, it appears that elimination rates increase in response to exposure, and tissue concentrations rapidly decrease to a low level.[9,15] 6:2 FTS has been shown to be biotransformed to shorter, more water-soluble PFASs (5:3 fluorotelomer carboxylic acid [5:3 FTCA], perfluorobutanoic acid [PFBA], PFPeA, and PFHxA).[45] This has been suggested as the main mechanism behind the rapid elimination,[15] because these compounds show little accumulation in fish.[9,13,14] It is possible that fish exposed to a 6:2 FTS point source acquire the enzymatic ability to eliminate 6:2 FTS at a fast rate. An increased enzyme activity could possibly be used as a biomarker of exposure to 6:2 FTS.

6:2 FTS has previously been found in invertebrates.[21,60] However, this study is one of the first to report 6:2 FTS bioaccumulation to such an extent. High levels have previously been found in earthworms (max 14 834 μg kg^{-1}) and in marine snails (>100 μg kg^{-1}) in the vicinity of firefighting training areas in Norway.[68] Invertebrates have different detoxification pathways and enzymes than fish and mammals, e.g., different expression of cytochrome P450 (CYP) enzymes.[69,70] Different accumulation potentials for polycyclic aromatic hydrocarbons (PAHs) among invertebrates and vertebrates have previously been suggested to be partly due to these differential biotransformation capacities.[71] Although PAHs and PFASs are two distinct chemical classes of contaminants with different toxicokinetics and dynamics, this explanation cannot be ruled out.

Environmental Implications. The results of this study suggest that 6:2 FTS has the potential to bioaccumulate in marine invertebrates. Marine invertebrates are food sources to higher trophic organisms like fish, birds, and mammalian species. Marine invertebrates are also used as food sources for humans. Possible effects of 6:2 FTS accumulation in invertebrates and subsequent effects of a repeated dietary exposure should be investigated further.

The observed different accumulation pattern between teleost fish and invertebrates suggests that future biota monitoring and risk assessment of AFFF contaminated areas, and other sites possibly contaminated with FTS and related compounds, should include invertebrates. Data on accumulation in aquatic invertebrates and possible effects of species differences and parameters, such as sex, size, and moulting stage, will provide vital contributions to future PFAS monitoring.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00927.

Raw data, statistical and analytical methods, and other materials in figures and tables (PDF)

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The authors declare no competing financial interest.

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Supplementary Information

Bioaccumulation of fluorotelomer sulfonates and perfluoroalkyl acids in marine organisms living in aqueous film-forming foam (AFFF) impacted waters

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Sampling, sample preparation, and analysis

Sampling

Sediments and small crabs were sampled from a radius of 20 m from the emission point. Sediments were sampled using a plexiglas tube (7.5 cm diameter) which was pushed into the sea floor to a depth of approximately 10 cm. Water depth varied between stations. Approximate water depths at the different stations were: A - 3 m, B – 1 m, C – 1 m, D – 1 m, E – 5 m, F – 5 m, H – 3 m.

Fish traps used for catching edible crab and fish were placed approximately 200 m from shore, in deeper water compared to sampling of small crabs and sediment, to enable sampling (as it was not possible to catch fish within 20 m from the emission points). Approximate water depths at the different stations were: A - 15 m, B – 5 m, C – 7 m, D – 7 m, E – 20 m, F – 20 m, H – 30 m.

Analysis

The list of target PFAS analysed varied between media (see table S4). Sediments were analysed for 30 PFAS compounds, water was analysed for 19 PFAS compounds, passive samplers were analysed for 15 PFAS compounds and biota were analysed for 22 PFAS compounds.

Analysis of PFAS were carried out at the accredited laboratory Eurofins GfA Lab Service GmbH (in Germany), according to DIN EN ISO/IEC 17025:2005. All extracts were analysed using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS).

SorbiCell conceptual basis and deployment

Passive samplers were used to measure total concentrations in the fjord water (sea water) at all stations. The conceptual basis of the passive sampler, the SorbiCell, is previously described[1] and summarized here. Passive samplers can be used to determine time integrated average concentrations without the need for high resolution water sampling. The SorbiCell sampler is an advective passive flow through sampler with an entrance filter, a tailored sorbent material for the compounds of interest, and a tracer salt for the calculation of the volume of water which has passed through the sampler. The entrance filter allows both freely dissolved and the small particle bound pollutant fraction (< 100 µm) to be adsorbed by the sorbent material. Containers for collecting the water which has flown through the sampler were used as a control for the calculated water volumes (based on the tracer salt).

The tailored sorbent for PFAS analysis was purchased from Eurofins Environment Testing Norway AS. SorbiCell cartridges were pre-wetted with Millipore water prior to deployment, using a syringe. This was done in order to expel all air from the tracer salt and resin matrices, thereby establishing good capillary contact with the surrounding water. Passive samplers were deployed in the fjord, as close as

possible to the emission point, 0.5 meters below the water surface. Passive samplers were collected 3 weeks after deployment, the cartridges were placed in sealed tubes which were put in cooled insulated containers, and sent for chemical analysis.

Extraction of water samples

Water was extracted for PFAS following method DIN 38407-F42, involving solid-phase extraction (SPE) followed by basic methanol elution, evaporation, and re-dissolving in methanol. Thirteen internal standards were used ($^{13}C_2$-H_4PFOS, $^{13}C_4$-PFOS, $^{13}C_2$-PFDoA, $^{18}O_2$-PFHxS, $^{13}C_8$-PFOSA, ^{13}C2-M_2PFTeDA, $^{13}C_3$-M_3PFBS, $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_8$-PFOA, $^{13}C_5$-PFNA, 13C_2-PFDA, and $^{13}C_2$-PFUnA).

Extraction of sediments

PFAS concentrations in sediments were quantified using method DIN 38414-S14, involving methanol or acetonitrile, ultrasonic extraction with a multi-step solvent clean-up, using SPE.

Extraction of passive samplers (SorbiCell)

SorbiCell were analysed for PFAS by extracting the sorbent using methanol.

Extraction of biotic tissue

Approximately 1.5 g material (0.92 g – 1.64 g tissue from crabs, snails and fish muscle, and 0.18 g-0.91 g fish liver) were extracted for PFAS analysis. Samples were freeze dried and 18 surrogate standards (^{13}C-PFOS, $^{13}C_2$-PFDoA, $^{18}0_2$-PFHxS, $^{18}0_2$-PFHxS, $^{13}C_8$-PFOSA, $^{13}C_2$-PFTeDA, ^{13}C-PFBS, ^{13}C-PFBS, $^{13}C_4$-PFHpA, $^{13}C_5$-PFPeA, $^{13}C_2$-6:2FTS, $^{13}C_2$-6:2FTS, $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_8$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, and $^{13}C_2$-PFUnA) were added before extraction with methanol in an ultrasonic bath. After vaporization, acetonitrile and hexane were added for solvent exchange, and the acetonitrile phase was isolated and cleaned up. Following this the acetonitrile was vaporized and dissolved in methanol. $^{13}C_4$-PFOA was used as internal (injection) standard. The LOQ was calculated based on sample intake weight. For results below the LOQ, the method LOQ was divided by the weight of sample intake in order to get the sample specific LOQ (raw data, see table S5). For data treatment of results below the LOQ, half the LOQ was used.

Data treatment and statistics

Biological parameters

Concentrations (C) in whole fish (µg/kg) were calculated using the weight of the whole fish (kg), the liver weight (kg), and the concentrations in liver and remaining tissue (µg/kg):

$$C\ whole\ fish\ (\mu g/kg) = \frac{(C\ remaining\ tissue\ (\mu g/kg)\ x\ weight\ remaining\ tissue\ (kg)) + (C\ liver\ (\mu g/kg)\ x\ weight\ liver\ (kg))}{weight\ whole\ fish\ (kg)}$$

Fulton's condition factor (K):

$$K = \frac{Whole\ body\ weight\ (g)}{Length\ (cm)^3} \times 100$$

Liver Somatic Index (LSI):

$$LSI = \frac{Liver\ weight\ (g)}{Total\ body\ weight\ (g)} \times 100$$

Statistical methods

Data handling was performed in Microsoft Excel 2013. Statistical analysis was carried out using R version 3.4.2.[2] Concentrations below the LOQ are treated as half the LOQ. The significance level (p) was set to 0.05 ($p \leq 0.05$).

PFOS concentrations in cod liver and whole fish were not normally distributed according to the Shapiro-Wilk w-test (function: shapiro.test). Some individuals had a considerably higher PFAS body burden compared to the general level, causing a positive skew in the dataset. Therefore, the non-parametric unpaired Wilcoxon Test/Mann–Whitney U test (function: wilcox.test) was used to test differences between PFOS concentrations in cod caught near the Air Station and cod caught at the Reference Station. Similarly, several groups in the dataset for the proportional levels of 6:2 FTS were positively skewed, hence significance testing was performed using the non-parametric Kruskal-Wallis test and Bonferroni correction (package: agricolae[4], functions: shapiro.test, kruskal.test, kruskal).

Potential trends between length, weight, Fulton's condition factor (K), or liver somatic index and Σ_{22} PFAS were evaluated using Spearman's rank correlation coefficient (Spearman's rho) (function: cor.test).

Differences in PFAS profiles between different organisms and tissues were evaluated using Principal Components analysis (PCA) (packages factoextra[5] and FactoMineR[6], functions: prcomp, fviz_pca) in combination with the multivariate PERMANOVA tool followed by Bonferroni correction (package vegan[3], functions: adonis, pairwise.adonis).

Supplementary tables

Table S1 Sampling time for storm water at the different stations.

Station	June 2015	January 2016	February 2016	Mars 2016	April 2016	May 2016	September 2016
A				X	X	X	
B	X	X	X		X	X	
C				X	X	X	
D	X	X	X		X	X	
E	X	X	X		X	X	
F						X[1]	X[1]
G				X	X	X	
H	X	X	X		X	X	
Ref.							

[1] *Sampled soil leachate water*

Table S2 Total number of analysed samples of snails, crabs and fish at each station

Station	A	B	C	D	E	F	G	H	Ref.
Carcinus maenas (whole organisms)	Mixed sample (n = 8)	1	Mixed sample (n = 4)	Mixed sample (n = 11)	n.f.	Mixed sample (n = 2)	n.f.	Mixed sample (n = 4)	Mixed sample (n = 4)
Hyas araneus (whole organisms)	Mixed sample (n = 2)	Mixed sample (n = 1)	Mixed sample (n = 5)	n.f.	Mixed sample (n = 7)	Mixed sample (n = 6)	n.f.	Mixed sample (n = 1)	Mixed sample (n = 4)
Cancer pagurus (hepatopancreas)	n.f.	n.f.	n.f.	2	1	1	3	n.f.	2
Gadus morhua (liver)	4	3	1	5	2	2	5	3	6
Gadus morhua (whole fish[1])	4	3	1	5	2	2	5	3	6
Pleuronectes platessa (liver)	2	n.f.	n.f.	2	1	n.f.	n.f.	n.f.	n.f.
Pleuronectes platessa (whole fish[1])	2	n.f.	n.f.	2	1	n.f.	n.f.	n.f.	n.f.
Microstomus kitt (liver)	n.f.	1	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
Microstomus kitt (whole fish[1])	n.f.	1	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.

[1] *Calculated concentration from concentration in remaining tissue after removal of liver and stomach content combined with liver concentration. n.f. = not found at the specific station*

Table S3.1 Fish weight, fork length, Fulton's condition factor (K), liver weight, and liver somatic index

Organism	Sampling station	Sample name	Weight (g)	Length (cm)	Fulton's K	Weight liver (g)	Liver somatic index
Atlantic cod	A	A-T-1	1670	59.2	0.80	- [1]	- [1]
		A-T-3	570	40.6	0.85	1.50	0.27
		A-T-4	1520	50.3	1.19	15.21	1.03
		A-T-5	1630	57.3	0.87	- [1]	- [1]
		A-T-6	720	43.3	0.89	3.01	0.44
	B	B-T-1	130	26.8	0.68	0.24	0.20
		B-T-2	260	31	0.87	0.32	0.14
		B-T-3	250	31.2	0.82	0.76	0.36
	C	C-T-1	1120	54.7	0.68	3.03	0.31
	D	D-T-2	1230	51	0.93	8.06	0.79
		D-T-3	700	43.9	0.83	1.71	0.26
		D-T-4	450	37.7	0.84	0.81	0.19
		D-T-5	1030	49	0.88	1.26	0.14
		D-T-6	320	35.4	0.72	1.17	0.40
	E	E-T-1	2800	66.2	0.97	10.26	0.42
		E-T-2	350	34.4	0.86	0.19	0.05
		E-T-3	80	24.9	0.52	- [1]	- [1]
	F	F-T-1	190	29.5	0.74	1.62	0.96
		F-T-2	210	30.1	0.77	0.18	0.09
	G	G-T-1	2020	63.6	0.79	17.72	0.89
		G-T-2	1770	61.3	0.77	14.74	0.83
		G-T-3	1970	61.7	0.84	60.50	3.17
		G-T-4	1190	-	-	8.93	0.76
		G-T-5	1500	57.5	0.79	3.85	0.31
	H	H-T-1	8340	92.2	1.06	242.49	3.27
		H-T-2	990	45	1.09	8.82	0.93
		H-T-3	1130	49.8	0.91	8.66	0.81
	Reference station	Ref-T-1	1620	56.7	0.89	17.03	1.11
		Ref-T-2	1470	54.3	0.92	18.95	1.33
		Ref-T-3	2420	63.8	0.93	18.26	0.83
		Ref-T-4	2120	63.1	0.84	18.81	0.92
		Ref-T-5	1810	55.6	1.05	14.32	0.83
		Ref-T-6	3210	71.5	0.88	79.77	3.02
European plaice	A	A-R-1	530	36.8	1.06	1.09	0.21
		A-R-2	360	33	1.00	2.21	0.68
	D	D-R-1	760	39.8	1.21	2.05	0.31
		D-R-2	430	35.2	0.99	1.55	0.40
	E	E-R-1	420	33.9	1.08	2.71	0.70
Lemon sole	B	B-L-1	340	34.5	0.83	0.42	0.13

[1] Liver was lost and liver weight could not be measured

Table S3.2 Crab weight, carapace length and sex

Organism	Sampling station	Sample type	Sample name	Male	Female	Weight (g) [1]	Length (cm) [1]
Great spider crab	A	Mixed sample	A-PK	1	1	-	-
Green shore crab			A-SK	5	2	-	-
Great spider crab	B		B-PK	1	0	-	-
Green shore crab			B-SK	0	1	-	-
Great spider crab	C		C-PK	3	1	-	-
Green shore crab			C-SK	2	2	-	-
Green shore crab	D		D-SK	7	4	-	-
Great spider crab	E		E-PK	3	4	-	-
Great spider crab	F		F-PK	3	3	-	-
Green shore crab			F-SK	2	0	-	-
Great spider crab	H		H-PK	1	0	-	-
Green shore crab			H-SK	2	2	-	-
Great spider crab	Reference station		Ref-PK	3	1	-	-
Green shore crab			Ref-SK	2	2	-	-
Edible crab	D	Individual	D-TK-1	Male		526	15.1
			D-TK-2	Male		350	14.1
	E		E-TK-1	Male		-	-
	F		F-TK-1	Male		912	17.7
	G		G-TK-1	Female		329	13.4
			G-TK-2	Female		384	13.4
			G-TK-3	Male		232	11.2
	Reference station		Ref-TK-1	Male		371	13.5
			Ref-TK-2	Male		452	14.9

[1] Small crabs (Great spider crab and Green shore crab) were analysed as mixed samples of whole organisms, and individual length and weight were not measured.

Table S4. Analysed PFAS compounds. Compounds are grouped according to chemical structure. Abbreviations are given in round brackets ( ). SED = sediment, WAT = water, PAS = passive sampler, BIO = biota

Compound	SED	WAT	PAS	BIO
4:2 Fluorotelomer sulfonate (4:2 FTS)	X			X
6:2 Fluorotelomer sulfonate (6:2 FTS)	X	X	X	X
8:2 Fluorotelomer sulfonate (8:2 FTS)	X	X	X	X
Perfluorobutanoic acid (PFBA)	X	X	X	X
Perfluoropentanoic acid (PFPeA)	X	X	X	X
Perfluorohexanoic acid (PFHxA)	X	X	X	X
Perfluoroheptanoic acid (PFHpA)	X	X	X	X
Perfluorooctanoic acid (PFOA)	X	X	X	X
Perfluorononanoic acid (PFNA)	X	X	X	X
Perfluorodecanoic acid (PFDeA)	X	X	X	X
Perfluoroundecanoic acid (PFUnA)	X	X	X	X
Perfluorododecanoic acid (PFDoA)	X	X		X
Perfluorotridecanoic acid (PFTrDA)	X	X		X
Perfluorotetradecanoic acid (PFTA)	X	X		X
Perfluorohexadecanoic acid (PFHxDA)	X			
Perfluorobutane sulfonic acid (PFBS)	X	X	X	X
Perfluorohexane sulfonic acid (PFHxS)	X	X	X	X
Perfluoroheptane sulfonic acid (PFHpS)	X	X		X
Perfluorooctane sulfonic acid (PFOS)	X	X	X	X
Perfluorodecane sulfonic acid (PFDS)	X	X	X	X
N-ethylperfluorooctane sulfonamide (EtFOSA)	X			
N-ethylperfluorooctane sulfonamide acetic acid (EtFOSAA)	X			
N-ethylperfluorooctane sulfonamide ethanol (EtFOSE)	X			
N-methylperfluorooctane sulfonamide acetic acid (MeFOSAA)	X			
N-methylperfluorooctane sulfonamide ethanol (MeFOSE)	X			
N-methylperfluorooctane sulfonamide (MeFOSA)	X			
Perfluorooctane sulfonamide acetic acid (FOSAA)	X			
Perfluoro-3,7-dimethyl-octanoic acid (PF-3,7-DMOA)	X			X
Perfluorooctane sulfonamide (PFOSA)	X	X	X	X
7H dodecane fluoroheptanoic acid (HPFHpA)	X			X
Total number of PFAS	30	19	15	22

Table S5. Ratio of liver to whole fish (including liver) concentrations. Of the 22-PFAS analysed only compounds detected in both liver and in remaining whole fish are included. Numbers in brackets indicate the total number of individuals with concentrations above detection limit for each compound.

Species/compound		Median	Average	Standard error of mean (SEM)	Max	Min
Atlantic cod (*Gadus morhua*)						
FTS	8:2 FTS [2]	3.87	3.87	0.76	4.63	3.10
Short chained PFCA	PFBA [2]	1.50	1.50	0.09	1.58	1.41
Long chained PFCA	PFNA [19]	2.04	2.87	0.40	7.25	1.16
	PFDeA [19]	2.56	2.80	0.32	6.23	0.99
	PFUnA [26]	2.19	2.81	0.33	7.97	1.24
	PFDoA [4]	3.31	3.43	0.33	4.32	2.78
	PFTrA [21]	2.72	3.46	0.57	10.79	0.75
Long chained PFSA	PFHxS [1]	3.40	3.40	-	3.40	3.40
	PFOS [30]	2.91	3.54	0.35	9.95	1.52
	PFOSA [12]	3.47	4.88	1.19	14.65	0.80
European place (*Pleuronectes platessa*)						
Long chained PFCA	PFNA [4]	3.54	3.05	0.58	3.78	1.33
	PFDeA [4]	2.80	2.43	0.42	2.94	1.19
	PFUnA [5]	3.16	2.68	0.51	3.86	1.28
	PFTrA [4]	2.54	2.57	0.51	3.64	1.55
Long chained PFSA	PFOS [5]	3.02	2.46	0.45	3.38	0.96
Lemon sole (*Microstomus kitt*)						
Long chained PFCA	PFOA [1]	1.93	1.93	-	1.93	1.93
	PFNA [1]	1.95	1.95	-	1.95	1.95
Long chained PFSA	PFOS [1]	2.40	2.40	-	2.40	2.40

Table S6. Relative fraction of analysed PFAS compounds in biota from the Air Station (stations A-H) given as a % of sum 22-PFAS (in bold). Concentrations below the LOQ are treated as half the LOQ. Standard error of means (SEM) are given in the row below (not for Lemon sole where n=1) .

	Atlantic cod *remaining tissue*	**Atlantic cod** *liver*	**European place** *remaining tissue*	**European place** *liver*	**Lemon sole** *remaining tissue*	**Lemon sole** *liver*	**Snail (Patellidae)** *Soft tissue*	**Green shore crab** *whole organisms*	**Great spider crab** *whole organisms*	**Edible crab** *hepatopancreas*
4:2 FTS	**1.81**	**2.71**	**1.69**	**2.04**	**4.53**	**4.97**	**1.80**	**1.58**	**1.81**	**0.74**
	0.16	0.22	0.38	0.33			0.42	0.66	0.51	0.16
6:2 FTS	**1.48**	**2.03**	**1.26**	**6.92**	**3.40**	**3.73**	**12.84**	**21.81**	**25.14**	**24.34**
	0.13	0.17	0.29	5.43			5.15	10.05	10.98	10.32
8:2 FTS	**2.37**	**3.95**	**1.69**	**6.49**	**4.53**	**4.97**	**6.58**	**1.75**	**1.86**	**4.40**
	0.26	0.53	0.38	3.43			1.50	0.62	0.49	2.20
PFBA	**2.39**	**1.78**	**0.84**	**3.09**	**2.27**	**2.48**	**0.91**	**0.79**	**0.90**	**1.36**
	0.86	0.30	0.19	1.47			0.21	0.33	0.26	0.48
PFPeA	**0.91**	**1.43**	**1.12**	**1.02**	**2.27**	**2.48**	**0.93**	**0.79**	**0.90**	**0.48**
	0.08	0.12	0.42	0.17			0.20	0.33	0.26	0.10
PFHxA	**0.91**	**1.35**	**0.84**	**1.02**	**2.27**	**2.48**	**0.91**	**0.79**	**0.90**	**0.37**
	0.08	0.11	0.19	0.17			0.21	0.33	0.26	0.08
PFHpA	**0.91**	**1.35**	**0.84**	**1.02**	**2.27**	**2.48**	**0.90**	**0.79**	**0.90**	**0.37**
	0.08	0.11	0.19	0.17			0.21	0.33	0.26	0.08
PFOA	**1.30**	**1.48**	**0.98**	**1.02**	**6.91**	**5.27**	**0.93**	**0.82**	**0.91**	**6.92**
	0.18	0.14	0.19	0.17			0.20	0.32	0.25	2.72
PFNA	**5.14**	**3.85**	**12.76**	**12.40**	**11.96**	**9.24**	**0.96**	**0.83**	**1.31**	**5.47**
	0.44	0.46	3.07	3.76			0.20	0.32	0.38	1.33
PFDeA	**4.57**	**3.57**	**8.65**	**6.54**	**2.27**	**2.48**	**0.92**	**1.04**	**1.53**	**2.65**
	0.40	0.46	1.53	1.74			0.21	0.28	0.43	0.67
PFUnA	**8.09**	**6.13**	**7.90**	**6.74**	**2.27**	**2.48**	**0.90**	**1.61**	**2.11**	**4.65**
	0.84	0.63	0.58	1.26			0.21	0.36	0.62	1.42
PFDoA	**1.58**	**1.50**	**1.05**	**1.02**	**2.27**	**2.48**	**0.90**	**1.25**	**0.90**	**1.18**
	0.20	0.11	0.20	0.17			0.21	0.26	0.26	0.43
PFTrA	**6.14**	**5.36**	**3.59**	**2.51**	**2.27**	**2.48**	**1.17**	**3.38**	**2.65**	**3.86**
	0.66	0.95	0.75	0.32			0.24	0.73	1.02	1.04
PFTA	**0.99**	**1.35**	**0.84**	**1.02**	**2.27**	**2.48**	**0.90**	**0.98**	**0.90**	**1.11**
	0.09	0.11	0.19	0.17			0.21	0.29	0.26	0.34
PFBS	**1.36**	**2.03**	**1.26**	**1.53**	**3.40**	**3.73**	**1.35**	**1.19**	**1.35**	**0.80**
	0.12	0.17	0.29	0.25			0.32	0.50	0.38	0.19
PFHxS	**1.51**	**2.08**	**1.72**	**1.53**	**3.40**	**3.73**	**1.36**	**2.28**	**1.53**	**3.22**
	0.10	0.15	0.66	0.25			0.31	0.44	0.31	0.58
PFHpS	**1.39**	**2.03**	**1.26**	**1.53**	**3.40**	**3.73**	**1.35**	**1.26**	**1.45**	**0.56**
	0.11	0.17	0.29	0.25			0.32	0.47	0.34	0.12
PFOS	**36.91**	**37.56**	**45.61**	**34.59**	**23.30**	**22.13**	**52.16**	**47.29**	**38.75**	**33.70**
	2.72	2.88	1.59	5.32			6.51	9.40	4.50	4.61
PFDS	**1.36**	**2.03**	**1.26**	**1.53**	**3.40**	**3.73**	**1.35**	**1.19**	**1.35**	**0.56**
	0.12	0.17	0.29	0.25			0.32	0.50	0.38	0.12
PF-3,7-DMOA	**1.81**	**2.97**	**1.69**	**2.04**	**4.53**	**4.97**	**1.80**	**1.58**	**1.81**	**0.81**
	0.16	0.33	0.38	0.33			0.42	0.66	0.51	0.13
PFOSA	**15.25**	**10.74**	**1.44**	**2.38**	**2.27**	**2.48**	**7.27**	**5.41**	**9.22**	**1.71**
	2.94	3.01	0.53	1.40			1.87	1.29	2.81	0.78
HPFHpA	**1.81**	**2.71**	**1.69**	**2.04**	**4.53**	**4.97**	**1.80**	**1.59**	**1.81**	**0.74**
	0.16	0.22	0.38	0.33			0.42	0.67	0.51	0.16

Table S7. Concentrations of 22-PFAS detected in biota. Concentrations below LOQ are denoted as < followed by the sample specific LOQ

Tissue		**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**
Sample name		**Snail A**	**Snail B**	**Snail B - 2**	**Snail C**	**Snail C - 2**	**Snail D**
Comment		Station A	Station B	Station B: 30 - 100 m from emission source[1]	Station C	Station C: 20 - 100 m from emission source[1]	Station D
4:2 FTS	µg/kg	< 0.0858	< 0.0849	< 0.0811	< 0.0848	< 0.0794	< 0.0977
6:2 FTS	µg/kg	< 0.0643	0.13	< 0.0608	< 0.0636	0.142	< 0.0733
8:2 FTS	µg/kg	0.0874	0.449	0.245	< 0.0848	< 0.0794	< 0.0977
PFBA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFPeA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFHxA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFHpA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFOA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFNA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFDeA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFUnA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFDoA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFTrA	µg/kg	< 0.0429	0.0666	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFTA	µg/kg	< 0.0429	< 0.0425	< 0.0406	< 0.0424	< 0.0397	< 0.0488
PFBS	µg/kg	< 0.0643	< 0.0637	< 0.0608	< 0.0636	< 0.0595	< 0.0733
PFHxS	µg/kg	< 0.0643	< 0.0637	< 0.0608	< 0.0636	< 0.0595	< 0.0733
PFHpS	µg/kg	< 0.0643	< 0.0637	< 0.0608	< 0.0636	< 0.0595	< 0.0733
PFOS	µg/kg	7.37	1.23	0.361	0.635	0.476	2.57
PFDS	µg/kg	< 0.0643	< 0.0637	< 0.0608	< 0.0636	< 0.0595	< 0.0733
PF-3.7-DMOA	µg/kg	< 0.0858	< 0.0849	< 0.0811	< 0.0848	< 0.0794	< 0.0977
PFOSA	µg/kg	0.636	0.274	0.438	0.0698	0.0735	0.129
HPFHpA	µg/kg	< 0.0858	< 0.0849	< 0.0811	< 0.0848	< 0.0794	< 0.0977
Sum PFAS excl. LOQ	µg/kg	8.1	2.15	1.04	0.705	0.692	2.7

[1] In four stations (B, C, E, and F), an additional sample of snails was collected approximately 100 m from the emission source

Tissue		**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Snail (*Patellidae*)**
Sample name		**Snail E**	**Snail E - 2**	**Snail F**	**Snail F – 2**	**Snail G**	**Snail H**
Comment		Station E: Stream outlet	Station E: 140 m from emission source[1]	Station F: soil leachate	Station F: 90 m east of emission source[1]	Station G	Station H: south side
4:2 FTS	µg/kg	< 0.0816	< 0.0905	< 0.0896	< 0.0988	< 0.0727	< 0.0909
6:2 FTS	µg/kg	3.68	0.926	56.3	1.11	0.146	< 0.0682
8:2 FTS	µg/kg	0.634	0.352	8.29	0.447	< 0.0727	< 0.0909
PFBA	µg/kg	< 0.0408	< 0.0452	0.136	< 0.0494	< 0.0364	< 0.0455
PFPeA	µg/kg	0.0632	< 0.0452	0.177	< 0.0494	< 0.0364	< 0.0455
PFHxA	µg/kg	< 0.0408	< 0.0452	0.0832	< 0.0494	< 0.0364	< 0.0455
PFHpA	µg/kg	< 0.0408	< 0.0452	0.0562	< 0.0494	< 0.0364	< 0.0455
PFOA	µg/kg	0.0475	< 0.0452	0.234	< 0.0494	< 0.0364	< 0.0455
PFNA	µg/kg	0.0647	< 0.0452	0.434	< 0.0494	< 0.0364	< 0.0455
PFDeA	µg/kg	0.0429	< 0.0452	0.135	< 0.0494	< 0.0364	< 0.0455
PFUnA	µg/kg	< 0.0408	< 0.0452	0.0571	< 0.0494	< 0.0364	< 0.0455
PFDoA	µg/kg	< 0.0408	< 0.0452	< 0.0448	< 0.0494	< 0.0364	< 0.0455
PFTrA	µg/kg	< 0.0408	0.0479	0.094	0.0827	< 0.0364	< 0.0455
PFTA	µg/kg	< 0.0408	< 0.0452	< 0.0448	< 0.0494	< 0.0364	< 0.0455
PFBS	µg/kg	< 0.0612	< 0.0679	< 0.0672	< 0.0741	< 0.0545	< 0.0682
PFHxS	µg/kg	< 0.0612	< 0.0679	0.196	< 0.0741	< 0.0545	< 0.0682
PFHpS	µg/kg	< 0.0612	< 0.0679	< 0.0672	< 0.0741	< 0.0545	< 0.0682
PFOS	µg/kg	14.3	3.37	12.6	2.04	4.21	0.19
PFDS	µg/kg	< 0.0612	< 0.0679	< 0.0672	< 0.0741	< 0.0545	< 0.0682
PF-3.7-DMOA	µg/kg	< 0.0816	< 0.0905	< 0.0896	< 0.0988	< 0.0727	< 0.0909
PFOSA	µg/kg	0.878	0.311	2.32	0.253	0.073	0.0683
HPFHpA	µg/kg	< 0.0816	< 0.0905	< 0.0896	< 0.0988	< 0.0727	< 0.0909
Sum PFAS excl. LOQ	µg/kg	19.7	5.01	81.1	3.94	4.43	0.258

[1] In four stations (B, C, E, and F), an additional sample of snails were sampled approximately 100 m from the emission source

Tissue		**Snail (*Patellidae*)**	**Snail (*Patellidae*)**	**Green shore crab (whole)**	**Green shore crab (whole)**	**Green shore crab (whole)**	**Green shore crab (whole)**	**Green shore crab (whole)**
Sample name		**Snail H - 2**	**Snail Ref.**	**A-SK**	**B-SK**	**C-SK**	**D-SK**	**F-SK**
Comment		Station H: north side	Reference station	Station A	Station B	Station C	Station D	Station F
4:2 FTS	µg/kg	< 0.0684	< 0.0734	< 0.219	< 0.108	< 0.124	< 0.153	< 0.220
6:2 FTS	µg/kg	0.121	< 0.0551	0.18	3.35	1.46	0.397	12.3
8:2 FTS	µg/kg	0.115	< 0.0734	< 0.219	0.273	< 0.124	< 0.153	< 0.220
PFBA	µg/kg	< 0.0342	< 0.0367	< 0.109	< 0.0538	< 0.0621	< 0.0766	< 0.110
PFPeA	µg/kg	< 0.0342	< 0.0367	< 0.109	< 0.0538	< 0.0621	< 0.0766	< 0.110
PFHxA	µg/kg	< 0.0342	< 0.0367	< 0.109	< 0.0538	< 0.0621	< 0.0766	< 0.110
PFHpA	µg/kg	< 0.0342	< 0.0367	< 0.109	< 0.0538	< 0.0621	< 0.0766	< 0.110
PFOA	µg/kg	< 0.0342	< 0.0367	< 0.109	0.071	< 0.0621	< 0.0766	< 0.110
PFNA	µg/kg	< 0.0342	< 0.0367	< 0.109	0.0739	< 0.0621	< 0.0766	< 0.110
PFDeA	µg/kg	< 0.0342	< 0.0367	< 0.109	0.106	0.0737	0.114	< 0.110
PFUnA	µg/kg	< 0.0342	< 0.0367	< 0.109	0.298	0.151	0.292	< 0.110
PFDoA	µg/kg	< 0.0342	< 0.0367	< 0.109	0.289	0.0752	0.152	< 0.110
PFTrA	µg/kg	< 0.0342	0.055	0.152	0.628	0.224	0.577	0.148
PFTA	µg/kg	< 0.0342	< 0.0367	< 0.109	0.188	< 0.0621	0.078	< 0.110
PFBS	µg/kg	< 0.0513	< 0.0551	< 0.164	< 0.0807	< 0.0931	< 0.115	< 0.165
PFHxS	µg/kg	< 0.0513	< 0.0551	< 0.164	0.709	0.307	0.162	< 0.165
PFHpS	µg/kg	< 0.0513	< 0.0551	< 0.164	0.137	< 0.0931	< 0.115	< 0.165
PFOS	µg/kg	0.805	0.0754	1.6	13.6	7.49	6.55	3.26
PFDS	µg/kg	< 0.0513	< 0.0551	< 0.164	< 0.0807	< 0.0931	< 0.115	< 0.165
PF-3.7-DMOA	µg/kg	< 0.0684	< 0.0734	< 0.219	< 0.108	< 0.124	< 0.153	< 0.220
PFOSA	µg/kg	0.0717	< 0.0367	0.309	1.59	0.28	0.863	0.529
HPFHpA	µg/kg	< 0.0684	< 0.0734	< 0.219	< 0.108	< 0.124	< 0.153	< 0.231
Sum PFAS excl. LOQ	µg/kg	1.11	0.13	2.24	21.3	10.1	9.19	16.2

Tissue		Green shore crab (whole)	Green shore crab (whole)	Great spider crab (whole)	Great spider crab (whole)	Great spider crab (whole)	Great spider crab (whole)	Great spider crab (whole)
Sample name		**H-SK**	**Ref-SK**	**A-PK**	**B-PK-1**	**C-PK**	**C-PK-2**	**E-PK**
Comment		Station H	Reference station	Station A	Station B	Station C	Station C: fish trap	Station E: 140 m from emission source
4:2 FTS	µg/kg	< 0.190	< 0.0994	< 0.199	< 0.107	< 0.141	< 0.112	< 0.142
6:2 FTS	µg/kg	0.515	< 0.0745	< 0.149	0.128	0.121	0.211	5.57
8:2 FTS	µg/kg	< 0.190	< 0.0994	< 0.199	< 0.107	< 0.141	< 0.112	< 0.142
PFBA	µg/kg	< 0.0952	< 0.0497	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFPeA	µg/kg	< 0.0952	< 0.0497	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFHxA	µg/kg	< 0.0952	< 0.0497	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFHpA	µg/kg	< 0.0952	< 0.0497	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFOA	µg/kg	< 0.0952	0.0525	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFNA	µg/kg	< 0.0952	0.0552	< 0.0996	< 0.0535	< 0.0703	0.201	< 0.0711
PFDeA	µg/kg	< 0.0952	0.0728	< 0.0996	0.0612	< 0.0703	0.222	< 0.0711
PFUnA	µg/kg	< 0.0952	0.177	< 0.0996	0.137	< 0.0703	0.211	0.0717
PFDoA	µg/kg	< 0.0952	0.0814	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFTrA	µg/kg	0.0989	0.28	< 0.0996	0.225	< 0.0703	0.224	0.0903
PFTA	µg/kg	< 0.0952	< 0.0497	< 0.0996	< 0.0535	< 0.0703	< 0.0559	< 0.0711
PFBS	µg/kg	< 0.143	< 0.0745	< 0.149	< 0.0803	< 0.105	< 0.0839	< 0.107
PFHxS	µg/kg	< 0.143	< 0.0745	< 0.149	< 0.0803	< 0.105	< 0.0839	0.124
PFHpS	µg/kg	< 0.143	< 0.0745	< 0.149	< 0.0803	< 0.105	< 0.0839	< 0.107
PFOS	µg/kg	0.478	0.399	1.26	0.964	0.905	3.79	3.21
PFDS	µg/kg	< 0.143	< 0.0745	< 0.149	< 0.0803	< 0.105	< 0.0839	< 0.107
PF-3.7-DMOA	µg/kg	< 0.190	< 0.0994	< 0.199	< 0.107	< 0.141	< 0.112	< 0.142
PFOSA	µg/kg	< 0.0952	< 0.0497	0.249	0.607	0.114	1.03	0.668
HPFHpA	µg/kg	< 0.192	< 0.0994	< 0.199	< 0.107	< 0.141	< 0.112	< 0.142
Sum PFAS excl. LOQ	µg/kg	1.09	1.12	1.51	2.12	1.14	5.89	9.73

Tissue		Great spider crab (whole)	Great spider crab (whole)	Great spider crab (whole)	Edible crab (Hepatopancreas)	Edible crab (Hepatopancreas)	Edible crab (Hepatopancreas)	Edible crab (Hepatopancreas)
Samplename		**F-PK**	**H-PK**	**Ref-PK**	**D-TK-1**	**D-TK-2**	**E-TK-1**	**F-TK-1**
Comment		Station F	Station H	Reference station	Station D:fish trap	Station D: fish trap	Station E: fish trap	Station F: fish trap
4:2 FTS	µg/kg	< 0.100	< 0.130	< 0.217	< 0.144	< 0.178	< 0.203	< 0.252
6:2 FTS	µg/kg	56.8	0.991	< 0.163	0.423	0.859	26.4	1.53
8:2 FTS	µg/kg	0.333	< 0.130	< 0.217	0.221	0.508	0.551	< 0.252
PFBA	µg/kg	< 0.0502	< 0.0650	< 0.108	0.0857	0.108	0.115	0.165
PFPeA	µg/kg	< 0.0502	< 0.0650	< 0.108	0.0726	< 0.0892	< 0.101	< 0.126
PFHxA	µg/kg	< 0.0502	< 0.0650	< 0.108	< 0.0718	< 0.0892	< 0.101	< 0.126
PFHpA	µg/kg	< 0.0502	< 0.0650	< 0.108	< 0.0718	< 0.0892	< 0.101	< 0.126
PFOA	µg/kg	0.0715	< 0.0650	< 0.108	0.298	0.243	0.791	1.76
PFNA	µg/kg	0.143	< 0.0650	< 0.108	0.571	0.502	0.344	1.05
PFDeA	µg/kg	0.103	< 0.0650	< 0.108	0.382	0.446	0.203	0.33
PFUnA	µg/kg	0.1	0.067	< 0.108	0.593	1.03	0.284	0.496
PFDoA	µg/kg	< 0.0502	< 0.0650	< 0.108	0.128	0.305	< 0.101	0.144
PFTrA	µg/kg	0.129	0.0716	0.159	0.436	0.734	0.213	0.435
PFTA	µg/kg	< 0.0502	< 0.0650	< 0.108	0.178	0.207	0.112	0.141
PFBS	µg/kg	< 0.0753	< 0.0975	< 0.163	< 0.108	< 0.134	< 0.152	< 0.189
PFHxS	µg/kg	0.452	< 0.0975	< 0.163	0.218	0.475	0.434	0.465
PFHpS	µg/kg	0.543	< 0.0975	< 0.163	< 0.108	< 0.134	< 0.152	< 0.189
PFOS	µg/kg	16.2	1.13	0.344	4.04	3.84	5.45	3.52
PFDS	µg/kg	< 0.0753	< 0.0975	< 0.163	< 0.108	< 0.134	< 0.152	< 0.189
PF-3.7-DMOA	µg/kg	< 0.100	< 0.130	< 0.217	< 0.144	< 0.178	< 0.203	< 0.252
PFOSA	µg/kg	0.588	0.147	0.26	0.474	0.117	0.228	< 0.126
HPFHpA	µg/kg	< 0.100	< 0.130	< 0.217	< 0.144	< 0.178	< 0.203	< 0.252
Sum PFAS excl. LOQ	µg/kg	75.5	2.4	0.764	8.12	9.37	35.1	10

Tissue		Edible crab (Hepatopancreas)	Edible crab (Hepatopancreas)	Edible crab (Hepatopancreas)	Edible crab (Hepatopancreas)	Remaining tissue	Liver	Remaining tissue
Sample name		**G-TK-2**	**G-TK-3**	**Ref-TK-1**	**Ref-TK-2**	**A-T-1**	**A-T-1**	**A-T-3**
Comment		Station G: fish trap	Station G: fish trap	Reference station fish trap	Reference station fish trap	Station A Atlantic cod	Station A Atlantic cod	Station A Atlantic cod
4:2 FTS	µg/kg	< 0.237	< 0.173	< 0.0947	< 0.121	< 0.110	< 0.279	< 0.0990
6:2 FTS	µg/kg	2.06	10.7	0.308	< 0.0956	< 0.0821	< 0.209	< 0.0742
8:2 FTS	µg/kg	< 0.237	6.15	0.386	< 0.121	< 0.110	< 0.279	< 0.0990
PFBA	µg/kg	0.388	0.266	0.338	< 0.0778	< 0.0548	< 0.140	0.287
PFPeA	µg/kg	< 0.118	0.139	< 0.0474	< 0.0604	< 0.0548	< 0.140	< 0.0495
PFHxA	µg/kg	< 0.118	< 0.0864	< 0.0474	< 0.0604	< 0.0548	< 0.140	< 0.0495
PFHpA	µg/kg	< 0.118	< 0.0864	0.0998	< 0.0604	< 0.0548	< 0.140	< 0.0495
PFOA	µg/kg	1.63	1	0.648	0.623	< 0.0548	< 0.140	< 0.0495
PFNA	µg/kg	0.873	1.08	0.733	0.819	0.109	0.279	0.0521
PFDeA	µg/kg	0.242	0.484	0.416	0.29	0.0736	0.179	< 0.0495
PFUnA	µg/kg	0.356	0.851	0.507	0.42	0.155	0.342	0.0643
PFDoA	µg/kg	< 0.118	0.23	0.129	0.0979	< 0.0548	< 0.140	< 0.0495
PFTrA	µg/kg	0.532	0.511	0.97	0.442	0.161	1.08	0.082
PFTA	µg/kg	< 0.118	0.152	0.173	0.0799	< 0.0548	< 0.140	< 0.0495
PFBS	µg/kg	< 0.178	0.67	< 0.0711	< 0.0906	< 0.0821	< 0.209	< 0.0742
PFHxS	µg/kg	0.469	0.924	0.416	0.569	< 0.0821	< 0.209	< 0.0742
PFHpS	µg/kg	< 0.178	< 0.130	< 0.0711	< 0.0906	< 0.0821	< 0.209	< 0.0742
PFOS	µg/kg	3.05	17	4.38	5.91	0.483	1.56	0.28
PFDS	µg/kg	< 0.178	< 0.130	< 0.0711	< 0.0906	< 0.0821	< 0.209	< 0.0742
PF-3.7-DMOA	µg/kg	< 0.237	0.249	0.188	< 0.121	< 0.110	< 0.279	< 0.0990
PFOSA	µg/kg	0.16	0.357	0.356	0.197	0.132	< 0.140	0.517
HPFHpA	µg/kg	< 0.237	< 0.173	< 0.0947	< 0.121	< 0.110	< 0.279	< 0.0990
Sum PFAS excl. LOQ	µg/kg	9.75	40.7	10.1	9.45	1.11	3.44	1.28

Tissue		Liver	Remaining tissue	Liver	Remaining tissue	Liver	Remaining tissue	Liver
Sample name		**A-T-3**	**A-T-4**	**A-T-4**	**A-T-5**	**A-T-5**	**A-T-6**	**A-T-6**
Comment		Station A Atlantic cod	Station A Atlantic cod	Station A Atlantic cod	Station A Atlantic cod	Station A Atlantic cod	Station A Atlantic cod	Station A Atlantic cod
4:2 FTS	µg/kg	< 0.476	< 0.0876	< 0.411	< 0.0997	< 0.426	< 0.102	< 0.411
6:2 FTS	µg/kg	< 0.357	< 0.0657	< 0.308	< 0.0748	< 0.319	< 0.0768	< 0.308
8:2 FTS	µg/kg	< 0.476	< 0.0876	< 0.411	< 0.0997	< 0.426	< 0.102	< 0.411
PFBA	µg/kg	< 0.238	< 0.0438	< 0.205	< 0.0499	< 0.213	0.131	0.208
PFPeA	µg/kg	< 0.238	< 0.0438	< 0.205	< 0.0499	< 0.213	< 0.0512	< 0.205
PFHxA	µg/kg	< 0.238	< 0.0438	< 0.205	< 0.0499	< 0.213	< 0.0512	< 0.205
PFHpA	µg/kg	< 0.238	< 0.0438	< 0.205	< 0.0499	< 0.213	< 0.0512	< 0.205
PFOA	µg/kg	< 0.238	< 0.0438	< 0.205	< 0.0499	< 0.213	< 0.0512	< 0.205
PFNA	µg/kg	< 0.238	0.0652	< 0.205	0.101	< 0.213	0.0769	0.308
PFDeA	µg/kg	< 0.238	0.0705	0.217	0.119	< 0.213	0.0777	0.353
PFUnA	µg/kg	0.335	0.156	0.457	0.246	0.253	0.176	0.874
PFDoA	µg/kg	< 0.238	< 0.0438	< 0.205	0.0646	< 0.213	< 0.0512	< 0.205
PFTrA	µg/kg	0.559	0.133	0.267	0.209	0.221	0.137	0.61
PFTA	µg/kg	< 0.238	< 0.0438	< 0.205	< 0.0499	< 0.213	< 0.0512	< 0.205
PFBS	µg/kg	< 0.357	< 0.0657	< 0.308	< 0.0748	< 0.319	< 0.0768	< 0.308
PFHxS	µg/kg	< 0.357	< 0.0657	< 0.308	< 0.0748	< 0.319	< 0.0768	< 0.308
PFHpS	µg/kg	< 0.357	< 0.0657	< 0.308	< 0.0748	< 0.319	< 0.0768	< 0.308
PFOS	µg/kg	1.85	0.53	2.13	0.383	0.56	0.413	2.5
PFDS	µg/kg	< 0.357	< 0.0657	< 0.308	< 0.0748	< 0.319	< 0.0768	< 0.308
PF-3.7-DMOA	µg/kg	< 0.476	< 0.0876	< 0.411	< 0.0997	< 0.426	< 0.102	0.7
PFOSA	µg/kg	1.56	0.207	< 0.205	0.149	< 0.213	0.27	< 0.205
HPFHpA	µg/kg	< 0.476	< 0.0876	< 0.411	< 0.0997	< 0.426	< 0.102	< 0.411
Sum PFAS excl. LOQ	µg/kg	4.31	1.16	3.07	1.27	1.03	1.28	5.55

Tissue		**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**
Sample name		**B-T-1**	**B-T-1**	**B-T-2**	**B-T-2**	**B-T-3**	**B-T-3**	**C-T-1**
Comment		Station B Atlantic cod	Station B Atlantic cod	Station B Atlantic cod	Station B Atlantic cod	Station B Atlantic cod	Station B Atlantic cod	Station C Atlantic cod
4:2 FTS	µg/kg	< 0.0887	< 0.628	< 0.106	< 0.422	< 0.0962	< 0.352	< 0.0897
6:2 FTS	µg/kg	< 0.0665	< 0.471	< 0.0796	< 0.317	< 0.0722	< 0.264	< 0.0673
8:2 FTS	µg/kg	< 0.0887	< 0.628	< 0.106	< 0.422	< 0.0962	0.366	< 0.0897
PFBA	µg/kg	< 0.0444	< 0.314	0.426	0.6	< 0.0481	< 0.176	< 0.0449
PFPeA	µg/kg	< 0.0444	< 0.314	< 0.0531	< 0.211	< 0.0481	< 0.176	< 0.0449
PFHxA	µg/kg	< 0.0444	< 0.314	< 0.0531	< 0.211	< 0.0481	< 0.176	< 0.0449
PFHpA	µg/kg	< 0.0444	< 0.314	< 0.0531	< 0.211	< 0.0481	< 0.176	< 0.0449
PFOA	µg/kg	< 0.0444	< 0.314	0.0727	< 0.211	0.051	< 0.176	0.0472
PFNA	µg/kg	0.0815	0.315	0.218	0.253	0.131	0.219	0.129
PFDeA	µg/kg	0.0833	< 0.314	0.12	0.308	0.126	0.206	0.0957
PFUnA	µg/kg	0.196	0.883	0.169	0.604	0.184	0.415	0.168
PFDoA	µg/kg	0.0734	0.319	< 0.0531	< 0.211	< 0.0481	< 0.176	< 0.0449
PFTrA	µg/kg	0.408	1.16	0.146	0.58	0.144	0.502	0.177
PFTA	µg/kg	0.0607	< 0.314	< 0.0531	< 0.211	< 0.0481	< 0.176	< 0.0449
PFBS	µg/kg	< 0.0665	< 0.471	< 0.0796	< 0.317	< 0.0722	< 0.264	< 0.0673
PFHxS	µg/kg	< 0.0665	< 0.471	< 0.0796	< 0.317	< 0.0722	< 0.264	< 0.0673
PFHpS	µg/kg	< 0.0665	< 0.471	< 0.0796	< 0.317	< 0.0722	< 0.264	< 0.0673
PFOS	µg/kg	1.44	7	0.677	1.49	1.15	2.59	0.422
PFDS	µg/kg	< 0.0665	< 0.471	< 0.0796	< 0.317	< 0.0722	< 0.264	< 0.0673
PF-3.7-DMOA	µg/kg	< 0.0887	< 0.628	< 0.106	< 0.422	< 0.0962	< 0.352	< 0.0897
PFOSA	µg/kg	0.908	3.2	< 0.0531	1.65	2	< 0.176	< 0.0449
HPFHpA	µg/kg	< 0.0887	< 0.628	< 0.106	< 0.422	< 0.0962	< 0.352	< 0.0897
Sum PFAS excl. LOQ	µg/kg	3.25	12.9	1.83	5.49	3.78	4.3	1.04

Tissue		Liver	Remaining tissue	Liver	Remaining tissue	Liver	Remaining tissue	Liver
Sample name		**C-T-1**	**D-T-2**	**D-T-2**	**D-T-3**	**D-T-3**	**D-T-4**	**D-T-4**
Comment		Station C Atlantic cod	Station D Atlantic cod	Station D Atlantic cod	Station D Atlantic cod	Station D Atlantic cod	Station D Atlantic cod	Station D Atlantic cod
4:2 FTS	µg/kg	< 0.480	< 0.107	< 0.459	< 0.0944	< 0.481	< 0.0922	< 0.476
6:2 FTS	µg/kg	< 0.360	< 0.0801	< 0.344	< 0.0708	< 0.361	< 0.0692	< 0.357
8:2 FTS	µg/kg	< 0.480	< 0.107	0.57	< 0.0944	< 0.481	0.0966	< 0.476
PFBA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFPeA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFHxA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFHpA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFOA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFNA	µg/kg	0.78	0.0921	< 0.229	0.0841	< 0.241	0.258	0.597
PFDeA	µg/kg	0.534	0.109	< 0.229	0.104	< 0.241	0.202	0.594
PFUnA	µg/kg	1.12	0.224	0.377	0.195	0.353	0.268	0.659
PFDoA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFTrA	µg/kg	1.97	0.129	0.257	0.153	< 0.241	0.18	0.364
PFTA	µg/kg	< 0.240	< 0.0534	< 0.229	< 0.0472	< 0.241	< 0.0461	< 0.238
PFBS	µg/kg	< 0.360	< 0.0801	< 0.344	< 0.0708	< 0.361	< 0.0692	< 0.357
PFHxS	µg/kg	< 0.360	< 0.0801	< 0.344	< 0.0708	< 0.361	0.0841	< 0.357
PFHpS	µg/kg	< 0.360	< 0.0801	< 0.344	< 0.0708	< 0.361	< 0.0692	< 0.357
PFOS	µg/kg	3.46	0.66	2.47	0.933	2.82	1.78	5.1
PFDS	µg/kg	< 0.360	< 0.0801	< 0.344	< 0.0708	< 0.361	< 0.0692	< 0.357
PF-3.7-DMOA	µg/kg	< 0.480	< 0.107	< 0.459	< 0.0944	< 0.481	< 0.0922	< 0.476
PFOSA	µg/kg	< 0.240	< 0.0534	< 0.229	2.54	8.78	0.293	< 0.238
HPFHpA	µg/kg	< 0.480	< 0.107	< 0.459	< 0.0944	< 0.481	< 0.0922	< 0.476
Sum PFAS excl. LOQ	µg/kg	7.87	1.21	3.67	4.01	12	3.16	7.32

Tissue		Remaining tissue	Liver	Remaining tissue	Liver	Remaining tissue	Liver	Remaining tissue
Sample name		**D-T-5**	**D-T-5**	**D-T-6**	**D-T-6**	**E-T-1**	**E-T-1**	**E-T-2**
Comment		Station D Atlantic cod	Station D Atlantic cod	Station D Atlantic cod	Station D Atlantic cod	Station E Atlantic cod	Station E Atlantic cod	Station E Atlantic cod
4:2 FTS	µg/kg	< 0.0893	< 0.408	< 0.0973	< 0.493	< 0.103	< 0.494	< 0.109
6:2 FTS	µg/kg	< 0.0670	< 0.306	< 0.0729	< 0.369	< 0.0770	< 0.370	0.157
8:2 FTS	µg/kg	< 0.0893	< 0.408	< 0.0973	1.14	< 0.103	< 0.494	0.215
PFBA	µg/kg	< 0.0446	< 0.204	< 0.0486	< 0.246	< 0.0514	< 0.247	0.102
PFPeA	µg/kg	< 0.0446	< 0.204	< 0.0486	< 0.246	< 0.0514	< 0.247	< 0.0547
PFHxA	µg/kg	< 0.0446	< 0.204	< 0.0486	< 0.246	< 0.0514	< 0.247	< 0.0547
PFHpA	µg/kg	< 0.0446	< 0.204	< 0.0486	< 0.246	< 0.0514	< 0.247	< 0.0547
PFOA	µg/kg	< 0.0446	< 0.204	< 0.0486	< 0.246	< 0.0514	< 0.247	0.0727
PFNA	µg/kg	0.118	0.236	0.195	1.45	1.06	3.03	0.266
PFDeA	µg/kg	0.0971	0.278	0.165	1.05	0.284	0.825	0.15
PFUnA	µg/kg	0.167	0.349	0.206	1.69	0.259	0.774	0.207
PFDoA	µg/kg	< 0.0446	< 0.204	< 0.0486	0.309	0.195	0.547	0.0728
PFTrA	µg/kg	0.134	0.231	0.0892	0.895	0.598	1.5	0.195
PFTA	µg/kg	< 0.0446	< 0.204	< 0.0486	< 0.246	0.0811	< 0.247	< 0.0547
PFBS	µg/kg	< 0.0670	< 0.306	< 0.0729	< 0.369	< 0.0770	< 0.370	< 0.0820
PFHxS	µg/kg	< 0.0670	< 0.306	< 0.0729	0.389	0.265	0.91	< 0.0820
PFHpS	µg/kg	< 0.0670	< 0.306	< 0.0729	< 0.369	0.109	< 0.370	< 0.0820
PFOS	µg/kg	1.31	4.57	1.56	16.1	18	70.4	2.77
PFDS	µg/kg	< 0.0670	< 0.306	< 0.0729	< 0.369	< 0.0770	< 0.370	< 0.0820
PF-3.7-DMOA	µg/kg	< 0.0893	< 0.443	< 0.0973	< 0.493	< 0.103	< 0.494	< 0.109
PFOSA	µg/kg	1.35	1.08	0.487	1.58	13.4	56.4	0.61
HPFHpA	µg/kg	< 0.0893	< 0.408	< 0.0973	< 0.493	< 0.103	< 0.494	< 0.109
Sum PFAS excl. LOQ	µg/kg	3.18	6.73	2.7	24.6	34.2	134	4.82

Tissue		**Liver**	**Remaining tissue**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**
Sample name		**E-T-2**	**E-T-3**	**F-T-1**	**F-T-1**	**F-T-2**	**F-T-2**	**G-T-1**
Comment		Station E Atlantic cod	Station E Atlantic cod	Station F Atlantic cod	Station F Atlantic cod	Station F Atlantic cod	Station F Atlantic cod	Station G Atlantic cod
4:2 FTS	µg/kg	< 1.45	< 0.0928	< 0.0773	< 0.391	< 0.0989	< 1.48	< 0.0833
6:2 FTS	µg/kg	< 1.09	< 0.0696	< 0.0580	< 0.293	< 0.0742	< 1.11	< 0.0625
8:2 FTS	µg/kg	< 1.45	< 0.0928	< 0.0773	< 0.391	< 0.0989	< 1.48	< 0.0833
PFBA	µg/kg	< 0.726	< 0.0464	< 0.0387	0.271	< 0.0494	< 0.739	< 0.0416
PFPeA	µg/kg	< 0.726	< 0.0464	< 0.0387	< 0.195	< 0.0494	< 0.739	< 0.0416
PFHxA	µg/kg	< 0.726	< 0.0464	< 0.0387	< 0.195	< 0.0494	< 0.739	< 0.0416
PFHpA	µg/kg	< 0.726	< 0.0464	< 0.0387	< 0.195	< 0.0494	< 0.739	< 0.0416
PFOA	µg/kg	< 0.726	0.122	< 0.0387	< 0.195	0.0822	< 0.739	< 0.0416
PFNA	µg/kg	< 0.726	0.172	0.158	0.327	0.146	< 0.739	0.102
PFDeA	µg/kg	< 0.726	0.106	0.142	0.246	0.114	< 0.739	0.17
PFUnA	µg/kg	< 0.726	0.194	0.301	0.422	0.297	0.775	0.389
PFDoA	µg/kg	< 0.726	< 0.0464	0.0711	< 0.195	0.0602	< 0.739	0.0812
PFTrA	µg/kg	< 0.726	0.216	0.31	0.233	0.182	< 0.739	0.221
PFTA	µg/kg	< 0.726	< 0.0464	0.0416	< 0.195	< 0.0494	< 0.739	< 0.0416
PFBS	µg/kg	< 1.09	< 0.0696	< 0.0580	< 0.293	< 0.0742	< 1.11	< 0.0625
PFHxS	µg/kg	< 1.09	< 0.0696	< 0.0580	< 0.293	< 0.0742	< 1.11	< 0.0625
PFHpS	µg/kg	< 1.09	< 0.0696	< 0.0580	< 0.293	< 0.0742	< 1.11	< 0.0625
PFOS	µg/kg	4.21	1.12	0.642	1.41	0.916	2.93	0.758
PFDS	µg/kg	< 1.09	< 0.0696	< 0.0580	< 0.293	< 0.0742	< 1.11	< 0.0625
PF-3.7-DMOA	µg/kg	< 1.45	< 0.0928	< 0.0773	< 0.391	< 0.0989	< 1.48	< 0.0833
PFOSA	µg/kg	9	0.747	0.29	0.371	0.584	5.56	< 0.0416
HPFHpA	µg/kg	< 1.45	< 0.0928	< 0.0773	< 0.391	< 0.0989	< 1.48	< 0.0833
Sum PFAS excl. LOQ	µg/kg	13.2	2.68	1.96	3.28	2.38	9.27	1.72

Tissue		**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**
Sample name		**G-T-1**	**G-T-2**	**G-T-2**	**G-T-3**	**G-T-3**	**G-T-4**	**G-T-4**
Comment		Station G Atlantic cod	Station G Atlantic cod	Station G Atlantic cod	Station G Atlantic cod	Station G Atlantic cod	Station G Atlantic cod	Station G Atlantic cod
4:2 FTS	µg/kg	< 0.268	< 0.0587	< 0.551	< 0.0833	< 0.280	< 0.0938	< 0.338
6:2 FTS	µg/kg	< 0.201	< 0.0440	< 0.413	< 0.0625	< 0.210	< 0.0703	< 0.253
8:2 FTS	µg/kg	< 0.268	< 0.0587	< 0.551	< 0.0833	< 0.280	< 0.0938	0.438
PFBA	µg/kg	< 0.134	< 0.0293	< 0.275	< 0.0417	< 0.140	< 0.0469	< 0.169
PFPeA	µg/kg	< 0.134	< 0.0293	< 0.275	< 0.0417	0.205	< 0.0469	< 0.169
PFHxA	µg/kg	< 0.134	< 0.0293	< 0.275	< 0.0417	< 0.140	< 0.0469	< 0.169
PFHpA	µg/kg	< 0.134	< 0.0293	< 0.275	< 0.0417	< 0.140	< 0.0469	< 0.169
PFOA	µg/kg	0.144	< 0.0293	< 0.275	< 0.0417	< 0.140	< 0.0469	0.171
PFNA	µg/kg	0.16	0.0772	< 0.275	0.0694	0.466	0.0774	0.277
PFDeA	µg/kg	0.169	0.0885	< 0.275	0.124	0.578	0.129	0.237
PFUnA	µg/kg	0.565	0.117	0.316	0.251	0.833	0.187	0.234
PFDoA	µg/kg	< 0.134	0.0322	< 0.275	0.0501	0.188	0.048	< 0.169
PFTrA	µg/kg	0.352	0.0691	< 0.275	0.0992	0.438	0.0969	< 0.169
PFTA	µg/kg	< 0.134	< 0.0293	< 0.275	< 0.0417	< 0.140	< 0.0469	< 0.169
PFBS	µg/kg	< 0.201	< 0.0440	< 0.413	< 0.0625	< 0.210	< 0.0703	< 0.253
PFHxS	µg/kg	< 0.201	< 0.0440	< 0.413	< 0.0625	< 0.210	< 0.0703	< 0.253
PFHpS	µg/kg	< 0.201	< 0.0440	< 0.413	< 0.0625	< 0.210	< 0.0703	< 0.253
PFOS	µg/kg	1.41	0.616	1.92	0.547	2.72	1.05	2.95
PFDS	µg/kg	< 0.201	< 0.0440	< 0.413	< 0.0625	< 0.210	< 0.0703	< 0.253
PF-3.7-DMOA	µg/kg	< 0.268	< 0.0587	< 0.551	< 0.0833	< 0.280	< 0.0938	< 0.338
PFOSA	µg/kg	< 0.134	0.132	< 0.275	< 0.0417	< 0.140	0.105	< 0.169
HPFHpA	µg/kg	< 0.268	< 0.0587	< 0.551	< 0.0833	< 0.280	< 0.0938	< 0.338
Sum PFAS excl. LOQ	µg/kg	2.8	1.13	2.24	1.14	5.42	1.69	4.31

Tissue		**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**
Sample name		**G-T-5**	**G-T-5**	**H-T-1**	**H-T-1**	**H-T-2**	**H-T-2**	**H-T-3**
Comment		Station G Atlantic cod	Station G Atlantic cod	Station H Atlantic cod	Station H Atlantic cod	Station H Atlantic cod	Station H Atlantic cod	Station H Atlantic cod
4:2 FTS	µg/kg	< 0.106	< 0.491	< 0.109	< 0.258	< 0.0989	< 0.352	< 0.0610
6:2 FTS	µg/kg	< 0.0792	< 0.369	< 0.0816	< 0.194	< 0.0741	< 0.264	0.0828
8:2 FTS	µg/kg	0.397	1.24	< 0.109	< 0.258	0.164	0.786	0.101
PFBA	µg/kg	< 0.0528	< 0.246	< 0.0544	< 0.129	< 0.0494	< 0.176	0.13
PFPeA	µg/kg	< 0.0528	< 0.246	< 0.0544	< 0.129	< 0.0494	< 0.176	< 0.0305
PFHxA	µg/kg	< 0.0528	< 0.246	< 0.0544	< 0.129	< 0.0494	< 0.176	< 0.0305
PFHpA	µg/kg	< 0.0528	< 0.246	< 0.0544	< 0.129	< 0.0494	< 0.176	< 0.0305
PFOA	µg/kg	< 0.0528	< 0.246	< 0.0544	< 0.129	< 0.0494	< 0.176	0.0489
PFNA	µg/kg	0.333	0.52	0.371	0.785	0.151	0.311	0.23
PFDeA	µg/kg	0.23	0.425	0.272	0.746	0.146	0.352	0.156
PFUnA	µg/kg	0.21	0.428	0.361	0.561	0.285	0.355	0.125
PFDoA	µg/kg	< 0.0528	< 0.246	0.0773	< 0.129	0.0603	< 0.176	< 0.0305
PFTrA	µg/kg	0.13	0.389	0.225	0.298	0.0988	< 0.176	0.0739
PFTA	µg/kg	< 0.0528	< 0.246	< 0.0544	< 0.129	< 0.0494	< 0.176	< 0.0305
PFBS	µg/kg	< 0.0792	< 0.369	< 0.0816	< 0.194	< 0.0741	< 0.264	< 0.0457
PFHxS	µg/kg	0.0838	< 0.369	< 0.0816	< 0.194	< 0.0741	< 0.264	0.0921
PFHpS	µg/kg	< 0.0792	< 0.369	< 0.0816	< 0.194	< 0.0741	< 0.264	0.0609
PFOS	µg/kg	4.26	11.7	0.901	2.83	1.16	2.16	4.05
PFDS	µg/kg	< 0.0792	< 0.369	< 0.0816	< 0.194	< 0.0741	< 0.264	< 0.0457
PF-3.7-DMOA	µg/kg	< 0.106	< 0.491	< 0.109	< 0.258	< 0.0989	< 0.352	< 0.0610
PFOSA	µg/kg	0.282	< 0.246	0.271	< 0.129	0.287	< 0.176	0.219
HPFHpA	µg/kg	< 0.106	< 0.491	< 0.109	< 0.258	< 0.0989	< 0.352	< 0.0610
Sum PFAS excl. LOQ	µg/kg	5.93	14.7	2.48	5.22	2.35	3.96	5.37

Tissue		**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**
Sample name		**H-T-3**	**Ref-T-1**	**Ref-T-1**	**Ref-T-2**	**Ref-T-2**	**Ref-T-3**	**Ref-T-3**
Comment		Station H Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod
4:2 FTS	µg/kg	< 0.571	< 0.0967	< 0.347	< 0.105	< 0.468	< 0.0738	< 0.541
6:2 FTS	µg/kg	< 0.428	< 0.0725	< 0.261	< 0.0785	< 0.351	< 0.0553	< 0.406
8:2 FTS	µg/kg	< 0.571	< 0.0967	< 0.347	< 0.105	< 0.468	< 0.0738	< 0.541
PFBA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	< 0.0369	0.689
PFPeA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	< 0.0369	< 0.271
PFHxA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	< 0.0369	< 0.271
PFHpA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	< 0.0369	< 0.271
PFOA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	< 0.0369	< 0.271
PFNA	µg/kg	0.374	< 0.0483	< 0.174	0.108	< 0.234	0.0902	< 0.271
PFDeA	µg/kg	< 0.286	< 0.0483	< 0.174	0.117	< 0.234	0.162	0.339
PFUnA	µg/kg	< 0.286	0.0768	< 0.174	0.217	0.315	0.47	1.01
PFDoA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	0.0941	0.304
PFTrA	µg/kg	< 0.286	< 0.0483	< 0.174	0.116	0.323	0.298	1.06
PFTA	µg/kg	< 0.286	< 0.0483	< 0.174	< 0.0523	< 0.234	< 0.0369	< 0.271
PFBS	µg/kg	< 0.428	< 0.0725	< 0.261	< 0.0785	< 0.351	< 0.0553	< 0.406
PFHxS	µg/kg	< 0.428	< 0.0725	< 0.261	< 0.0785	< 0.351	< 0.0553	< 0.406
PFHpS	µg/kg	< 0.428	< 0.0725	< 0.261	< 0.0785	< 0.351	< 0.0553	< 0.406
PFOS	µg/kg	9.53	0.304	1.4	0.555	1.61	0.441	1.29
PFDS	µg/kg	< 0.428	< 0.0725	< 0.261	< 0.0785	< 0.351	< 0.0553	< 0.406
PF-3.7-DMOA	µg/kg	< 0.571	< 0.0967	< 0.347	< 0.105	< 0.468	< 0.0738	< 0.541
PFOSA	µg/kg	< 0.286	< 0.0483	< 0.174	0.142	< 0.234	0.214	0.986
HPFHpA	µg/kg	< 0.571	< 0.0967	< 0.347	< 0.105	< 0.468	< 0.0738	< 0.541
Sum PFAS excl. LOQ	µg/kg	9.91	0.38	1.4	1.25	2.25	1.77	5.68

Tissue		**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**	**Liver**	**Remaining tissue**
Sample name		**Ref-T-4**	**Ref-T-4**	**Ref-T-5**	**Ref-T-5**	**Ref-T-6**	**Ref-T-6**	**A-R-1**
Comment		Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Ref. station Atlantic cod	Station A European plaice
4:2 FTS	µg/kg	< 0.0823	< 0.390	< 0.108	< 0.414	< 0.0903	< 0.485	< 0.116
6:2 FTS	µg/kg	< 0.0617	< 0.292	< 0.0810	< 0.310	< 0.0677	< 0.364	< 0.0873
8:2 FTS	µg/kg	< 0.0823	< 0.390	< 0.108	< 0.414	< 0.0903	< 0.485	< 0.116
PFBA	µg/kg	< 0.0412	< 0.195	< 0.0540	< 0.207	< 0.0452	0.555	< 0.0582
PFPeA	µg/kg	< 0.0412	< 0.195	< 0.0540	< 0.207	< 0.0452	< 0.242	< 0.0582
PFHxA	µg/kg	< 0.0412	< 0.200	< 0.0540	< 0.207	< 0.0452	< 0.242	< 0.0582
PFHpA	µg/kg	< 0.0412	< 0.195	< 0.0540	< 0.207	< 0.0452	< 0.242	< 0.0582
PFOA	µg/kg	< 0.0412	< 0.195	< 0.0540	< 0.207	< 0.0452	< 0.242	< 0.0582
PFNA	µg/kg	0.216	0.395	0.113	< 0.207	0.15	0.257	0.101
PFDeA	µg/kg	0.143	0.271	0.0992	< 0.207	0.21	0.365	0.115
PFUnA	µg/kg	0.213	0.379	0.18	< 0.207	0.38	0.663	0.17
PFDoA	µg/kg	< 0.0412	< 0.195	< 0.0540	< 0.207	0.103	< 0.242	< 0.0582
PFTrA	µg/kg	0.166	0.322	0.158	< 0.207	0.395	0.825	0.141
PFTA	µg/kg	< 0.0412	< 0.195	< 0.0540	< 0.207	< 0.0452	< 0.242	< 0.0582
PFBS	µg/kg	< 0.0617	< 0.292	< 0.0810	< 0.310	< 0.0677	< 0.364	< 0.0873
PFHxS	µg/kg	< 0.0617	< 0.292	< 0.0810	< 0.310	< 0.0677	< 0.364	< 0.0873
PFHpS	µg/kg	< 0.0617	< 0.292	< 0.0810	< 0.310	< 0.0677	< 0.364	< 0.0873
PFOS	µg/kg	0.964	2.82	0.569	1.02	0.709	1.66	0.939
PFDS	µg/kg	< 0.0617	< 0.292	< 0.0810	< 0.310	< 0.0677	< 0.364	< 0.0873
PF-3.7-DMOA	µg/kg	< 0.0823	< 0.390	< 0.108	< 3.55	< 0.0903	< 0.485	< 0.116
PFOSA	µg/kg	0.192	0.274	< 0.0540	< 0.207	0.0744	0.917	< 0.0582
HPFHpA	µg/kg	< 0.0823	< 0.390	< 0.108	< 0.414	< 0.0903	< 0.485	< 0.116
Sum PFAS excl. LOQ	µg/kg	1.9	4.46	1.12	1.02	2.02	5.24	1.47

Tissue		Liver	Remaining tissue	Liver	Remaining tissue	Liver	Remaining tissue	Liver
Sample name		**A-R-1**	**A-R-2**	**A-R-2**	**D-R-1**	**D-R-1**	**D-R-2**	**D-R-2**
Comment		Station A European plaice	Station A European plaice	Station A European plaice	Station D European plaice	Station D European plaice	Station D European plaice	Station D European plaice
4:2 FTS	µg/kg	< 0.501	< 0.103	< 0.438	< 0.101	< 0.476	< 0.107	< 0.340
6:2 FTS	µg/kg	3.25	< 0.0770	< 0.329	< 0.0754	< 0.357	< 0.0801	< 0.255
8:2 FTS	µg/kg	2.25	< 0.103	< 0.438	< 0.101	0.965	< 0.107	< 0.340
PFBA	µg/kg	< 0.250	< 0.0514	0.663	< 0.0503	< 0.238	< 0.0534	< 0.170
PFPeA	µg/kg	< 0.250	0.0537	< 0.219	< 0.0503	< 0.238	< 0.0534	< 0.170
PFHxA	µg/kg	< 0.250	< 0.0514	< 0.219	< 0.0503	< 0.238	< 0.0534	< 0.170
PFHpA	µg/kg	< 0.250	< 0.0514	< 0.219	< 0.0503	< 0.238	< 0.0534	< 0.170
PFOA	µg/kg	< 0.250	< 0.0514	< 0.219	0.0543	< 0.238	< 0.0534	< 0.170
PFNA	µg/kg	< 0.250	0.144	0.535	0.917	3.5	0.858	1.14
PFDeA	µg/kg	< 0.250	0.0978	0.29	0.56	1.5	0.475	0.567
PFUnA	µg/kg	0.28	0.119	0.468	0.383	1.22	0.37	0.476
PFDoA	µg/kg	< 0.250	< 0.0514	< 0.219	< 0.0503	< 0.238	< 0.0534	< 0.170
PFTrA	µg/kg	0.26	0.0618	< 0.219	0.132	0.485	0.137	0.213
PFTA	µg/kg	< 0.250	< 0.0514	< 0.219	< 0.0503	< 0.238	< 0.0534	< 0.170
PFBS	µg/kg	< 0.375	< 0.0770	< 0.329	< 0.0754	< 0.357	< 0.0801	< 0.255
PFHxS	µg/kg	< 0.375	0.0842	< 0.329	< 0.0754	< 0.357	< 0.0801	< 0.255
PFHpS	µg/kg	< 0.375	< 0.0770	< 0.329	< 0.0754	< 0.357	< 0.0801	< 0.255
PFOS	µg/kg	1.79	0.922	3.17	1.8	5.47	2.32	2.23
PFDS	µg/kg	< 0.375	< 0.0770	< 0.329	< 0.0754	< 0.357	< 0.0801	< 0.255
PF-3.7-DMOA	µg/kg	< 0.501	< 0.103	< 0.438	< 0.101	< 0.476	< 0.107	< 0.340
PFOSA	µg/kg	0.901	< 0.0514	< 0.219	< 0.0503	< 0.238	< 0.0534	< 0.170
HPFHpA	µg/kg	< 0.501	< 0.103	< 0.438	< 0.101	< 0.476	< 0.107	< 0.340
Sum PFAS excl. LOQ	µg/kg	8.74	1.48	5.12	3.84	13.1	4.16	4.63

Tissue		Remaining tissue	Liver	Remaining tissue	Liver
Sample name		**E-R-1**	**E-R-1**	**B-L-1**	**B-L-1**
Comment		Station E European plaice	Station E European plaice	Station B Lemon sole	Station B Lemon sole
4:2 FTS	µg/kg	< 0.104	< 0.381	< 0.119	< 0.330
6:2 FTS	µg/kg	< 0.0783	< 0.286	< 0.0894	< 0.248
8:2 FTS	µg/kg	< 0.104	< 0.381	< 0.119	< 0.330
PFBA	µg/kg	< 0.0522	0.662	< 0.0596	< 0.165
PFPeA	µg/kg	< 0.0522	< 0.190	< 0.0596	< 0.165
PFHxA	µg/kg	< 0.0522	< 0.190	< 0.0596	< 0.165
PFHpA	µg/kg	< 0.0522	< 0.190	< 0.0596	< 0.165
PFOA	µg/kg	< 0.0522	< 0.190	0.0907	0.175
PFNA	µg/kg	0.746	2.6	0.157	0.307
PFDeA	µg/kg	0.587	1.75	< 0.0596	< 0.165
PFUnA	µg/kg	0.522	1.83	< 0.0596	< 0.165
PFDoA	µg/kg	0.0848	< 0.190	< 0.0596	< 0.165
PFTrA	µg/kg	0.139	0.458	< 0.0596	< 0.165
PFTA	µg/kg	< 0.0522	< 0.190	< 0.0596	< 0.165
PFBS	µg/kg	< 0.0783	< 0.286	< 0.0894	< 0.248
PFHxS	µg/kg	< 0.0783	< 0.286	< 0.0894	< 0.248
PFHpS	µg/kg	< 0.0783	< 0.286	< 0.0894	< 0.248
PFOS	µg/kg	2.78	8.54	0.306	0.735
PFDS	µg/kg	< 0.0783	< 0.286	< 0.0894	< 0.248
PF-3.7-DMOA	µg/kg	< 0.104	< 0.381	< 0.119	< 0.330
PFOSA	µg/kg	0.194	< 0.190	< 0.0596	< 0.165
HPFHpA	µg/kg	< 0.104	< 0.381	< 0.119	< 0.330
Sum PFAS excl. LOQ	µg/kg	5.06	15.8	0.554	1.22

Supplementary figures

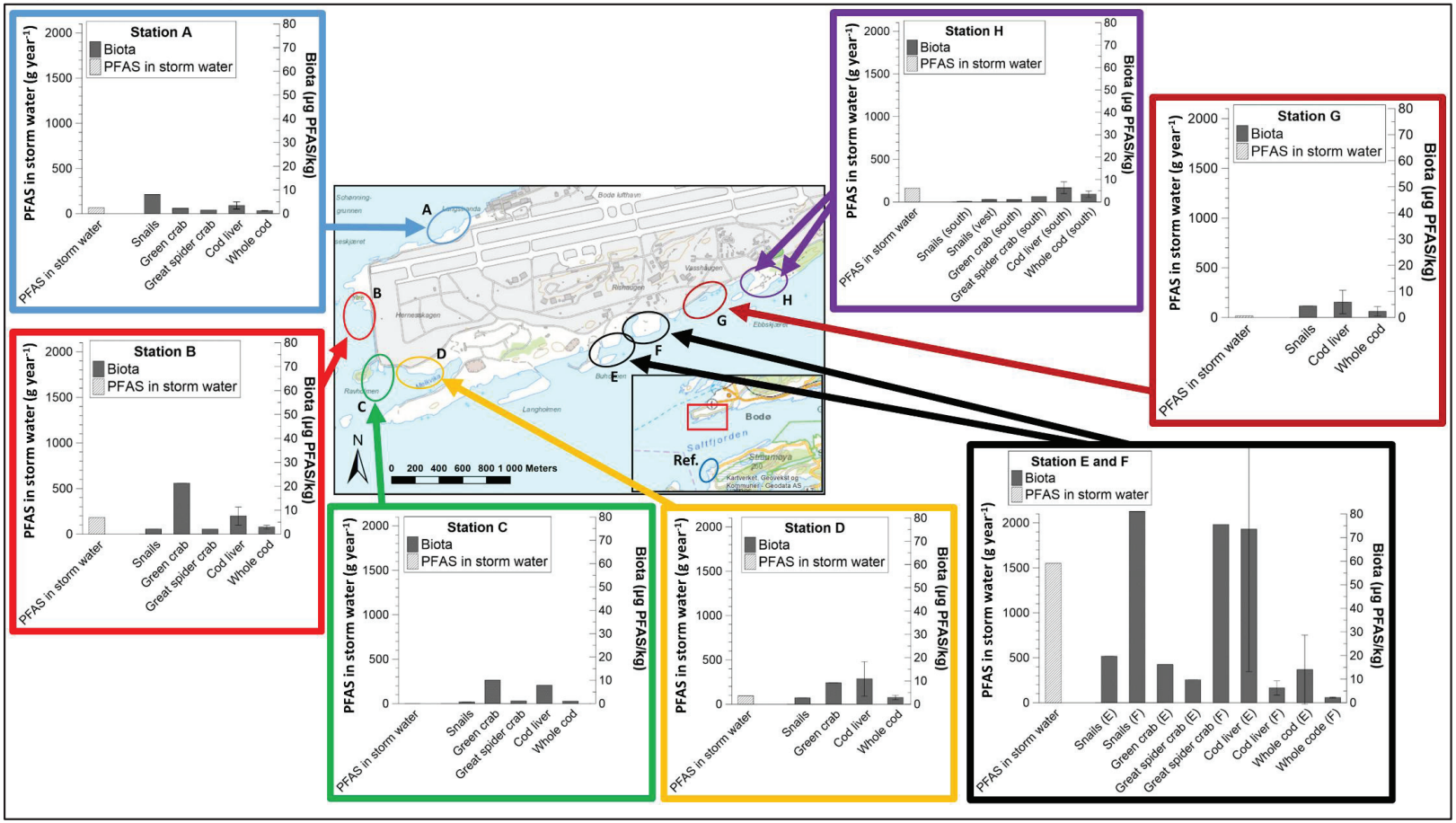

Figure S1. Map of the Air Station, including sampling stations, calculated amount of PFAS release with storm water, and concentrations in biota.

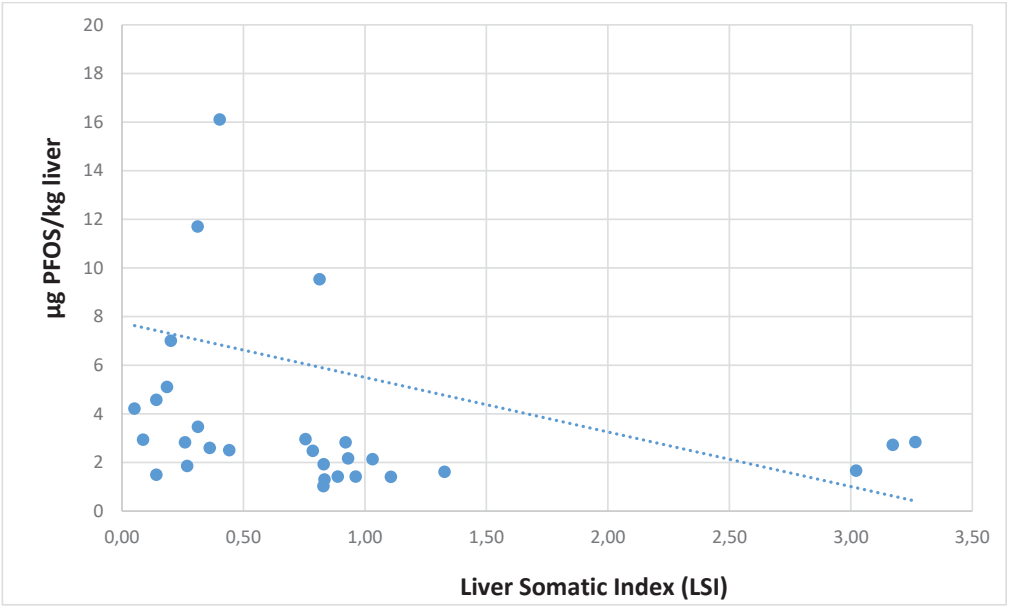

Figure S2. PFOS concentrations in liver of Atlantic cod vs. Liver Somatic Index (LSI)

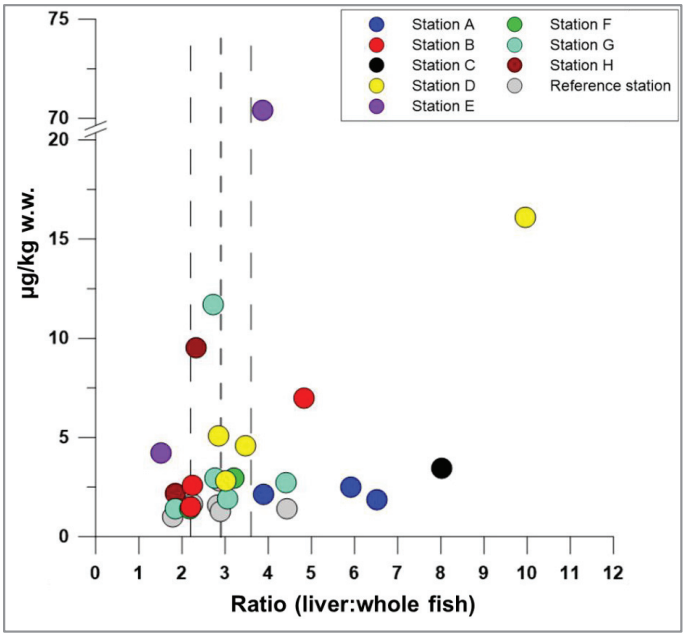

Figure S3. PFOS liver concentrations in Atlantic cod plotted against the ratio of PFOS concentrations liver to whole fish. Each circle represent one individual, caught at the respective station. Dashed lines show median ratio ± the median absolute deviation (MAD).

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Paper V

The fate of poly- and perfluoroalkyl substances in a marine food web influenced by land-based sources in the Norwegian Arctic

Firefighting training station at Svalbard airport. Photo: Håkon Austad Langberg

Appendix: Paper V

The fate of poly- and perfluoroalkyl substances in a marine food web influenced by land-based sources in the Norwegian Arctic

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Abstract

Although poly- and perfluorinated alkyl substances (PFAS) are ubiquitous in the Arctic, their sources and fate in Arctic marine environments remain unclear. Herein, abiotic media (water, snow, and sediment) and biotic media (plankton, benthic organisms, fish, crab, and glaucous gull) were sampled to study PFAS uptake and fate in the marine food web of an Arctic Fjord in the vicinity of Longyearbyen (Svalbard, Norwegian Arctic). Samples were collected from locations impacted by a firefighting training site (FFTS) and a landfill as well as from a reference site. Mean Σ_{14}PFAS concentration in the landfill leachate was 643.6±84 ng L^{-1}, while it was 365±8.0 ng L^{-1} in a freshwater pond and 57±4.0 ng L^{-1} in a creek in the vicinity of the FFTS. These levels were an order of magnitude higher than in coastal seawater of the nearby fjord (maximum level Σ_{14}PFAS= 10.1±1.2 ng L^{-1}, at the FFTS impacted site). PFOS was the most predominant compound in all seawater samples and in freshly fallen snow (63–93% of Σ_{14}PFAS). In freshwater samples from the Longyear river and the reference site, PFCA ≤ C_9 were the predominant PFAS (37–59%), indicating that both local point sources and diffuse sources contributed to the exposure of the marine food web in the fjord. Σ_{14}PFAS concentrations increased from zooplankton (1.1±0.32 µg kg^{-1} ww) to polychaete (2.8±0.8 µg kg^{-1} ww), crab (2.9±0.7 µg kg^{-1} ww whole-body), fish liver (5.4±0.87 µg kg^{-1} ww), and gull liver (62.2±11.2 µg kg^{-1}). PFAS profile changed with increasing trophic level from a large contribution of 6:2 FTS, FOSA and long-chained PFCA in zooplankton and polychaetes to being dominated by short-chained PFCA and linear PFOS in fish and gull liver. The PFOS isomer profile (branched *versus* linear) in the active FFTS and landfill was similar to historical ECF PFOS. A similar isomer profile was observed in seawater, indicating major contribution from local sources. However, a PFOS isomer profile enriched by the linear isomer was observed in other media (sediment and biota). Substitutes for PFOS, namely 6:2 FTS and PFBS, showed bioaccumulation potential in marine invertebrates. However, these compounds were not found in organisms at higher trophic levels.

Introduction

The presence of poly- and perfluoroalkyl substances (PFAS) in the environment has attracted significant attention and research during the two last decades.[1, 2] PFAS are a group of man-made chemicals and are classified and subdivided based on their characteristic functional groups. The most commonly studied PFAS groups include perfluoroalkyl carboxylates (PFCA) and perfluoroalkane sulfonates (PFSA), fluorotelomer alcohols (FTOH), sulfonamido ethanols (FOSE), and fluorotelomer sulfonates (FTS).[3] Several PFAS are regulated nationally and/or internationally through the Stockholm Convention (www.pops.int) and their use has been, or is currently being phased out. However, they have been replaced by other substitute PFAS, which are of unknown environmental concern.[4] Perfluorooctane sulfonate (PFOS) is one of the most widely known PFSA being detected worldwide in the aquatic and the terrestrial environment, including humans.[5, 6] PFOS and its precursors were only manufactured with electrochemical fluorination (ECF) which yields a mixture of linear and branched isomers with known percentages (70±1.1% and 30±0.8%, respectively).[7, 8]

The extremely broad product application range for PFAS has resulted in the ubiquitous detection of these persistent chemicals, even in remote environments such as the Arctic.[9, 10] PFAS are considered priority chemicals of emerging concern for the Arctic.[11] The transport pathways that result in PFAS ultimately ending up in the Arctic ecosystem is a focus of current research. The most frequently used PFAS are amphiphobic and ionic, and hence, not expected to be prone to long-range atmospheric transport.[12] Oceanic long-range transport is a known transport pathway for ionic PFAS.[13] However, the observation of the occurrence of neutral precursors in outdoor air[14-17] suggests that precursors with long atmospheric lifetimes have the potential to be transported over long distances and subsequently degraded in the atmosphere to environmental stable perfluoroalkyl acids (PFAA).[18] Once PFAA are formed in the atmosphere, they deposit to the surface through wet or dry deposition.[19] Degradation of these precursor compounds (e.g. fluorotelomer alcohols and polyfluorinated sulfonamides based chemicals) may increase environmental loads as it leads to the formation of PFAA.[20, 21] In addition, recent field and laboratory studies have suggested water-to-air transfer of PFAA through sea spray aerosol as an important additional source of PFAAs to the atmosphere.[22, 23]

High concentrations of PFAS have been reported in Arctic environments influenced by local sources such as landfills, sewage discharge and airports.[9, 24] The use of aqueous film forming foams (AFFF) for firefighting training activities at airports has previously been noted to be a significant point source of PFAS to a variety of environmental media.[4, 25] The disposal of PFAS containing consumer products (food wrappings, non-stick cook ware, stain-resistant coatings, cleaning products, etc.) has also resulted in elevated PFAS levels in landfill leachate.[26-28] In the Svalbard archipelago, further studies are

needed to elucidate the contribution of such local sources to the Arctic environment as well as how these sources affect the marine food web. Further, the direct link between the release from local sources and accumulation in the Arctic marine environment has not been studied previously.

Hence, the main objective of the present study is to investigate the fate of PFAS released by certain point sources in a marine food web in the Norwegian Arctic. Thus, the PFAS distribution patterns in terrestrial, limnic and marine abiotic matrices (water, snow and sediments) and biota at various trophic levels in the marine food web was investigated.

MATERIALS AND METHODS

The study sites

Longyearbyen is the largest settlement on Svalbard, with approximately 2400 inhabitants.[29] During the tourist season, up to 100,000 visitors, arriving by cruise ship or plane at the small local airport are recorded each year.[30] Following the cessation of most coal mining activities in 2018, both tourism and education drive the local economy. The mean temperature varies from -16°C in February to +6°C in July, and the annual precipitation is approximately 200 mm (Norwegian Meteorological Institute). The following point sources were included in this study (Figure 1), representing the main point sources of the study area: Svalbard Airport (N 78°14', E 15°30'), situated approximately five kilometres northwest of Longyearbyen centre and a decommissioned landfill in Adventdalen (N 78°10', E 15°56'). Diffuse sources to the marine environment include wastewater from the municipality and the airport which is discharged without pre-treatment into Adventfjord, at approximately 60 m depth 2 km off the coast,[31] and runoff from the municipality. It was estimated that Longyearbyen city annually releases about 285,000 m^3 of untreated wastewater into Adventfjord.[32] To investigate the PFAS load from diffuse sources, the Longyear river (N 78°13', E 15°38') which runs through Longyearbyen and is by glacier and snow melt, was sampled, as well as a meltwater creek (N 78°12', E 15°12'), which is fed by snow melt. A snow sample, collected directly after a precipitation event, was sampled from a nearby mountain side, Breinosa (N 78°09', E 16°03'), which could represent PFAS from atmospheric deposition.

Svalbard airport was opened in 1975 and has two firefighting training stations (FFTS), one decommissioned area north-east of the runway and one newer active training area south-east of the runway (Figure 1). The main source of contamination at the airport site is AFFF containing PFAS used during training which is assumed to have been transported with run-off to Adventfjord during the short spring snow melting season. The landfill received municipal and industrial waste between 1991

and 2007. From 2007, most municipal waste from Longyearbyen was transported to mainland Norway for incineration and mainly non-degradable waste (e.g. gypsum, steel, concrete and slag) has been disposed of at the landfill [33].

Water samples

To investigate the contribution of PFAS to the marine food web from the active FFTS, runoff water from a creek running from the FFTS to the coast was collected in duplicate using 2.5 L methanol rinsed polyethylene bottles (FFTS-creek, Figure 1). Water from the pond down gradient of the old FFTS, receiving runoff from the airport, was also collected (FFTS-pond, Figure 1). At the landfill site, leachate water was sampled (Landfill). To investigate the contribution from the various sources, seawater was sampled from four representative stations located in the fjord system (Adventfjord and Isfjord, St1-St3, Figure 1), and one reference location (St4, Fig. 1). All of these water samples were collected in June 2018. From each of the marine sampling stations in the fjord, surface (1 m below surface), subsurface (mid water column) and deep seawater (1 m above the seabed) were sampled using a Ruttner Water Sampler (KC Denmark A/S). Seawater samples were analysed without filtration thus representing total water concentrations. Station 1 is impacted by the active FFTS and located close to where the creek drains into the fjord (N 78°14', E 15°33'), while station 2 is impacted by the old FFTS site (FFTS-pond) and it receives general runoff from the airport (N 78°15', E 15°29'). Station 3 is located directly outside the Longyearbyen settlement, where the Longyearbyen river flows into the fjord (N 78°14', E 15°39'). Station 3 is also affected by water from Adventdalen, where the landfill is located. The reference station, Station 4 is located in the fjord, Isfjord, approximately 10 km from any known PFAS source (airport, landfill or settlement). This station was chosen as a background site that reflects the coastal waters of the fjord. However, it cannot be excluded that this site may be affected by these sources. Runoff from a small meltwater creek near station 4 draining to Isfjord was sampled to represent PFAS from atmospheric deposition (Ref-creek, N 78°12', E 15°12'). The Longyear river is a meltwater river receiving meltwater from the adjacent glaciers (Longyearbreen and Larsbreen glaciers). This was sampled to represent atmospheric deposition and contamination from Longyearbyen town before draining into Adventfjord (LY-river, N 78°13', E 15°38'). A surface snow sample was collected on the mountainside above the active coal mine (Snow sample, N 78°09', E 16°03', 545 above mean sea level, Figure 1) in October 2018. Surface snow (0 – 10 cm depth) was collected following recent precipitation during the previous 7 days and so it presumably represents newly deposited PFAS. The snow was melted and analyzed as an aqueous sample. Sampling data are presented in Table S1 and Figure S1.

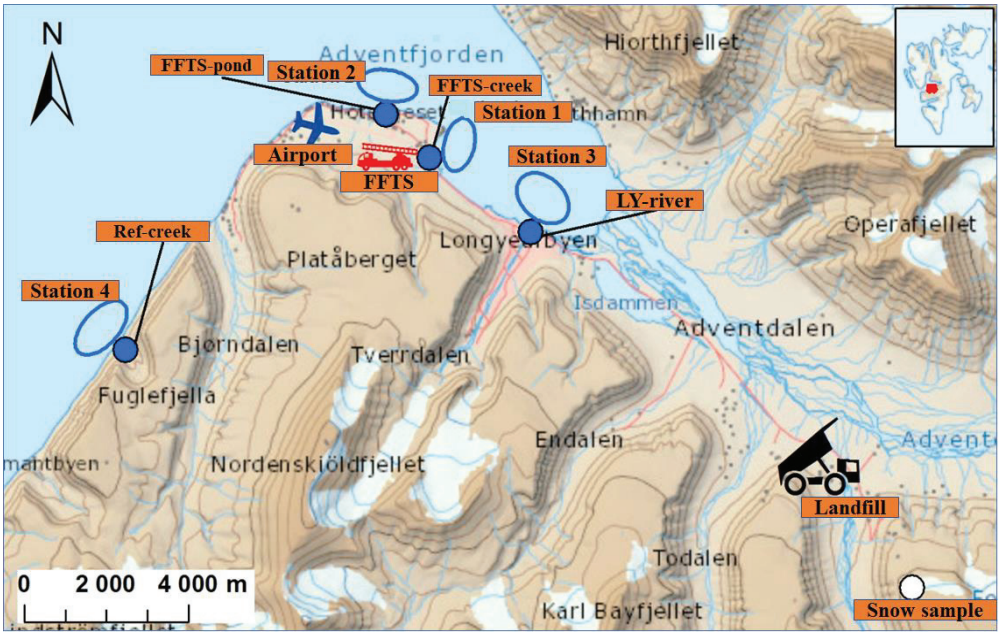


Figure 1. Marine sampling stations (blue circles representing St1, 2, 3 and 4), sampling points for freshwater samples (blue dots for Ref-creek, FFTS-pond, FFTS-creek, LY-river), the landfill, and snow sample (white dot) locations in the vicinity of Longyearbyen (Svalbard, Norway, source:toposvalbard.npolar.no).

Sediment and biota samples

Bottom sediments (0-5 cm depth) were collected in triplicate at the four marine stations (St1-St4) using a van Veen grab sampler. Sediment from the upper centimetres of the landfill leachate drainage channel was also collected. Marine biota samples were collected at the four marine stations (St1-St4). To determine PFAS levels in benthic organisms, polychaetes were collected (approximately 10 g from each station) from the sediments sampled and individuals from the same station were pooled into one representative sample (Table S2). Polychaetes were depurated overnight in seawater in order to separate sediment-bound PFAS from accumulated PFAS. Pelagic zooplankton (copepods, mainly *calanus* spp.) was collected and triplicate samples from each station were pooled for analyses (approximately 20 g per station, Table S2). One to 14 crabs (*Hyas araneus)* were collected from each station and one to seven individuals were analysed (Table S3). Two local fish species were collected: sculpin (*Myoxocephalus scorpius*) (n=29) and wolffish (*Anarhichas lupus*) (n=3) from stations St1, St2 and St4. Liver and muscle samples were obtained from each fish individually and analysed separately (See Table S4 and Figure S2 for fish and liver weights). Twenty glaucous gulls specimen (*Larus hyperboreus*) were sampled in the proximity of Svalbard airport at *Adventpynten* (between station 1 and 2) in April 2018 and liver samples were obtained (biological parameters of the collected glaucous

gulls are shown in Table S5). None of biota species investigated is on the IUCN Red List Categories. PFAS levels in biota are calculated on a wet weight basis (ww), while concentrations in sediment are given on dry weight basis (dw) due to the potential variability in moisture content.

Sample Preparation and HPLC–MS/MS Analysis

Two previously published analytical methods were adopted with some modification for the analysis of abiotic and biotic samples.[34, 35] The methods were subjected to a comprehensive validation before being applied for the simultaneous quantification of all the selected PFAS (see Table S6). A detailed description of the methods is available in the supplementary information. Briefly, sediment and biota samples were extracted with methanol. Clean-up of methanol extracts was conducted using active carbon (EnviCarb, Sigma-Aldrich Co., PA, USA). Water and melted snow samples were extracted on Oasis® Waters (Mildford, MA, USA) weak-anion exchange (WAX) SPE cartridges (6 mL volume, 0.5 g). The quantitative determination of PFAS was done with high-performance liquid chromatography (HPLC) using an Agilent 1200 series HPLC (Agilent Technologies, Waldbronn, Germany) and an Agilent 6460 (Agilent Technologies, Santa Clara, CA, USA) triple quadrupole mass spectrometer equipped with a Jet stream electrospray ion source.

Quality assurance, quality control, and method validation

All samples were analysed under standardized conditions (NS-EN ISO/IEC 17025 - TEST 137) and spiked with a mixture of 12 internal standards (ISTDs) (see Table S7 and S8) before extraction. In order to monitor contamination during transportation and sample preparation, field and laboratory blank samples made of Milli-Q water (for water samples) and sodium sulfate standard - 99.99% (for sediment, and each organism type) were included and processed as real samples. Potential contamination resulting from the HPLC system was avoided by using a delay column (Agilent Eclipse Plus C_{18}, 4.6 × 50 mm, 3.5 µm), installed after the mixing valve, and before the autosampler [36]. This helps to resolve problems related to PFAS that originate from the instrumental contamination, as depicted in Figure S4. Additionally, a methanol blank was injected after every 10 samples. None of the targeted PFAS were detected in the methanol blanks, indicating the absence of carryover effects. Instrument limit of detection (LOD) and lower limit of quantification (LOQ) were determined by the compound specific amount corresponding to a signal to noise ratio (S/N) = 3 (LOD) and 10 (LOQ). These calculations were based on the three lowest calibrations standards prepared in solvent (0.05, 0.1, 5 pg μL^{-1}). For compounds not detected in procedural blank samples, the method detection limit (MDL) was determined as the concentration resulting in S/N = 3, based on the three lowest calibrations standards (0.1, 0.5, 5 pg μL^{-1}) prepared in real sample extracts. MDLs for compounds detected in

procedural blank samples were determined as C+3SD, where C is the mean concentration measured in blanks and SD is the standard deviation. No blank correction was made for these compounds. Signals detected below LOD were presented as non-detected (nd), while levels detected above LOD but below the calculated MDL, were reported as <LOQ (see Table S9).

In addition to the 19 PFAS targeted in this study, the proportion of total branched PFOS isomers were quantified. All target PFAS were quantified using internal standard calibration curves with eight concentration points (R^2 >0.99). For seawater, standards including both native and internal standards were prepared in similar matrix extracts. Samples with minimal PFAS concentrations were used for matrix matched calibration (see the supplementary information for details, Table S10) which has resulted in better recovery. In sediment and biota matrices, matrix-matched calibration remained necessary for the quantification of 6:2 FTS, which showed unacceptable recoveries >140% which was attributed to a lack of exactly-matched, isotopically-labelled ISTD. However, due to the lack of PFAS free biota material, and the observed low salinity in meltwater samples, these matrices were analysed with solvent matched calibration for PFAS other than 6:2 FTS. The proportion of total branched PFOS isomers was calculated using the chromatographic peak area against the calibration curve of the linear PFOS isomer.[37, 38] For this, concentrations were calculated using the average of m/z 499/80 and 499/99 ions for both PFOS isomers, as described in Riddell et al.[39] However, in order to enhance the selectivity, 499/99 ion was selected for PFOS quantification in fish and gull livers samples due to endogenous interferences associated with the m/z 499→80 transition. [40] For each sample type, matrix spiked apparent recovery percentages of all target PFAS were calculated from samples with low-contamination levels (4-6 replicates) spiked at two concentration levels (1.0 and 25 μg kg^{-1} for sediment and biota; 3.0 and 25 ng L^{-1} for water). Most target PFAS showed acceptable recoveries (40-125%, Table S11). Additionally, relative recoveries of internal standards were also calculated based on their linear calibration curves applying [$^{13}C_8$]-PFOA as a recovery standard (see Table S12). N-Methyl Perfluorooctanesulfonamido Ethanol (N-MeFOSE), N-Methyl Perfluorooctanesulfonamide (N-MeFOSA), N-Ethyl Perfluorooctanesulfonamido Ethanol (N-EtFOSE), and N-Ethyl Perfluorooctanesulfonamide (N-EtFOSA) showed unacceptable low recoveries for several matrices, and consequently were excluded from the dataset. PFBA was excluded from quantification due to some concerns of interference affecting the results which could not be excluded with only one MRM transition. Therefore, 14 PFAS (and Br-PFOS) were quantified. Analyte names, acronyms, CAS numbers, and structures of the 14 target compounds are shown in Table S6.

Statistics and data handling

Principal component analysis (PCA) was performed to investigate the main patterns of variation in PFAS profiles within the dataset after a normalization to sum PFAS concentrations. For PCA, the R-software (R-Studio Version 1.1.143 based on R version 3.5.2.) was used under the GNU public license (Boston, MA, USA) with prcomp function and the package ggbiplot. The non-parametric unpaired Wilcoxon Test/Mann–Whitney U test was applied for testing the differences in PFAS concentrations between FFTS-impacted sites and the background reference site and between female and male crabs and Glaucous gull individuals. The Spearman's correlation test was used for testing the correlation between $\sum_{14}$PFAS concentrations and biological parameters for individual organisms and to investigate the correlation among individual PFAS. The significance threshold was set to $p < 0.05$. Values reported in the current paper, indicate average values and ± standard error of the mean (SEM). For compounds detected at concentrations <LOQ, values were set at half LOQ for the summation of Σ_{14}PFAS.

RESULTS AND DISCUSSION

Concentration and distribution patterns of PFAS in water: point sources

PFAS concentration and distributions patterns for the 14 target PFAS are shown in Fig. 2 and PFAS concentrations in all water samples are listed in Table S13. The highest $\sum_{14}$PFAS concentrations were detected in the landfill leachate (643±84 ng L^{-1}). These $\sum_{14}$PFAS levels were similar to the concentrations reported in the leachate of Norwegian landfills (median 630 ng L^{-1}) and in Spain (639-1379 ng L^{-1}).[33, 41] Higher values have been found in landfill leachates in USA (2000 to 29000 ng L^{-1}) and Australia (2000 to 15000 ng L^{-1}).[27, 41, 42] Water samples collected from the pond that receives drainage water from the Svalbard airport (FFTS-pond) and a creek downstream from the FFTS (FFTS-creek) also showed elevated $\sum_{14}$PFAS concentrations (365±8.0 and 57.4±4.0 ng L^{-1}, respectively). This is in agreement with a recent study conducted in Longyearbyen where Skaar et al.[35] reported high $\sum_{9}$PFAS concentrations in run-off water samples collected in June 2015 at 600 m downstream of the local FFTS at Svalbard airport in Longyearbyen (113±2.9 ng L^{-1}).

The predominant PFAS in the FFTS-creek, which receives runoff from the firefighting training area where AFFF is actively used, were PFOS (35% of $\sum_{14}$PFAS), PFHxS (22%), PFHxA (18%), PFOA (11%), PFHpA (6%) and smaller percentages of the remaining compounds (≤ 3% per compound). The occurrence of 6:2 FTS at 1.46±0.08 ng L^{-1} (2.5% of $\sum_{14}$PFAS) might indicate the use of new AFFF formulations at the FFTS, as 6:2 FTS and related compounds have replaced PFOS after the phase-out in the 2000s according to the Norwegian Aviation Organisation.[43] A similar profile was identified in the

FFTS-pond which is close to the old firefighting training area and receives general runoff from the airport (without runoff from the active FFTS). The leachate water from the decommissioned Longyearbyen landfill was characterized by a high relative contribution of PFCA C_{6-11} (43% of $\sum_{14}$PFAS of which PFOA accounts for approximately 20%) and the sum of linear and branched PFOS representing 48% of $\sum_{14}$PFAS. The formation of PFCA e.g. PFHxA and PFOA from the degradation of fluorotelomers, precursors to PFCA, can be a potential source for PFCA in the landfill leachate.[44] A similar PFAS pattern is reported for landfill leachate from Spain, where PFOA was the predominant compound at 43% of the total PFAS.[41]

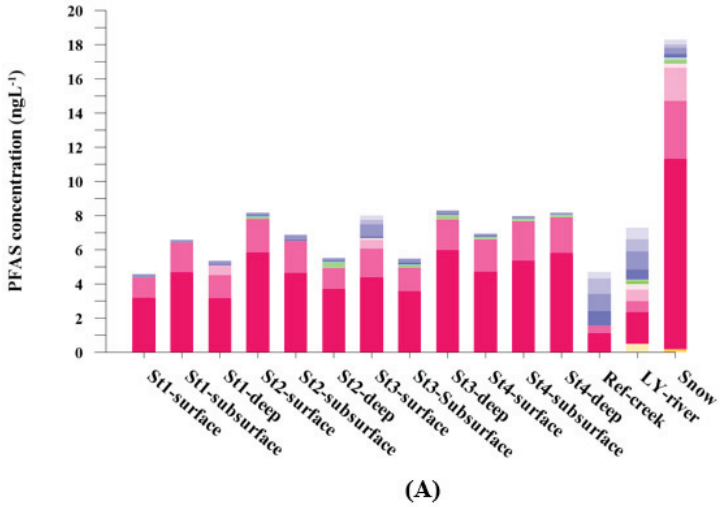
Concentration and distribution patterns of PFAS in water: diffuse sources

The $\sum_{14}$PFAS concentrations in samples from LY-river, Ref-creek, the snow sample as well as in the seawater samples from Adventfjord were lower than the concentrations reported in freshwater at the landfill and the FFTS pond (Fig. 2, Table S13). In the LY-river sample, the predominant PFAS were PFHxA, PFHpA, PFOA, PFHxS, and PFOS. The concentrations of PFCA C_{6-12} in LY-river reported in the current study (6.44 ng L^{-1}) were higher than previously reported (3.51 ng L^{-1})[45] (Table S13). This could be related to the season and the water-flow in the river, where the previously reported samples were taken during May 2006.

In the Ref-creek sample, a similar concentration as in the LY-river was found and the predominant PFAS were PFOA and PFOS (19 and 20% respectively). The $\sum_{14}$PFAS in the snow sample from the mountain side was somewhat higher (18.70 ng L^{-1}, Table S13), and was dominated by PFHxS (17 %) and PFOS (64 %). The PFOA concentration in the snow sample (0.360 ±0.007 ng L^{-1}, Table S13) was similar to a previous study in which snow was sampled near Longyearbyen town (0.396 ± 0.161 ng L^{-1}).[45] However, ∑PFAS (1.47 ng L^{-1}) and PFOS (0.118 ± 0.052 ng L^{-1}) concentrations were much lower in that particular study.[45]

In the seawater samples, PFOS was the most dominant compound (Fig. 2, Table S13). Depth profiles in the fjord based on the three sampling levels (surface, subsurface, and bottom waters) showed that PFAS were detected throughout the water column of Adventfjord (St1-St4). At station 3 and station 4, which was the reference station, $\sum_{14}$PFAS concentrations increased with depth, indicating a PFAS contribution from the deep marine water in contact with the bottom sediments. In contrast, in station 2, which receives direct runoff from the airport, $\sum_{14}$PFAS decreased with depth, while in station 1 (impacted by the active FFTS) the highest $\sum_{14}$PFAS value was found in the mid water column. In a previous study where surface water samples were collected in the coastal zone just outside Longyearbyen in Adventfjord during May 2006 the $\sum_{14}$PFAS concentrations were 0.73 ng L^{-1} [45], which

289 is lower than reported herein. Although this may indicate a temporal increase in PFAS levels in
290 Adventfjord, the differing concentrations may also be due to seasonal variations in runoff from the
291 point-sources caused by snow-melting and/or precipitation events. Nevertheless, the PFAS
292 concentrations in Adventfjord are higher than those previously reported for the open North Sea and
293 Norwegian Sea (0.01-0.07 ng L^{-1}) [46], indicating that the local point-sources contribute to the levels of
294 PFAS in Adventfjord.



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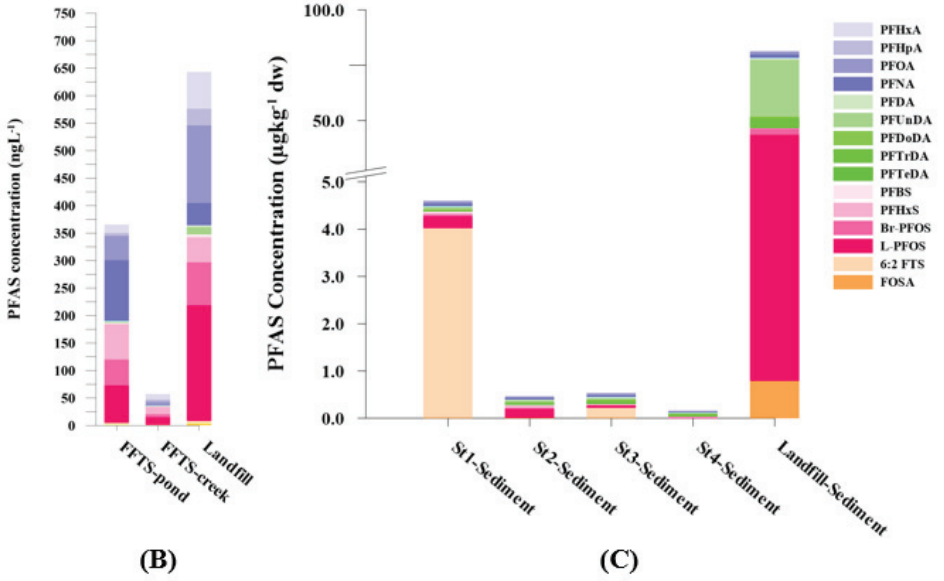

296
297 *Figure 2. Distribution and average concentrations of PFAS in abiotic samples in the vicinity of*
298 *Longyearbyen (Svalbard) (A) and (B) aqueous samples from the fresh water and marine environment*
299 *(standard error of the mean is given in Table S13). (C) marine sediment samples (St1-4) and landfill*
300 *sediments (n=3 at each station, standard error of the mean is given in Table S14). (Levels <LOQ were*
301 *treated as zero in this figure).*

302 **Contribution of different PFAS sources to water pollution**

303 The differences in the PFAS distribution patterns between water samples were considered to be
304 indicative of the different input from the different PFAS sources. A principle component analysis (PCA),
305 using PFAS profiles, i.e. individual PFAS are expressed as percentages of the $\sum_{14}$PFAS, was used to
306 investigate groupings between sample locations (Figure S5). The PCA revealed that the water samples
307 were distributed into five distinct groups: 1) marine water samples, 2) the snow sample, 3) LY-river, 4)
308 FFTS-pond, FFTS-creek, and 5) Landfill leachate and Ref-creek.

309 Concentrations of PFHxA, PFBS and PFOS were 1.7 to 5 times higher in the LY river compared to Ref
310 creek. The samples from LY-river represent glacial meltwater as well as run-off from the town of
311 Longyearbyen, whereas the Ref-creek sample represents meltwater from the annual snowpack. PFBS
312 is known as a major contaminant in wastewater effluents.[47] Thus, a significant local source of PFAS
313 originating from the Longyearbyen settlement has most likely resulted in the elevated PFAS
314 concentrations in the downstream part of the LY-river.[45] In contrast, PFHpA and PFNA were detected
315 at higher concentrations in the Ref-creek than in the LY-river, which might indicate that their source
316 is more due to atmospheric transport than a local source. Previously, PFOA and long-chain PFCA were
317 detected on particles collected from the Arctic atmosphere.[9] Due to their limited commercial
318 production ,[48] the presence of long chain PFCA with C≥10 in the river and the snow, points towards
319 long range transport and atmospheric oxidation of PFAS precursors to terminal end products, and
320 their subsequent atmospheric deposition.[21,14] However, these compounds were detected at LOQ
321 concentrations as depicted in Table S13.

322 The concentration ratio of PFOA to PFNA (C_8:C_9) in Ref-creek was 1.2 ± 0.2, whereas it was 1.9±0.1 in
323 the LY-river sample. Ratios observed in an Arctic ice core, which was presumed to receive input solely
324 from the atmosphere degradation of precursors were 1.5 ± 0.8.[21] Further study of remote Arctic ice
325 cores found that PFCA molar ratios of even-odd pairs were typically less than 2 and and greater than
326 0.5.[49] This is close to the ratio of C_8:C_9 in the snow sample in this study (1.63±0.04). Although this is
327 inline with the C_8:C_9 ratios from remote Arctic locations, further snow sampling is required to
328 understand if this as a result of atmospheric precursor degradation at this site, given its proximety to
329 known sources.

330 Possible sources of PFAS in snow could include marine aerosols,[50] direct local contamination[35] and
331 long range transport of PFAS precursors and, their subsequent degradation and deposition.[21] Previous
332 studies in Longyearbyen concluded that direct local inputs[45] were more important than inputs from
333 the atmospheric degradation of precursors or marine aerosols.

The concentration of L-PFOS (6.07 ng/L, 54.7% of $\sum_{14}$PFAS) in the snow sample in this study was significantly higher than PFOS previously reported in snow and ice cores at remote sites in Svalbard and the wider Arctic.[35] This suggests a significant local source, such as from firefighting training at the active coal mine (1.3 km from the sampling site), or from known local PFAS sources such as the FFTS (16.1 km).

Concentration and distribution patterns of PFAS in sediment

Figure 2 shows the concentration of PFAS in the sediments sampled at the landfill leachate channel and Adventfjord. All individual concentrations are listed in Table S14. Concentrations of $\sum_{14}$PFAS were higher in the sediment from the landfill (81.65±2.13 μg kg^{-1}) than in sediment from the fjord (maximum $\sum_{14}$PFAS = 4.61±3.92 μg kg^{-1}) (Fig. 1, Table S14), reflecting, similar to in the water samples, the difference in PFAS input. In sediment collected from the landfill, ∑PFOS (average concentration 45.4±1.54 μg kg^{-1}) contributed 55% and PFUnDA contributed 31% to $\sum_{14}$PFAS (Table S14). The high concentrations of PFAS in the sediment from the landfill are likely due to a combination of settling leachate particles as well as sorption of PFAS to the peat that dominated sediments at the landfill site.[51] It has previously been reported that FTOH in sediments can be biodegraded to PFCA[44] and this may explain the presence of long chain PFCAs in sediment samples of the landfill (PFCA C_{10}, C_{11}, C_{12}, C_{13} and C_{12} at 0.86, 25.5, 0.69, 4.21, and 0.04 μg kg^{-1} respectively) given that these compounds only have a limited number of direct applications in products. It is worth mentioning that PFAS emission from this landfill is considered low as the cold climate of Svalbard limits the volume of leachate production which has been estimated as 25 000 m^3 per year.[33]

Concentrations in the marine sediments from Adventfjord were generally low (Fig. 3, Table S14). However, the $\sum_{14}$PFAS in the marine sediment samples collected in the vicinity of FFTS influenced sites (St1 and St2; $\sum_{14}$PFAS=2.54±1.64) were significantly higher (Mann–Whitney-U-test, $p < 0.02$) than $\sum_{14}$PFAS in sediment samples from the reference station $\sum_{14}$PFAS=0.160±0.027 (Figure 2, Table S14). This confirms that there is a contribution from local sources to levels of PFAS observed in the marine sediments. 6:2 FTS was detected in all samples collected from station St1 (influenced by the active FFTS) at an average concentration of 4.0 μg kg^{-1}. 6:2 FTS was the most predominant compound (86% of $\sum_{14}$PFAS) at this station followed by PFOS (10%). PFOS was the most dominant compound in sediment samples collected from St2 (influenced by airport runoff), accounting for 45% of $\sum_{14}$PFAS. This indicates that this station was influenced by the FFTS. Long chain PFCAs (C_8-C_{14}) are the most predominant compounds (69% of $\sum_{14}$PFAS) in sediment collected from the background station, St4, followed by the PFBS (18%) and PFOS (7%), indicating at least a different source.

Concentration and distribution patterns of PFAS in pelagic marine biota - zooplankton

Figure 3 shows the PFAS concentrations (µg kg^{-1} ww) in zooplankton (dominated by *Calanus* spp.) collected from St1, St2, St3 and St4. PFAS were quantified in zooplankton at low concentrations (0.342-2.03 µg kg^{-1} ww). This can be attributed to the low levels of PFAS observed in the water column. Long chain PFCA (C_8-C_{13}) dominated the profiles at St1 (67% of $\sum_{14}$PFAS,) and St4 (48% of $\sum_{14}$PFAS) with a maximum concentration observed for PFUnDA (0.045µg kg^{-1} ww). 6:2 FTS dominated the profile at St2 which is directly impacted by FFTS emissions (accounting for 82% of $\sum_{14}$PFAS, 1.9 µg kg^{-1} ww). 6:2 FTS was the second most predominant PFAS in St1 which is also impacted by FFTS emissions (accounting for 26% of $\sum_{14}$PFAS, 0.19 µg kg^{-1} ww). The occurrence of 6:2 FTS in nine of the twelve zooplankton samples confirms its bioaccumulation potential which has been reported recently for invertebrates near a military airport.[25] Although neither PFHxA, nor PFHpA, were detected in any zooplankton samples, the short chain PFAS, PFBS was detected in four of the twelve zooplankton samples investigated at a maximum concentration of 0.735 µg kg^{-1} ww, confirming that PFSA are more bioaccumulative than PFCA.[52] Studies reporting PFAS concentrations in zooplankton in the Arctic are sparse in the scientific literature. PFOS was found at similar concentrations in zooplankton collected in the Baltic Sea 0.10±0.02 µg kg^{-1} ww.[53] A higher concentration range has been reported for PFOS in zooplankton from the Canadian Arctic, 1.1-2.6 µg kg^{-1} ww.[54]

Zooplankton plays an important role in the marine Arctic food web by transferring energy and carbon based nutrients from the primary producers (phytoplankton) to higher trophic levels.[55] Therefore, the bioconcentration of PFAS in zooplankton found in this study indicates an important exposure route of the marine ecosystem.

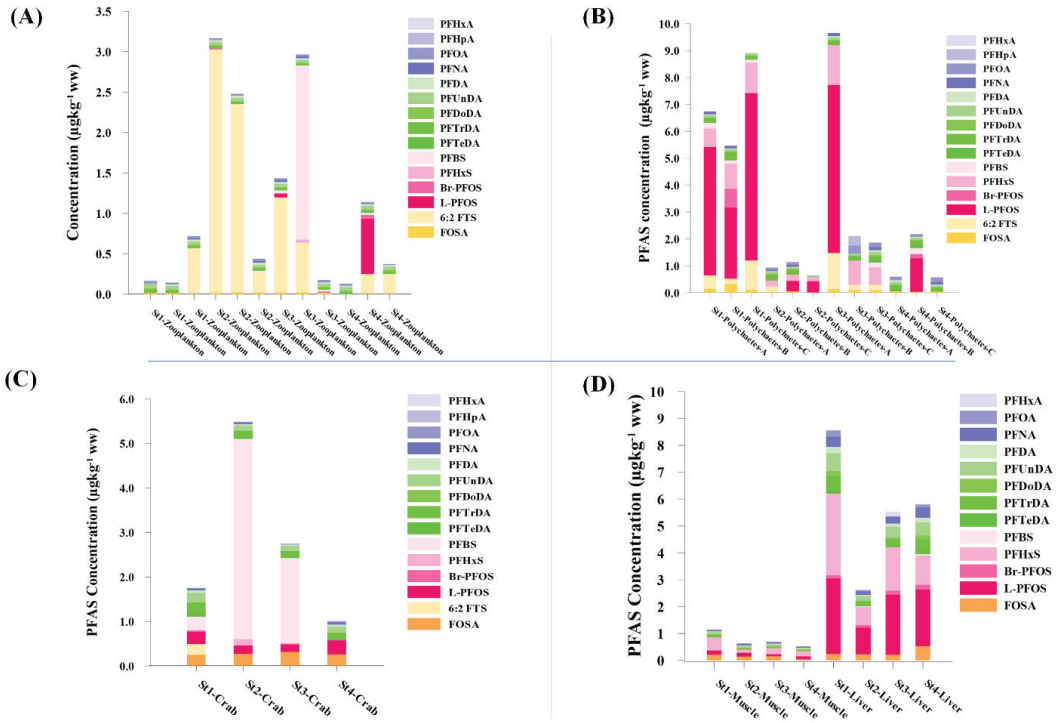

Figure 3. Average concentration of PFAS (μg kg^{-1} ww) detected in biota samples in the vicinity of Longyearbyen (Svalbard); (A) zooplankton; (B) Polychaetes; (C) Local crab samples (standard error of the mean is given in Table S17); (D) Local fish samples (muscle and liver) collected in the vicinity of Longyearbyen (Svalbard, standard error of the mean is given in Table S19 and S20).

Concentration and distribution patterns of PFAS in benthic invertebrates- Polychaetes

Unlike pelagic organisms, benthic organisms live in direct contact with the sediments, and therefore have the potential to scrape, tear, and filter sediment.[56, 57] Ingesting sediments and absorbing the released PFAS represent their main exposure pathways.[58] Polychaetes are representatives of the local benthic marine ecosystems and are expected to be indicators of the local PFAS exposure due to the relative immobility of polychaete species.[59] $\sum_{14}$PFAS in pooled polychaetes samples collected from the sediment samples was found in the range of 0.90 to 7.0 μg kg^{-1} ww (Figure 3 and Table S17). Similar to in the marine sediments, the maximum average $\sum_{14}$PFAS was observed in samples collected from the FFTS impacted station St1 (7.0±0.95 μg/kg) and the minimum $\sum_{14}$PFAS was observed in samples collected from the reference station (St4, 1.1±1.7 μg/kg). However, this difference was not found to be statistically significant ($p>0.05$). PFOS was the predominant PFAS in most polychaete samples accounting for 22% (St4) to 67% (St1) of the $\sum_{14}$PFAS. Long chain PFCA ($C_{9\text{-}14}$), PFOS, and FOSA were detected in all polychaete samples from all stations. 6:2 FTS was also detected in three of the four samples at low concentrations (<LOQ – 0.60 μg kg^{-1} ww) with the exception of the reference station

(St4). On average, 6:2 FTS occurs at the highest concentration in the active FFTS influenced station St1 (0.60 μg kg^{-1} ww), followed by station St3 (0.58 μg kg^{-1} ww). The detection of 6:2 FTS in polychaetes and sediment might indicate that sediment is a potential source for this PFAS in the marine ecosystem. In a previous study 6:2 FTS was detected in benthic invertebrates collected from the Canadian High Arctic at 0.43 ± 0.74 μg kg^{-1} ww.[60] Much higher concentrations (up to 630 mg kg^{-1} ww were measured in earthworms collected from a AFFF impacted site at a major Canadian Airport.[61] Therefore the present study confirms the bioaccumulation potential of 6:2 FTS in invertebrates. PFHpA was detected at St 2 at concentrations of 0.12 μg kg^{-1} ww. Since PFHpA was not detected in sediment samples, this might indicate that this short chain PFCA is a biotransformation product of PFAS precursors. Ruus et al.[62] also reported PFAS at the same concentration range in polychaetes collected from the densely populated Oslo Fjord (0.1 to 1.6 μg kg^{-1} ww). The levels of PFAS found in the current study were, however, considerably lower than those measured by Lescord et al. 2015 [60] in Canadian benthic invertebrates in Arctic fresh water lakes influenced by AFFF from airport activities (12-466 μg kg^{-1} ww).

Concentration and distribution patterns of PFAS in crabs

Concentrations of PFAS determined in 18 samples (whole body) of great spider crab (*Hyas Araneus*) (body weight = 76±8g) collected from the four stations are shown in Table S18 and Figure 3. PFCA ($C_{6,7,12}$) were not detected in any crab samples, indicating that these compounds were not enriched in crab tissues at detectable concentrations. In general, somewhat higher PFAS levels in crabs collected from contaminated sites (Stations St1-3, $\sum_{14}$PFAS=3.75±0.77 μg kg^{-1} ww, p=0.059) 1.28±0.95) were found compared to the reference station (St4, $\sum_{14}$PFAS=1.28±0.95 μg kg^{-1} ww). Long chain PFCA ($C_{8-11,13,14}$), FOSA, and PFOS were the predominant compounds in local crab samples with average percentage contributions to Σ_{14}PFAS of 28, 18, and 15%, respectively. However, PFBS dominated the profile of crab samples collected from the contaminated stations (St1-3) with average percentage contributions to Σ_{14}PFAS of 33% but was not detected in any crab sample collected from the reference station (St4, n=7).

PFHxS was found in a single crab collected at St2 at 0.14 μg kg^{-1} ww. FOSA was detected in all individuals collected from all stations at trace concentration ranging from 0.1 to 0.4 μg kg^{-1} ww. 6:2 FTS was quantified in only two crab individuals collected from station St1 at an average concentration of 0.66±0.43 μg kg^{-1} ww. A comparison between PFAS concentrations detected in crab samples from FFTS influenced sites (St1 and St2) and in those collected at the reference site (St4) is shown in Figure 6. $\sum_{14}$PFAS in FFTS contaminated crabs was significantly higher than in individuals from the reference site. This clearly indicates the contribution of the local sources to the levels of PFAS in crabs.

No correlation was observed between the biological parameters of crab individuals (size and weight, data not shown) and the concentrations of $\sum_{14}$PFAS. Similarly, no correlation was observed between crab sex and $\sum_{14}$PFAS levels. However, the highest $\sum_{14}$PFAS (9.5 µg kg^{-1}) was observed in a female individual collected from the FFTS impacted station (St2), and the lowest $\sum_{14}$PFAS (0.37 µg kg^{-1}) was observed in a male crab collected from the reference station (St4).

Previous studies reporting the concentration of PFAS in crabs are limited. In general, levels of PFAS determined here were in the lower range compared to previously reported levels for a military airport in Norway.[25] Langberg et al.[25] reported average levels of 5.50 ± 0.80 and 3.92 ± 0.79 µg kg^{-1} ww for PFOS in green shore crab (*Carcinus maenas*) and great spider crab respectively, collected at a military airport in Norway. These levels are higher than PFOS levels found in the current study (average 0.28±0.04 µg kg^{-1} ww). Similar, the authors reported higher 6:2 FTS concentrations (5.57-56.8 µg kg^{-1}) in great spider crab collected nearby the emission source compared to the average concentration observed at St1 in the present study where two individuals had quantifiable concentrations of 6:2 FTS (0.66±0.43 µg kg^{-1} ww). Higher PFOS concentrations (3.70–39.00 µg kg^{-1} ww) were also reported for mud crab (claw meat) from a contaminated Australian coastal estuary.[63] PFOS at relatively high levels (38–82 µg kg^{-1} dry weight) were measured in swimming crab collected from a river located in an industrial area of Tianjin, China.[64]

PFBS was detected at higher whole body concentrations (up to 8.5 µg kg^{-1} ww at St 2) than reported by Langberg et al.[25] and was detected in 1 to 3 individuals at all impacted stations (St1-3). This indicates that PFBS has a bioaccumulation potential in crabs. This contradicts the pharmacokinetics reported for PFAS in rats, monkeys, and humans,[65] although PFBS has been recently reported at 0.08 ± 0.11 µg kg^{-1} ww (whole body) in crabs (*Goniopsis cruentata*),[66] and at trace levels in polar bear plasma (max 0.69 µg kg^{-1}).[53, 67-69] Alternatively, PFBS in sediment can be an additional source for the invertebrates investigated. Higher PFBS concentrations were measured in fish tissues (<LOD to 16.90 ng/g of ww) from Yadkin-Pee Dee River, USA.[70] Penland et. al.[70] assumed that the biotransformation of an unquantified PFBS precursor may be responsible for the unexpected high level of this compound.

Concentration and distribution patterns of PFAS in marine fish

PFAS levels were determined in muscle and liver samples of individuals from two species (sculpin and wolffish, as described earlier) collected from St1-St4, as summarized in Figure 3 and table S19 and S20. Overall, low levels of PFAS were found in fish muscle samples (range $\sum_{14}$PFAS of 0.170-1.68 µg kg^{-1} ww) compared to liver samples ($\sum_{14}$PFAS ranged from 0.72 to 24.0 µg kg^{-1} ww). However, compared to

water concentrations, PFAS enrichment (bioaccumulation) was seen for several PFAS in both muscle and liver (see Table S19 and S20).

For muscle samples (sculpin: n=26 and wolffish: n=3) long chain PFCA (C_{8-14}), FOSA, PFHxS, as well as PFOS were detected in all samples investigated, whereas the short chain PFCA (PFHxA and PFHpA), and 6:2 FTS were not detected in any muscle sample. Likewise, PFBS was not detected in any muscle sample, and only in the liver of tow sculpin individuals at around 0.9 µg kg^{-1} ww concentration. PFOS was the predominant compound detected in all liver samples (sculpin: n=13 and wolffish: n=4) at an average concentration of ∑PFOS 2.2±0.27 µg kg^{-1} ww. The average contribution of PFOS to $\sum_{14}$PFAS in fish liver was 40±5%, and 18±2 % in muscle. The higher abundance of PFOS in liver confirms that PFOS tends to bioaccumulate in the liver compared to muscle tissue. This is in agreement with previous studies conducted on PFAS and PFOS specifically.[71-74] In contrast, PFHxS showed a high contribution to $\sum_{14}$PFAS in muscle (31±11%; maximum concentration=0.48 µg kg^{-1} ww) compared to liver (28±4%; maximum concentration= 3.0 µg kg^{-1} ww). Likewise, the contribution of long chain PFCA (C_{8-14}) to $\sum_{14}$PFAS was 33±5% and 26±3% in fish muscle and liver, respectively. PFUnDA was the most predominant of these long chain PFCA detected at a maximum concentration of 0.127 µg kg^{-1} ww (in muscle) and 1.55 µg kg^{-1} ww (in liver) of individuals collected from St1. Quantifiable concentrations of PFHxA (0.16±0.10µg kg^{-1} ww, average for 3 individuals out of 10) were detected in liver of individuals collected from St 3.

As expected for the benthic sculpin species, which do not migrate over significant distances,[75] muscle samples of individual collected from the FFTS influenced stations (St1 and 2) showed significantly higher $\sum_{14}$PFAS concentration (0.955±0.127 µg kg^{-1} ww; p=0.030) than in individuals from the reference site (St4) (0.523±0.127 µg kg^{-1} ww). Although, this difference is insignificant in liver samples (5.34±1.74 and 5.20 ±2.89 µg kg^{-1} ww in FFTS impacted station and the reference site, respectively), the highest average $\sum_{14}$PFAS concentration was observed in liver of fish collected from the FFTS impacted station (St1; 24.0 µg kg^{-1} ww) and the lowest was observed in the liver of the individual collected from the reference station (St4; 0.72 µg kg^{-1} ww). There were no significant differences in PFAS concentrations observed between the two investigated fish species, although differences in specific accumulation and elimination behaviour of individual PFAS have been found for different fish species in Lake Ontario [73].

Overall, the PFAS profile in fish investigated here is consistent with the PFAS profile of fish collected from AFFF impacted waters.[76] Data for PFAS levels in Arctic coastal fish populations is limited. In a previous study, PFOS and FOSA dominated in livers from the same sculpin species (*Myoxocephalus scorpius*) sampled close to a city or settlement from Iceland and the Faroe islands.[74] PFHxA constituted a significant proportion of the ∑PFAS in sculpin livers from Iceland.[74] These authors reported similar

PFAS concentrations ($\sum_8$PFAS <10 μg kg^{-1} ww) in sculpins collected from Faroe Islands, and higher PFAS concentrations ($\sum_8$PFAS >60 μg kg^{-1} ww) in those from Iceland.

Based upon the current results, bioaccumulation factors (BAF) were calculated for selected PFAS where concentrations were above the LOQ for both water and fish (Table S21). The Log BAFs of the investigated PFAA in the fish liver were higher than in the muscle, which is consistent with a recent studiy.[77] For instance, the tendency of PFOS to bioconcentrate in liver rather than fish muscle is clearly shown (Table S19 and S20), as previously reported [78]. This is most likely due to the affinity of PFAS to bind to proteins involved in fatty acid transport and metabolism such as liver fatty acid binding proteins [79, 80]. In line with several previous studies, Log BAFs of PFCA positively correlate with the perfluorinated carbon chain length.[73, 77] Log BAF increased from PFOA (Log BAF_{muscle}=2.09±0.103 and Log BAF_{liver}=2.87±0.210) to PFDA (Log BAF_{muscle}=3.19±0.161 and Log BAF_{liver}=3.78±0.357). However, PFUnDA showed lower Log BAF (Log BAF_{muscle}=2.61±0.110 and Log BAF_{liver}=3.41±0.221), possibly due to a decreased gill permeability.[73] A similar trend was observed for forage fish from Etobicoke and Spring Creeks nearby Toronto International Airport where the author reported comparable Log BAF_{liver} values.[81] However, differences in fish species and diets are the important factors for PFAS accumulation, and hence determine BAF values.

In the current study, PFOS liver/muscle concentration ratios calculated for individual fish ranged between 5 and 52 with an average of 18. These ratios are comparable to most previously reported values for different fish species collected from various locations. For instance, Pan et al.[71] reported ratios for PFOS ranging from 6.9 to 42 for fish species collected from Chinese rivers. Becker et al.[82] reported a value of 9.5 for PFOS in chub from a German river. In addition, Nania et al.[83] reported a ratio of 61.5 for different pelagic and benthic marine fishes collected from the Mediterranean Sea, which is comparable to the range in the current study.

Concentration and distribution patterns of PFAS in Glaucous gull *(Larus hyperboreus)*

The occurrence of a multitude of organic pollutants (including PFAS) in seabirds is one of the main causes of concern for seabird species in the Norwegian Arctic. Previous analyses of glaucous gull samples collected from Svalbard have detected several organic pollutants accumulated in their tissues.[84-86] It has been estimated that the breeding population of the glaucous gull on Bjørnøya in the Svalbard archipelago declined with 65% from 1986 to 2010 mainly due to elevated pollutant levels.[87]

Glaucous gull represents a high trophic level in the Arctic marine food web. In this study, 20 glaucous gulls were collected in the vicinity of Longyearbyen and analysed for PFAS. In total, 9 PFAS could be quantified in 20 glaucous gull livers as shown in Table S22 and Figure 4. PFOS was the predominant

PFAS detected in all individual samples at concentrations varying from 12.7-433 μg kg^{-1} ww, representing approximately 80% of $\sum_{14}$PFAS. Haukås et al.[88] reported a concentration of 65.8±22.4 μg kg^{-1} ww (n=9) for PFOS in glaucous gull livers collected in the Eastern Barents Sea close to Svalbard, which is slightly higher than the PFOS concentration reported herein (55.0±20.5 μg kg^{-1} ww). Tomy et al.[54] reported PFOS concentrations (20.2±3.9 μg kg^{-1} ww) in glaucous gulls livers sampled in 2007 from Eastern Arctic background locations which were approximately 40% of the herein reported concentrations.

The second most abundant PFAS group was the odd-numbered long chain length PFCA (C_9, C_{11}, C_{13}), which were detected at high concentration (3.16±0.375, 4.38±0.556, 1.55±0.351μg kg^{-1} ww, respectively) compared to the even-length PFCA homologues (8, 10, and 12 14, at 0.101±0.025, 1.95±0.190, 0.710±0.078 and 0.182±0.015 μg kg^{-1} ww respectively). This means that the odd-numbered PFCA was higher than the adjacent shorter even-numbered PFCA. This is in agreement with recent studies conducted on PFASs in plasma samples of Glaucous gull from Svalbard.[86, 89] This observation has also been made for other Arctic biota, including fish, birds and mammals.[90] Long-range transport and degradation of FTOHs is assumed as a source for the observed long-chain PFCAs in arctic animals[18]. Strong positive correlations were observed between PFOA and PFNA and between PFDA and PFUnDA ($r>0.7$, $p<0.001$), confirming their similar source. In contrast PFCA showed strong negative correlations with PFOS, suggesting a different source and transformation pathway ($r>0.8$, $p<0.001$). Assuming that the source of the long-chain PFCAs is the transformation of typically even-numbered FTOHs which degrade into odd and even-numbered PFCAs at similar yield, the abundance of odd-numbered PFCAs of higher chain length can be attributed to the higher bioaccumulation.[18] For instance, 8:2 FTOH forms both PFOA and PFNA in equal yields, but as PFNA is more bioaccumulative [91], suggesting that Glaucous gull samples carry a higher load of PFNA than the even-numbered homologue PFOA. Likewise, the degradation of 10:2 FTOH and 12:2 FTOH and the subsequent bioaccumulation interpret the higher abundance of PFUnDA compared to PFDA and PFTrDA compared to PFDoDA.

Overall, high individual variability in distribution of PFAS in the livers of the collected Glaucous gulls was observed, indicating individual differences in their feeding habits. Glaucous gulls have opportunistic feeding habits throughout the year, feeding on food items from human wastes, and preying on other seabirds, such as little auks (*Alle alle*) and black-legged kittiwakes (*Rissa tridactyla*), as well as fish, crabs and amphipods.[92, 93, 94]

At Svalbard, the glaucous gull (*Larus hyperboreus*) is considered the most important avian predator and occupies the same ecological niche as birds of prey further south.[94] Most bird species in Svalbard

migrate to Greenland and the open Barents Seas outside the nesting season.[87] Some glaucous gulls also winter in the restricted ice-free waters near shore off Svalbard [87], although the wintering locations of the sampled individuals are not known. Food related uptake is today considered the main source of PFAS for seabirds, however other factors can drive accumulation patterns of PFAS such as metabolic capabilities, habitat use, or migration.[60, 95] Although there were no significant sex related differences in PFAS levels among the individuals investigated, female individuals showed a relatively higher $\sum_{14}$PFAS concentration 68.2±14.7 than male individual 53.0±18.0. This agrees with recent studies where sex-related differences in PFAS concentrations were reported.[86, 89] Since the gulls were sampled prior to breeding, it is likely that they have been exposed to and accumulated PFAS when feeding in their wintering grounds. Thus, the PFAS body burdens of the bird constitutes of a mixture of PFAS compounds that have accumulated during feeding in their unknown wintering grounds, and in Adventfjord following their return to Svalbard. This makes it difficult to conclude on the dominant source. Nevertheless, the $\sum_{14}$PFAS liver concentrations in the present gulls were twice those in the fish livers, clearly documenting biomagnification of PFAS. Two gulls had relatively high concentrations of PFHxS, that could be related to local sources, but also could indicate that they wintered in the same area.

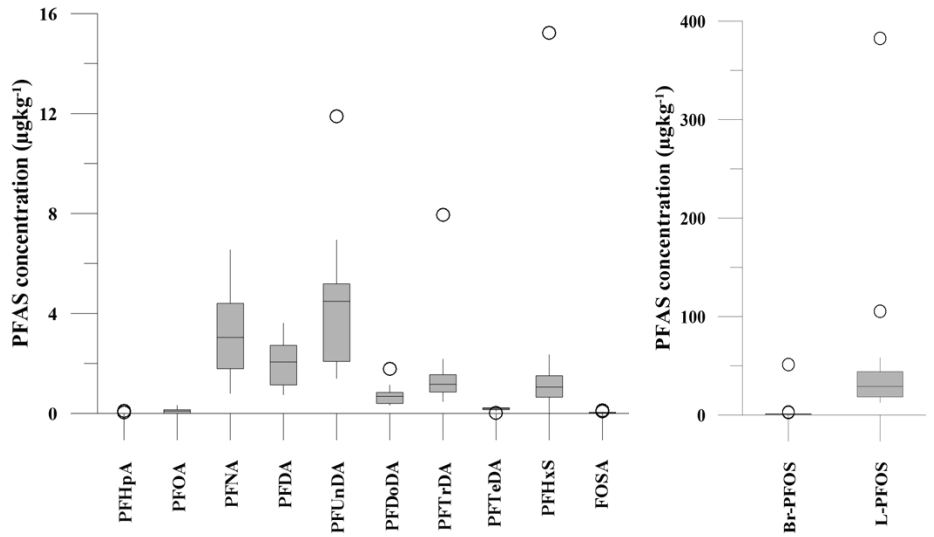

Figure 4. PFAS concentration measured in glaucous gull individuals (n=20) collected in the vicinity of Longyearbyen (Svalbard) sampled in 2018. The horizontal bisecting lines show the medians; boxes show the first and third quartiles; whiskers represent the interquartile range. The circles represent concentrations >1.5 times the interquartile range from the edge of the box.

Pattern of perfluorooctane sulfonate (PFOS) isomers in the local marine environment

The production of PFOS and perfluorooctanesulfonyl fluoride (POSF) based products by 3M was carried out using electrochemical fluorination (ECF) which resulted in 70±1.1% of the linear isomer and 30±0.8% of the branched isomer.[7, 8] Therefore, comparing the profile of PFOS isomers (branched and linear) in environmental samples with their profile in the technical mixture produced by ECF could provide insights in to the transport and distribution of PFOS in the environment.[96-98] Further, elevated percentages of branched PFOS isomers (Br-PFOS) caused by the preferential transformation of branched PFOS precursors can be used as an indicator of the contribution from PFOS precursors.[99] However, this can be complicated by the fact that PFOS isomer patterns can be significantly influenced by differences in sorption and by the differential uptake and elimination of Br-PFOS compared to L-PFOS.[99, 100] Figure 5 and Table S23 show the relative distribution of total branched PFOS isomer (Br-PFOS) and linear PFOS (L-PFOS) in abiotic and biotic samples investigated in the current study.

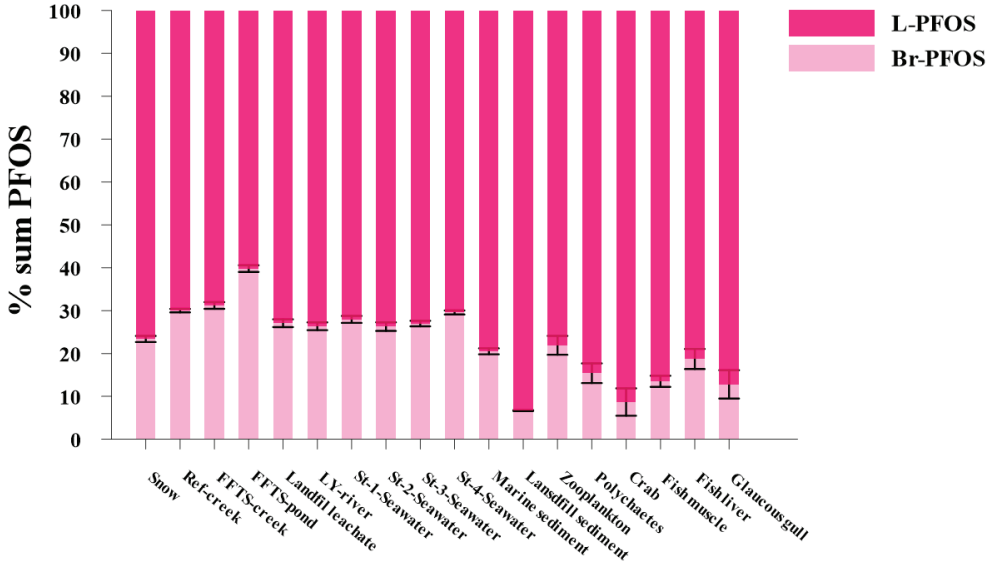

Figure 5. Relative distribution (mean±SEM) of the sum [∑] branched PFOS isomer (Br-PFOS) versus linear PFOS (L-PFOS) in abiotic and biotic samples in the Longyearbyen area. (error bars show ±standard error of mean, SEM).

Abiotic samples

From Figure 5 it is clear that the percentage of the isomers varies between sample matrices. overall, it is notable that a reduced contribution of branched PFOS content was observed in most biota and sediment samples compared to water. For water samples, the PFOS isomer profile in run-off from the active FFTS area (FFTS-creek), appeared similar to the historical 3M ECF PFOS (30±0.8% branched

609 isomers), with Br-PFOS contribution of 30.0±0.78% of total PFOS. Likewise, the isomer profiles
610 observed in LY-river and landfill leachate (26.3±0.91 % and 27.1±0.91% Br-PFOS, respectively) are
611 comparable to the historical 3M ECF profile. Similar isomer profiles were observed in seawater
612 samples (Br-PFOS contribution of 26-29 % of total PFOS), suggesting that a large proportion of the
613 PFOS contamination in seawater can be attributed to these local sources.

614 In the pond affected by the drainage from the airport and the old FFTS station, a higher Br-PFOS
615 percentage was found (39.8±0.78% of total PFOS). A similar PFOS isomer profile was observed in AFFF
616 impacted sample collected at the training ground of a FFTS at Bergen airport, Norway.[97] The reason
617 for this branched enrichment at the pond is unclear, however the preferential degradation of the
618 branched precursors of PFOS used at the FFTS and stronger sorption/uptake of L-PFOS are possible
619 reasons. [97, 101, 102] The limited water exchange between FFTS-pond water and seawater might be the
620 reason for the observed branched enriched profile which allowed steady increase in the percentage
621 of branched isomers over time, while water exchange reduces the branched isomers in seawater and
622 river water. The deficiency in branched PFOS found in the surface snow sample could be explained by
623 the preferential sorption of L-PFOS to the suspended particulate matter fraction.[102]. It should be noted
624 that the Br-PFOS percentage did not correlate with the total PFOS concentration change (Figure S7).
625 It has previously been reported that L-PFOS binds more strongly to organic matter than Br-PFOS,
626 owing to its greater hydrophobicity.[100] Compared to the marine sediment from Adventfjord, sediment
627 samples collected from the Longyearbyen landfill showed a higher contribution of L-PFOS. This can be
628 attributed to the peat like nature of the landfill sediments in which PFAS can partition.[51]

629 Biotic samples

630 The biotic samples were dominated by L-PFOS with percentages ranging from 78 to 91. This is in
631 agreement with several previous studies.[103] For instance, in minnow (*Hemiculter lcucisculus*), and
632 white shrimp (*Exopalaemon*), L-PFOS was found to contribute 78.6% and 95.5% of the total PFAS,
633 respectively [103]. Similarly, L-PFOS was found in more than 88% of the biota collected from Lake
634 Ontario [100] and was predominant in herring gull and polar bear from the Great Lakes and Arctic.[104]
635 These results indicate the selective bioaccumulation of L-PFOS in biota and/or the preferential
636 excretion of Br-PFOS, which has been documented in different laboratory studies [105, 106].

637 The PFOS isomer pattern found in all benthic organisms investigated (polychaetes, crab, benthic fish)
638 was similar to that found in sediment and more enriched in L-PFOS than in pelagic organisms 21.9±2.2
639 (zooplankton. This greater relative percentage of Br-PFOS in the lowest tropic level could be due to
640 the exposure of zooplankton to PFOS precursors (e.g. N-EtFOSE), where branched PFOS precursors are

biotransformed at a higher rate compared to the linear precursors which leads to an enriched branched PFOS isomer profiles [99]. Some systematic analytical bias resulting from matrix-induced ionization should be anticipated which is not unusual.[107] Therefore, isomer specific analytical method applying exactly-matched isotopically-labelled internal standards for all isomers is needed for accurate isomer profiles. However, this does not diminish the importance of the observed relative differences of the isomer profiles between the samples.

Changes in distribution pattern of PFAS in the local environment

In this study, the PFAS distribution was characteristically different for the respective sampled media types. As shown in Figure 6 and Figure S6, the abiotic samples from the assumed point source zones (FFTS-pond, -creek and landfill) contained high percentages of short and long-chained PFCA, specifically PFCA C_6 to C_9. This is also characteristic for the samples from LY-river and the assumed background sample Ref-creek. However, the source zones also contained 6:2 FTS. The snow sample was dominated by the long-chained PFSA (PFOS), similar to the profile observed in seawater. However, the snow sample contained a higher percentage of short-chained PFHxS. The marine sediment samples were dominated by the long chain PFCA >C_{10} in addition to 6:2 FTS and PFOS and contained short chain PFSA. Zooplankton was characterised by the presence of 6:2 FTS and long chain PFCA in addition to the presence of PFBS and PFOS. Similar to sediment, PFAS composition in the benthic organism polychaetes and crabs was dominated by long chain PFCA, PFOS, and PFBS in addition to some FOSA, and 6:2 FTS. The characteristic PFAS profiles in fish and glaucous gull were composed of a high proportion of PFOS.

The relative contribution of total PFOS to $\sum_{14}$PFAS increased from zooplankton (30%), polychaetes (36%), crab (30%), fish (40 %), to glaucous gull (72%), which indicates a high biomagnification potential of PFOS compared to other PFAS as previously reported.[103, 108, 109 88] Transformation of PFOS precursor compounds[110] has been suggested to be one reason for this.[103] Supporting this, the relative contribution for FOSA, which is a PFOS precursor, decreased in our samples from zooplankton (71%) to crab and polychaetes (21,6 and 5 % respectively) to 0.09% in glaucous gull. This suggests that the biotransformation of this precursor increases with increasing trophic level and consequently contributes to the relative amount of PFOS in the sampled organisms.[54, 111]

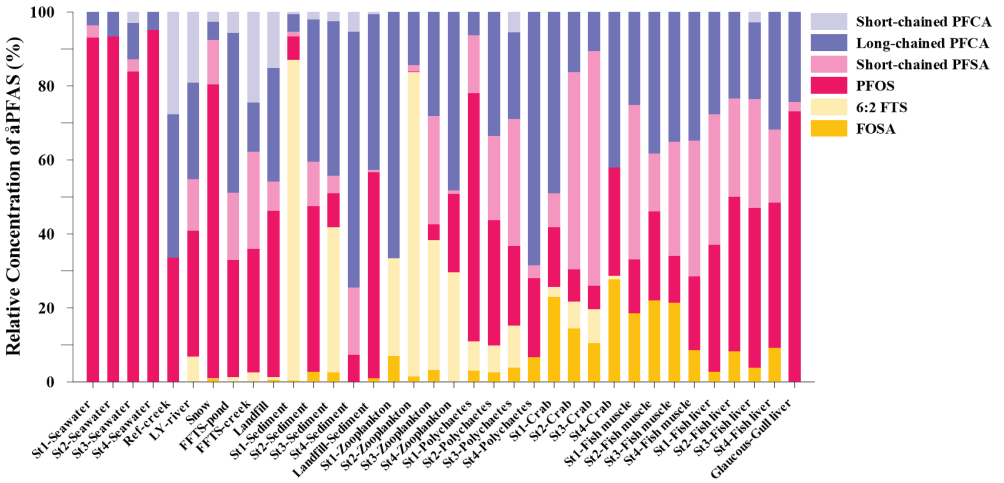

Figure 5. Average relative composition profile [%] for PFAS in abiotic and biotic samples collected from Adventfjord and Isfjord, near the Svalbard Airport. (Levels <LOQ were treated as zero in this figure). Short-chained PFCA: PFHxA and PFHpA; long-chained PFCA: C8-C14; Short-chained PFSA: PFBS and PFHxS; Long-chained PFSA: PFOS.

CONCLUSION

The firefighting training stations (FFTS) at Svalbard airport and diffuse release from the local settlement were the major local PFAS sources. The high concentration observed in landfill leachate illustrates the wide application of PFAS in consumer products. Thus, local anthropogenic activity represents a significant source of PFAS. The much lower concentrations detected in the seawater samples suggests that following release from the point sources, significant dilution of PFAS occurred by seawater circulation in the coastal waters of Adventfjord.

In the marine biota, PFAS levels increased from zooplankton to polychaete, crab, fish liver and gull liver. The distribution among the 14 target PFAS changed with increasing trophic level from low percentages of L-PFOS in in zooplankton and polychaetes to being dominated by linear PFOS in fish (40%) and gull liver (73%). Although the possible contribution of local sources to the relatively high PFAS concentrations in glaucous gulls cannot be evaluated, the high concentrations in their livers clearly demonstrates the biomagnification potential of PFAS, in particular L-PFOS. Results in the current study indicate bioaccumulation potential of compounds that have been taken into use as substitutes for PFOS, namely 6:2 FTS and PFBS in marine invertebrates, however they were not found in organisms at higher trophic levels. Toxicological information of this compounds remains unclear. Hence, further studies are needed to investigate the effect of exposure to these PFAS at the base of the marine food web.

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Appendix: Paper V

The fate of poly- and perfluoroalkyl substances in a marine food web influenced by land-based sources in the Norwegian Arctic

SUPPLEMENTARY INFORMATION

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Sample collection data

Table S1. Properties of investigated water samples

Location	Water samples (L)	Field		Laboratory	
		EC (µS/cm)	Temp. (ºC)	pH	Temp. (ºC)
Landfill	1.5	2550	5.20	7.60	13.20
LY-river	1.5	218	2.40	6.10	11.00
FFTS-pond	1.5	308	3.90	6.50	11.20
FFTS-creek	1.5	237	6.90	6.40	10.40
Ref-creek	1.5	62.4	-	5.80	19.90

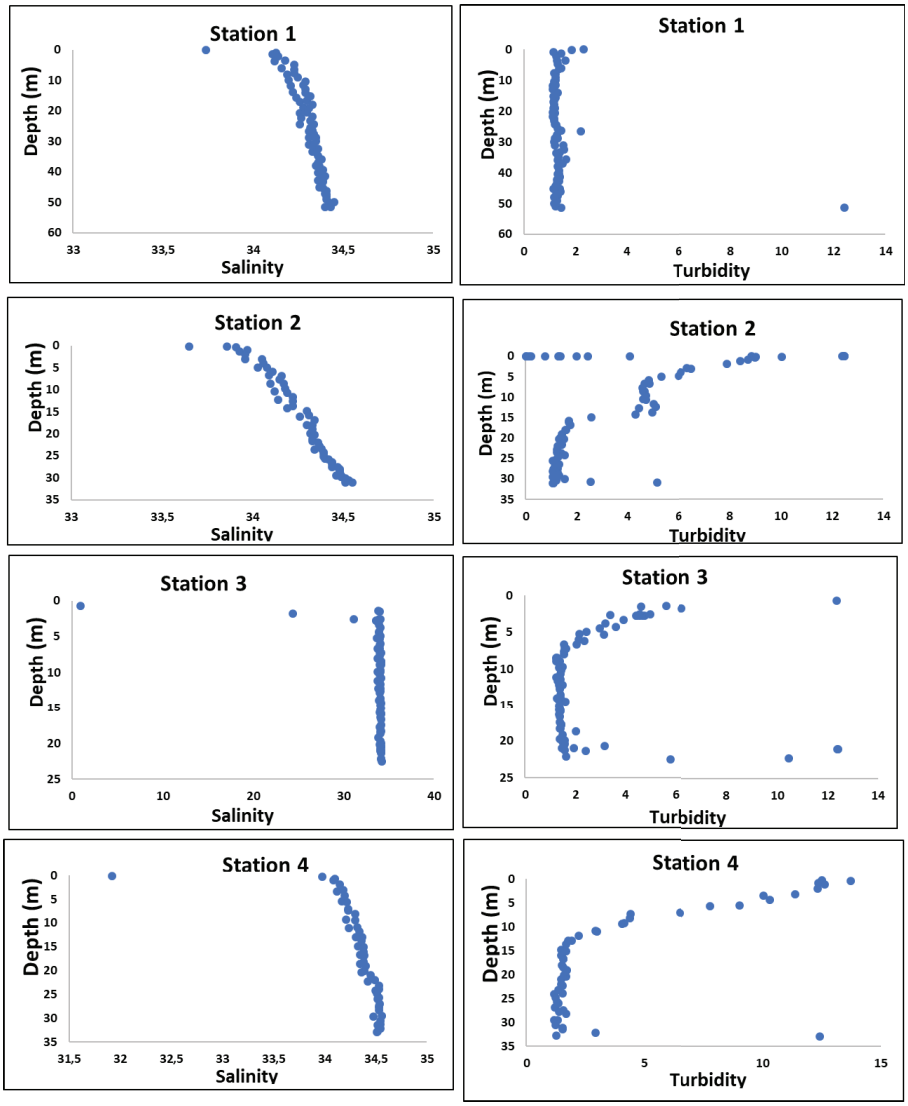


Figure S1. Turbidity and salinity depth profile at stations 1-4 in Adventfjorden.

Table S2. Weight of collected plankton and polychaete samples from different stations

Station	Plankton (g)	Polychaete (g)
St1	24.88	11.08
St2	25.59	10.84
St3	16.51	12.14
St4	36.01	9.00

Table S3. Biological parameters for collected crab individuals (Hyas araneus) from Adventfjorden/Isfjorden.

Station	Sample Name	Sex	Wdith (cm)	Length (cm)	Weight (g)
St1	Cr-1	M	6.5	8.6	123.89
	Cr-2	M	5.3	6.8	77.45
	Cr-3	M	5.1	7.2	77.45
	Cr-4	M	3.6	5.5	43.84
	Cr-5	M	3.6	5.3	38.09
	Cr-6	F	3.4	4.6	21.71
	Cr-7	M	4.4	6.3	54.88
	Cr-8	M	4.2	5.8	38.78
	Cr-9	M	5.5	7.4	116.01
	Cr-10	M	3.4	4.6	22.29
	Cr-11	M	2.7	4.0	13.27
	Cr-12	M	5.1	7.4	97.95
	Cr-13	M	5.1	7.4	93.72
	Cr-14	M	4.7	6.9	96.38
St2	Cr-1	M	6.1	7.6	108.51
	Cr-2	M	5.4	7.3	88.08
	Cr-3	F	4.4	5.4	32.19
	Cr-4	M	6.2	8.7	108.59
	Cr-5	M	3.3	4.5	19.83
	Cr-6	M	6.7	8.9	184.38
	Cr-7	M	6.3	8.4	118.62
	Cr-8	F	3.2	4.6	20.02
	Cr-9	M	3.5	4.9	25.56
	Cr-10	M	2.9	4.3	17.83
	Cr-11	M	6.1	8.0	157.00
	Cr-12	M	4.3	5.9	53.88
	Cr-13	M	5.7	7.9	107.90
	Cr-14	M	6.0	8.2	155.52
St3	Cr-1	-	-	-	-
St4	CR-1	F	5.6	6.8	59.48
	Cr-2	F	5.0	6.6	64.12
	Cr-3	F	4.6	5.8	46.13
	Cr-4	F	4.8	6.5	69.15
	Cr-5	M	6.4	8.2	150.49
	Cr-6	M	6.5	8.4	126.04
	Cr-7	M	4.9	6.4	76.93
	Cr-8	F	5.0	6.8	73.33
	CR-9	F	5.0	6.9	91.29

Table S4. Biological parameters of collected fish. SC: sculpin (Myoxocephalus scorpius). WF: wolffish (Anarhichas lupus).

Station	Sample Name	Weight (g)	Length (cm)	Liver weight (g)	Muscle sample (g)
St1	SC-1	126.6	21.6	2.97	11.77
	SC-2	61.79	18.1	1.49	6.95
	SC-3	529.88	30.9	32.61	21.1
	SC-4	263.76	25.7	15.07	14.18
	WF-1	856.1	45.8	26.1	30.76
St2	SC-1	279.3	27	11.79	20.58
	SC-2	243.9	25.9	17.18	16.73
	SC-3	358.22	27.5	22.02	17.3
	WF-1	2220	56.4	41.01	50.09
St3	SC-1	151.08	22.8	6.16	21.17
	SC-2	109.8	21	1.57	18.17
	SC-3	127.17	21.1	5.93	6.69
	SC-4	367.97	29.3	14.2	19.86
	SC-5	217.39	22.5	15.45	12.3
	SC-6	78.49	18.2	2.09	6.93
	SC-7	229.4	24.4	10.94	15.12
	SC-8	88.48	16.9	2.88	1213
	SC-9	73.22	18.1	1.34	9.14
	SC-10	69.92	17.4	1.89	5.54
	SC-11	102.77	19.1	7.78	9.37
St4	SC-1	75.35	18.2	2.13	14.81
	SC-2	131.72	21.18	3.32	19.45
	SC-3	62.52	17.8	0.56	8.76
	SC-4	87.93	20.3	1.71	11.46
	SC-5	232.83	26.4	5.39	24.28
	SC-6	89.69	19.4	2.75	11.99
	SC-7	113.88	21.3	3.23	7.19
	SC-8	92.3	19.1	2.66	7.48
	WF-1	780	43.5	13.56	62.93

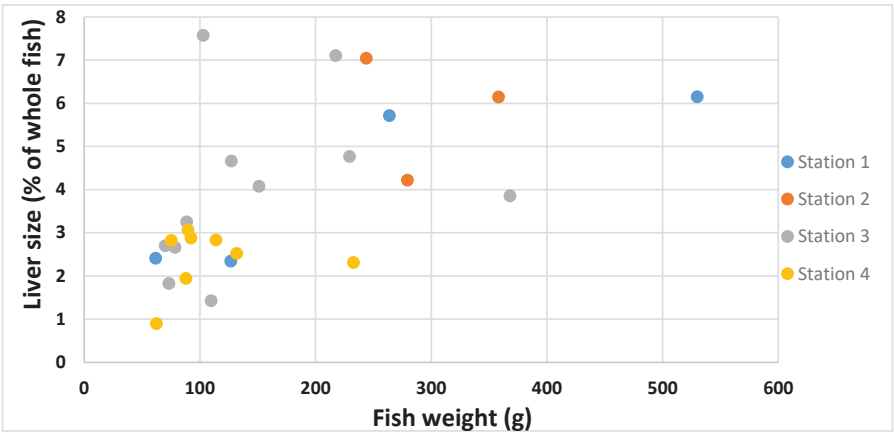


Figure S2. Sculpin (Myoxocephalus scorpius) relative liver size versus individual weight

Table S5. Biological parameters of collected glaucous gulls (Larus hyperboreus).

Sample Code	Sex	Body mass (g)	Liver mass (g)	Gonad mass (g)	Heart mass (g)
G-1	male	1860	38.94	2.2	18.07
G-2	female	1340	30.71	1.25	12.07
G-3	female	1580	36.22	1.83	14.9
G-4	female	1610	37.7	1.81	11.6
G-5	female	1573	41.26	2.11	13.31
G-6	female	1855	39.45	1.79	14.97
G-7	female	1371	37.11	1.27	11.27
G-8	male	2196	40	3.11	15.91
G-9	male	2141	38.87	na	15.57
G-10	male	1947	44.17	2.78	16.84
G-11	female	1355	35.46	1.32	11.25
G-12	male	1943	40.19	5.19	14.38
G-13	female	1434	33.01	0.49	11.8
G-14	female	1363	26.1	1.62	12.61
G-15	male	2026	43.2	3.92	18.12
G-16	male	2210	43.9	3.41	17.12
G-17	female	1700	50.06	4.3	12.99
G-18	female	1640	36.7	1.98	13.91
G-19	male	2011	29.21	2.38	16.3
G-20	female	1407	45.29	0.61	11.92

Detailed description of the chemical analysis

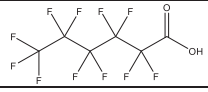
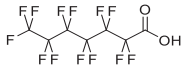
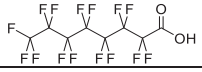
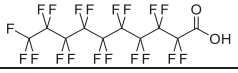
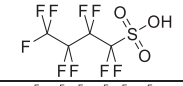
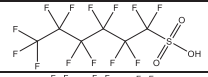
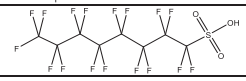
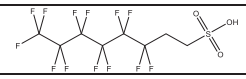
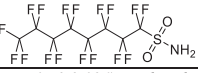
Standards and Chemicals

The following chemicals were applied for sample preparation and clean-up for subsequent LC/MS analysis: Glacial acetic acid (CH_3COOH, ACS reagent, ≥99.7%, Merck KGaA, Darmstadt, Germany), Q-guard 1 (MilliQ water purification, Billerica, MA, USA), Methanol (MeOH, HPLC grade, VWR International AS, Oslo, Norway), ammonium acetate ($NH_4CH_3CO_2$, 98.0%, Merck, Darmstadt, Germany), sodium hydroxide (NaOH, Sigma-Aldrich, ≥97.0%, St. Louis, MO), hydrochloric acid (HCl, 35%, Sigma-Aldrich, St. Louis, MO). All PFAS and their isotopically labeled internal standards (ISTDs) (Table S6) and analytical standards (all >98%) were produced by Wellington Laboratories (Guelph, Canada) and supplied by Greyhound Chromatography and Allied Chemicals (Merseyside, England).

1. Preparation of water samples

Water samples were prepared according to [1, 2] with some modifications. Unfiltered water samples (750 mL each, spiked 50µL of 500 ng mL^{-1} ISTDs mix) were extracted by solid-phase extraction (SPE) using mixed mode reverse phase/weak anion exchange (WAX); Oasis® WAX (500 mg, 6 cc, 60 µm, Waters, Milford MA, USA). The SPE cartridges were placed on a vacuum manifold and were conditioned by 4 mL of 0.1 % ammonia in methanol followed by 4 mL of methanol and 4 mL of Mill-Q water. SPE-cartridges were kept wet using additional 4 mL of Milli-Q water before loading the samples through a reservoir adapter and polypropylene (PP) tubing (o. d. 1/8"). Samples were loaded by the aid of a mild vacuum (water jet) and the flow rate was kept at 1-3 drop per second. The cartridges were cleaned with 4 mL acetate buffer of pH 4 and dried under vacuum for 15 min. Afterwards, the cartridges were eluted using 4 mL of methanol followed by 4 mL of 0.1% NH_3 in methanol. The eluates were collected in 15 mL polypropylene centrifuge tubes (VWR International, Radnor, PA, USA). The resulting eluates were dried at 37 °C under a gentle stream of N_2 (AGA, Oslo, Norway, N_2 5.0 quality) using a Reacti-Therm III evaporating unit (Thermo Fisher Scientific Inc., Rockford, USA). Twenty microliters of recovery standard (500 ng mL^{-1}) were added to each sample followed by addition of 450 µL MeOH. The residues were re-dissolved in 0.5 mL of methanol using vortex mixing (VWR mixer mini vortex 230V EU, VWR International, Radnor, PA, USA), filtered through a 0.2 µm nylon membrane microcentrifuge filter (Spin-X, Costar, Corning Inc., Corning, NY, USA), and transferred into PP vials for HPLC-MS/MS.

Table S6. The 14 poly- and perfluoroalkyl substances (PFAS) quantified in the Longyearbyen study

Analyte Name	Acronym	CAS #	Formula	Structure*	LogP**	LogD (7.4)**	Log *Koc*
PFCA							
Perfluorohexanoic acid	PFHxA	307-24-4	$F(CF_2)_5COOH$		5.97	0.15	1.31[3]
Perfluoroheptanoic acid	PFHpA	375-85-9	$F(CF_2)_6COOH$		6.86	1.11	1.63[3], 2.1[4]
Perfluorooctanoic acid	PFOA	335-67-1	$F(CF_2)_7COOH$		7.75	1.82	1.89–3.5[5-7 3, 8]
Perfluorononanoic acid	PFNA	375-95-1	$F(CF_2)_8COOH$		8.64	2.84	2.36–4.0[3-5, 7]
Perfluorodecanoic acid	PFDA	335-76-2	$F(CF_2)_9COOH$		9.53	3.62	2.96–4.6[3-5, 7]
Perfluoroundecanoic acid	PFUnDA	2058-94-8	$F(CF_2)_{10}COOH$		10.42	4.23	3.3–5.1[3-5, 7]
Perfluorododecanoic acid	PFDoDA	307-55-1	$F(CF_2)_{11}COOH$		11.31	4.58	5.6 ± 0.2[4]
perfluorotetradecanoic acid	PFTriDA	72629-94-8	$F(CF_2)_{12}COOH$		12.19	4.97	-
Perfluorododecanoate	PFTeDA	376-06-7	$F(CF_2)_{13}COOH$		13.08	5.77	-
PFSA							
Perfluorobutane sulfonic acid	PFBS	375-73-5	$F(CF_2)_4SO_3H$		3.68	-1.56	1.22[8], 1.79[3]
Perfluorohexane sulfonic acid	PFHxS	355-46-4	$F(CF_2)_6SO_3H$		5.25	-0.54	2.05–3.7[3, 4, 7]
Perfluorooctane sulfonic acid	PFOS	1763-23-1	$F(CF_2)_8SO_3H$		7.03	0.66	2.6–3.8[3-8]
FTSA							
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2	$F(CF_2)_6(CH_2)_2SO_3H$		3.47	-1.00	-
preFOS							
Perfluorooctane sulfonamide	FOSA	754-91-6	$C_8H_2F_{17}NO_2S$				4.2–4.5[6, 7]

**All structures were prepared with ChemDraw Professional (version 15.0.0.106), PerkinElmer Informatics, Inc. (Boston, Massachusetts, USA) ** Predicted data is calculated with ACD/Labs Percepta Platform − PhysChem Module, Toronto, CA*

2. Preparation of snow sample

A snow sample was collected according to [1]. An aluminum shovel was precleaned, rinsing with MilliQ and then MeOH and transported wrapped in MeOH rinsed aluminum foil. An LDPE container was precleaned by washing with soapy water, rinsing several times with tap water, rinsed 5 times with MilliQ and then rinsed 3 times with MeOH. Surface snow was then collected with the precleaned shovel and the sampling container sealed. The snow was then melted at 5°C and two 1.5 L duplicates were taken. This was then extracted unfiltered the same as the water samples in Section 1.

3. Preparation of biota and sediment samples

A previously published method was adopted with some modification[9]. About 0.5-2.5 g of homogenized biological material was weighed in a 15 ml Falcon tube (VWR International. LLC Radnor. USA). Fifty microliters of ^{13}C-labeled PFAS internal standards mix (Wellington laboratories) mixture solution (500 ng mL^{-1}) was added. Ten milliliters of MeOH were added to each sample and the sample was further homogenized with a sharp spatula. Samples were then sonicated at room temperature (20-22 ℃) for ten minutes. Subsequently, the samples were mechanically shaken using Stuart Reciprocating shaker (SSL2, Bibby Scientific Ltd., Staffordshire, UK) for 30 minutes. The shaking was followed by centrifugation 10 min at 3000 rpm. The supernatant was removed with a plastic pipette and transferred to a new plastic tube. This stage was repeated by adding 4 ml of MeOH in the second extraction. The volume of the combined supernatants is reduced to 4 mL (37 °C) under a gentle flow of nitrogen gas (N_2) (AGA, Oslo, Norway, N_2 5.0 quality) using a Reacti-Therm III evaporating unit (Thermo Fisher Scientific Inc., Rockford, USA). Regarding the sediment sample, air-dried 5 g sediment was extracted as biota with an additional step with addition of 2 mL of NaOH solution (200 mM) prior to the extraction and 200 µL HCl solution (2 M) after the extraction according to [10]. About 0.5g of active coal Envi-Carb (ENVI-Carb™ 122, Sigma-Aldrich, Oslo, Norway) was added to each sample extract, the extract was then mixed and centrifuged for 10 min. The supernatant was removed and transferred to a new plastic tube. This step was repeated by adding an aliquot of methanol (1 mL) to the remaining deposits, and the supernatant was added to the corresponding tube. The supernatant was dried at 37 °C under N_2-gas (AGA, Oslo, Norway, N_2 5.0 quality) using a Reacti-Therm III evaporating unit (Thermo Fisher Scientific Inc., Rockford, USA). Twenty microliters of recovery standard (500 ng mL^{-1}) were added to each sample followed by addition of 450 µL MeOH. The samples were then vortexed (VWR mixer mini vortex 230V EU, VWR International, Radnor, PA, USA), and subsequently filtered through a 0.2 µm microcentrifuge filter (Spin-X, Costar, Corning Inc., Corning, NY, USA). The resulting sample was finally transferred to polypropylene vials, and immediately analysed with HPLC–MS -QqQ.

4. HPLC–ESI–QqQ analysis

An Agilent 1200 series HPLC (Agilent Technologies, Waldbronn, Germany) coupled with an Agilent 6460 (Agilent Technologies, Santa Clara, CA, USA) triple quadrupole mass spectrometer (MS-QqQ) was used for quantification of PFASs. A Zorbax Eclipse plus C18 RRHD (2.1 x 100 mm, 1.8 µm) (Agilent, Palo Alto, USA) column was used for separation and quantification of the target compounds at 25 ˚C. The injection volume was 10 µL. The analytical column was protected with a respective Guard Cartridge (4 µm x 3.0 mm ID). Separation was conducted by a binary mobile phase gradient consisting of (A) Aqueous solution of $NH_4CH_3CO_2$ (5 mM) and (B) pure MeOH with a mobile phase flow rate of 0.2 mL/min. The initial mobile phase proportion was 15 % (B) which was held for 5 min. B was then linearly increased to 99 % over 5 min and held for 7 min. B was then linearly changed to 1% until the end of the quantitative analysis (total run = 26 min.). Analytes were ionized in an Agilent Jet Stream electrospray ion source in negative ionization mode. The ion source parameters were as follows; gas temperature was 300 °C and gas flow was 5 l/min, nebulizer pressure was 25 psi, sheath gas temperature was 400 °C, sheath gas flow was 8 l/min.

The produced ions were monitored in negative dynamic multiple reaction monitoring (dMRM). Table S2 contains information on the ion transitions monitored and their individual settings. Agilent MassHunter software (Version B.07.00 /Build 7.0.457.0, 2008) was used for instrument control, method validation and quantification. Combined chromatograms of the MRM transition for the product ions for each analyte are shown in Figure S3.

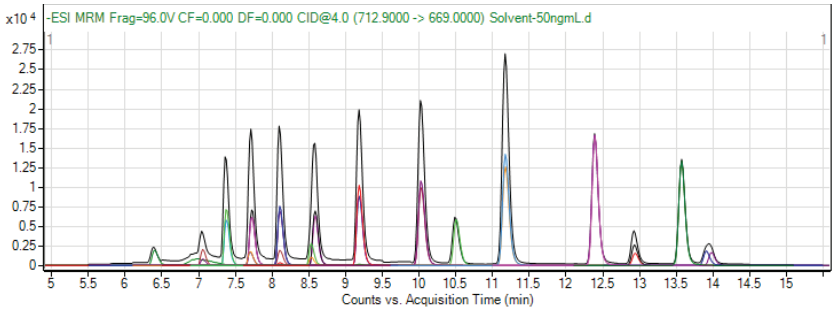


Figure S3. Extracted and Overlaid MRM of all compounds at 50 pg/µL

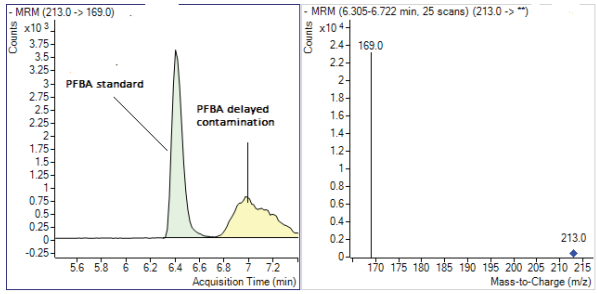


Figure S4. Extracted MRM of PFBA at 50 pg/µL

Table S7. Monitored ion transitions (dMRM) of target PFASs and their individual instrument settings; Retention time (RT) Precursor ion (Prec Ion), product ion (PI), Collision Energy (CE), Fragmentor voltage (FV), Retention time Window (ΔRT), and Polarity. For Acronyms and structure information on the target compounds, see table S6. ISTD used: internal standard used.

Acronym	ISTD	RT (min)	ΔRT	Prec Ion (m/z)	PI 1 (m/z)	PI 2 (m/z)	PI 3 (m/z)	CE1 (V)	CE2 (V)	CE3	Fragmentor (V)
PFBA	[$^{13}C_5$]-PFHxA	6.4	4	213	169			1			61
PFHxA	[$^{13}C_5$]-PFHxA	7.6	4	313	269	119		0	19		66
PFHpA	[$^{13}C_4$]-PFHpA	7.9	4	363	319	168.9		0	10		71
PFOA	[$^{13}C_4$]-PFOA	8.3	4	413	369	169		0	12		76
PFNA	[$^{13}C_5$]-PFNA	8.7	4	463	419	219		4	4		86
PFDA	[$^{13}C_2$]-PFDA	9.2	4	513	469	169		4	4		86
PFUnDA	[$^{13}C_2$]-PFUnDA	9.9	4	563	519	169		4	10		86
PFDoDA	[$^{13}C_2$]-PFDoDA	10.6	4	613	569			4			96
PFBS	[$^{18}O_2$]-PFHxS	7.2	4	299	99	80		25	35		121
PFHxS	[$^{18}O_2$]-PFHxS	7.9	4	398.9	99	80		45	45		151
Br-PFOS	[$^{18}O_2$]-PFHxS	8.3	4	499	99	80	130	61	61	61	200
L-PFOS	[$^{13}C_4$]-PFOS	8.4	4	499	99	80	130	61	61	61	200
6:2 FTS	[$^{18}O_2$]-PFHxS	8.1	4	427	407	81		15	15		145
FOSA	[$^{2}H_3$]-MeFOSA	10.5	4	497.9	78			33			141

Table S8. Monitored ion transitions (dMRM) of internal standards used and their individual instrument settings; Retention time (RT) Precursor ion (Prec Ion), product ion (PI), Collision Energy (CE), Fragmentor voltage (FV), Retention time Window (ΔRT), and Polarity.

Acronym	RT (min)	ΔRT	Prec Ion (m/z)	PI (m/z)	CE (V)	Fragmentor
[$^{13}C_8$]-PFOA	8.34	4	421	376	0	76
[$^{13}C_4$]-PFBA	6.58	4	217	172	1	61
[$^{13}C_5$]-PFHxA	7.66	4	318	273	0	66
[$^{13}C_4$]-PFHpA	7.99	4	367	322	0	66
[$^{13}C_4$]-PFOA	8.35	4	417	372.1	0	76
[$^{13}C_5$]-PFNA	8.79	4	468	423	4	76
[$^{13}C_2$]-PFDA	9.34	4	515	470	4	86
[$^{13}C_2$]-PFUnDA	9.94	4	565	520	4	96
[$^{13}C_2$]-PFDoDA	10.86	4	615	570	4	96
[$^{18}O_2$]-PFHxS	7.97	4	403	84	49	146
[$^{13}C_4$]-PFOS	8.74	4	503	80	61	180
[$^{2}H_3$]-MeFOSA	9.34	4	515	169	25	136

Validation of the Analytical Method

1. Recovery and detection limits

The apparent recoveries for all PFAS and their ISTDs from spiked samples were calculated using the following equation:

$$\text{Apparent Recovery\%} = 100 * \frac{\text{C (sample)} - \text{C (matrix blank)}}{\text{C (spiked)}}$$

Where C (sample) is the calculated concentration in the spiked sample, C (matrix blank) is the calculated background concentration in the matrix used, and C(spiked) is the concentration spiked into the sample.

Four and six replicates of each sample type (water, sediment, fish muscle, fish liver, plankton, worms, crab, and gull liver) were prepared and spiked with a mixture of all target PFASs and their ISTDs, while matrix blanks were spiked with only ISTDs. Six seawater samples were spiked at final concentration of 25 ng/L and four seawater samples were spiked at final concentration of 3 ng/L. For sediment and biota, 4 samples were spiked at 1 ng/g and six samples were spiked at 25 ng/g. All spiked samples with their blanks were then extracted and treated as real sample. The obtained recoveries are presented in Table S11. In general, most PFAS showed satisfying recoveries (42 – 120%) in the initial method validation as shown in Table S11. For N-MeFOSE, N-MeFOSA, N-EtFOSE, and N-EtFOSA, however, unacceptable recovery rates from some matrices were achieved, and were consequently excluded from further quantitative analysis from these matrices (red highlighted in Table S11). Sample specific recovery rates for all internal standards (ISTD) from different samples were calculated applying known concentrations of [$^{13}C_8$]-PFOA as a recovery standard (Table S12). Instrumental limit of detection (LOD), instrumental lower limit of quantification (LOQ) , and method detection limit (MDL) in abiotic and biotic samples, values are summarised in Table S9.

2. Matrix effect

Matrix effects (ME) caused by some co-eluting components from the residual matrix, are common in HPLC-ESI-QqQ methods [11]. ME influences the ionization efficiency of the target analytes. Typically, this results in suppression or enhancement of target compound signal [12]. In general, MEs are not reproducible among various sample sets or even replicates of the same set of samples and, therefore, compromise the quantitative analysis if not appropriately assessed [13], [14]. Therefore, here we evaluated MEs as we have investigated complex environmental samples. ME was estimated applying the following equation, where Sm and Ss represent the slopes of the matrix matched and solvent matched calibration curves respectively.

$$ME\% = \left[\left(\frac{Sm}{Ss}\right) - 1\right] \times 100$$

The results are summarized n Table S10. ME% values outside the range −20% to +20% indicate significant effects. Therefore, in sediment and biota samples, all PFASs experienced significant effect. We found that the use of ISTDs was not compensated for these effects, therefore, calibration standards including both native and ISTDs were prepared in similar matrix extracts using real samples collected from the reference in order to confirm the linear range of the method for reliable quantification.

3. Blank samples

Milli-Q water and clean sodium sulfate were used in the field during abiotic and biotic sample collection in order to monitor for possible contamination during sample collection, transport, and storage and analyzed as field blanks. Certain PFAS; PFBA, PFOA, and 6:2 FTS were detected in some of these blank samples at average concentration of 0.12, 0.010, and 0.034 ng/mL, respectively.

Table S9. Instrument limit of detection (ILOD), instrument limit of quantification (ILOQ), and method detection limit (MDL). For abbreviations and structure information on the target compounds see table S6

Compound	ILOD (ng/mL)	ILOQ (ng/mL)	MDL-Water (ng/L)	MDL-Fish liver (ng/g)	MDL-Fish Muscle (ng/g)	MDL-Sediment (ng/g)	MDL-Crab (ng/g)	MDL-Plankton (ng/g)	MDL-Worms (ng/g)	MDL-Gull liver (ng/g)
PFBA	0.007	0.022	0.150	0.094	0.02	0.320	0.80	0.600	5.3	0.08
PFHxA	0.012	0.040	0.270	0.060	0.030	0.003	0.003	0.003	0.040	0.045
PFHpA	0.015	0.051	0.340	0.015	0.020	0.002	0.003	0.003	0.011	0.0033
PFOA	0.004	0.015	0.180	0.020	0.010	0.045	0.012	0.003	0.017	0.010
PFNA	0.010	0.033	0.070	0.040	0.050	0.008	0.010	0.003	0.015	0.013
PFDA	0.004	0.014	0.080	0.030	0.090	0.040	0.003	0.002	0.060	0.040
PFUnDA	0.010	0.030	0.220	0.030	0.020	0.020	0.020	0.003	0.060	0.010
PFDoDA	0.050	0.160	0.110	0.070	0.050	0.030	0.060	0.002	0.018	2.24
PFTrDA	0.040	0.150	0.100	0.030	0.010	0.030	0.040	0.005	0.015	0.17
PFTeDA	0.040	0.140	0.090	0.090	0.070	0.030	0.040	0.009	0.014	0.80
PFBS	0.050	0.160	0.110	0.016	0.050	0.018	0.020	0.005	0.016	0.27
PFHxS	0.021	0.070	0.790	0.016	0.010	0.011	0.101	0.090	0.010	0.20
PFOS	0.060	0.190	0.240	0.050	0.040	0.014	0.063	0.030	0.010	0.30
6:2 FTS	0.040	0.010	1.08	0.015	0.060	0.030	0.050	0.410	0.05	0.38
FOSA	0.010	0.030	0.070	0.003	0.010	0.010	0.150	4.55	0.04	0.06
N-MeFOSE	0.070	0.220	0.150	0.079	0.010	2.00	0.070	1.30	0.22	0.51
N-MeFOSA	0.010	0.040	0.030	0.047	0.010	0.08	0.170	6.25	0.04	0.51
N-EtFOSE	0.010	0.040	0.030	0.015	0.014	0.030	1.11	1.54	0.04	2.50
N-EtFOSA	0.040	0.130	0.090	0.016	0.016	0.010	0.270	8.82	0.13	0.17

Table S10. Matrix effect (ME %); negative values indicate ion suppression and positive values indicate signal enhancement. For abbreviations and structure information on the target compounds see table S6

Compound	Water	Sediment	Crab	Plankton	Gull liver	Fish Liver	Fish Muscle
PFBA	-95.2	-80.0	-98.6	-89.9	-96.6	-99.0	-79.1
PFHxA	-86.2	-74.5	-96.5	-63.1	-89.1	-99.4	-76.9
PFHpA	-70.1	-68.1	-96.6	-50.5	-84.3	-98.6	-77.2
PFOA	-56.4	-66.6	-92.7	-51.5	-92.3	-98	-77.2
PFNA	-40.0	-64.9	-90.4	-34.5	-76.0	-96.9	-49.9
PFDA	-21.2	-68.3	-86.3	-38.8	-79.3	-97.4	-48.7
PFUnDA	1.80	-67.1	-80.3	-40.9	-73.0	-95.3	-41.8
PFDoDA	-12.1	-64.4	-71.3	-65.4	-73.0	-91.8	-29.3
PFTrDA	-16.1	-65.9	-77.0	-39.0	-89.4	-96.1	-40.8
PFTeDA	-16.1	-68.5	-97.4	-67.4	-94.0	-95.3	-40.2
PFBS	-61.5	-77.3	-93.5	-69.6	-89.1	-98.0	-67.2
PFHxS	-7.90	-70.0	-92.0	-55.3	-84.8	-97.9	-62.9
PFOS	-23.8	-70.8	-87.8	-55.4	-79.2	-97.8	-51.3
6:2 FTS	126.5	-57.7	-45.8	126.1	-21.1	-83.8	166.8
FOSA	-28.6	-68.9	-81.8	-67.8	-88.6	-99.5	-53.2
N-MeFOSE	-27.9	-69.2	-95.6	-96.0	-96.7	-99.8	-71.1
N-MeFOSA	-28.2	-70.1	-93.6	-88.6	-96.9	-98.3	-67.5
N-EtFOSE	-27.6	-78.5	-99.4	-96.3	-99.2	-99.9	-94.3
N-EtFOSA	-24.2	-74.8	-97.1	-92.5	-98.2	-98.7	-88.3

Table S11. Recovery rates percent (mean± relative standard deviation) for all target compounds determined by repeated spiking of different type of samples. For abbreviations and structure information on the target compounds, see table S6 (colored cells indicate compounds with low recoveries, that were not quantified). Accepted recovery % :40-125%. Recoveries of 6:2 FTS were determined using matrix matched calibration curves.

Compound	Seawater		Fish muscle		Fish liver		Sediment		Crab		Plankton		Worm	Gull	
	3 ng/L	50 ng/L	1 ng/g	25 ng/g	1 ng/g	25 ng/g	1 ng/g	25 ng/g	1 ng/g	25 ng/g	1 ng/g	25 ng/g	25 ng/g	1 ng/g	25 ng/g
	(n=4)	(n=6)	(n=4)	(n=6)	(n=4)	(n=6)	(n=4)	(n=6)	(n=4)	(n=6)	(n=4)	(n=6)	(n=3)	(n=4)	(n=6)
PFBA	54±42	95±14	80±15	107.2±6.7	76±7	98±11	-	68±11	82±17	57±31	138±26	106±25	111±13	113.8±3.5	110.6±1.5
PFHxA	104±5	116±1	81.9±9.9	111.2±5.9	81.9±9.9	111.2±5.9	119.0±8.3	113.5±2.6	124.9±7.6	121.3±9.1	110.3±1.0	113.6±4.3	108.1±3.3	113.8±3.5	110.6±1.5
PFHpA	108±6	116±1	92.4±12.9	95.1±9.2	92.4±12.9	95.1±9.2	110.6±9.6	109.2±3.4	101.4±	108.5±5.9	101.5±6.6	101.2±4.0	97.0±3.9	104.0±3.7	100.4±4.9
PFOA	111±3	118±2	106.8±5.1	113.0±5.4	106.8±5.1	113.0±5.4	96.4±10.7	122.3±5.8	98.8±5.9	123.5±5.7	115.4±4.2	116.1±2.1	114.0±2.9	119.8±2.5	114.2±5.3
PFNA	109±2	117±1	114.3±9.4	107.3±2.8	114.3±9.4	107.3±2.8	89.4±12.8	114.8±4.2	98.9±10.9	125.6±11.3	107.0±5.7	104.8±1.6	106.4±3.2	111.3±2.5	116±4
PFDA	109±2	116±1	114.8±8.1	106.5±3.8	114.8±8.1	106.5±3.8	117.7±4.6	112.6±2.4	116.4±5.4	113.8±10.3	103.1±1.5	109.4±3.9	106.3±3.1	110.5±3.1	108±4
PFUnDA	106±2	119±2	126.0±5.3	115.3±1.6	126.0±5.3	115.3±1.6	126.5±3.9	121.0±2.4	131.7±0.5	122.4±6.0	115.2±0.40	120±4	118.6±2.5	129.3±3.3	118±4
PFDoDA	101±2	130±1	118.3±6.8	102.2±16.4	118.3±6.8	102.2±16.4	118.4±4.0	116.0±3.1	120.3±5.1	111.3±12.7	108.2±1.2	113.3±4.3	110.32.0	114.7±3.2	128.9±2.7
PFTrDA	72±4	117±4	114.7±6.0	100.3±6.7	114.7±6.0	100.3±6.7	128.8±6.5	117.9±12.7	69.0±12.2	94.3±21.7	93.7±3.7	96.8±4.1	102.1±4.2	52.0±18.5	107±4
PFTeDA	50±4	75±4	86.1±5.7	80.2±6.5	86.1±5.7	80.2±6.5	192.2±8.6	109.8±27.6	84.1±4.0	82.3±8.9	40.2±63.	110±10	89.3±15.0	47.3±37	95±16
PFBS	115±6	117±1	59.9±6.9	51.0±14.4	59.9±6.9	51.0±14.4	72.6±5.3	89.0±5.2	121.1±42.4	116.9±9.2	76.8±6.3	75.7±6.1	124.2±16.9	68.4±5.1	75.1±1.8
PFHxS	111±2	120.0±0.8	98.8±9.8	94.8±5.1	98.8±9.8	94.8±5.1	85.5±7.4	112.8±3.1	114.1±9.4	125.5±5.9	102.8±3.2	101.7±1.7	99.4±2.2	102.±2.3	73.4±2.8
L-PFOS	112±3	118±2	120.8±9.7	104.0±1.6	120.8±9.7	104.0±1.6	92.0±10.9	125.4±2.6	113.5±9.6	125.2±5.8	119.7±8.0	113.5±2.1	110.5±4.8	-	121±16
6:2 FTS	94±6	119±3	50±34	88.7±7.1	107±2	108±11	107±10	103±16	88±11	89±7.0	125±10	127±2.0	124±2.0	109±9.0	109±6.0
FOSA	53±51	92±7	51.3±12.7	52.4±4.9	51.3±12.7	52.4±4.9	104.7±25.1	79±26	115.8±11.9	111.5±22.4	52±14	57±6	79.7±9.9	62.7±3.7	72.8±5.0
N-MeFOSE	7±55	6±32	43±45	43±33	34±29	93±29	84±18	67±28	37±7	32±21	33±12	23±46	42±22	84±37	92±14
N-MeFOSA	-	0.3±17	63±25	18±61	64±12	68±10	12±26	13±34	38±6	28±32	26±14	13±29	53±20	84±13	110±17
N-EtFOSE	11±52	9±21	50±13	103±67	105±20	88±13	108±14	44±63	25±4	8±96	7±194	2±27	4±6	95±12	74±11
N-EtFOSA	0.6±83	0.7±11	8±68	8±41	72±13	71±14	44±6	13±36	36±2	11±29	25±67	5±7	13±14	55±32	76±15

Table S12. Recovery rates percent (mean± relative standard deviation) for all internal standards determined by repeated spiking of different type of samples. For abbreviations and structure information on the target compounds, see table S6.

Compound	Seawater (n=8)	Fish muscle (n=8)	Fish liver (n=8)	Glaucous gull (n=8)	Worms (n=3)	Plankton (n=8)	Sediment (n=5)	Crab avg (n=8)
[$^{13}C_4$]-PFBA	11.6±20.6	48.1±23.7	9.6±131.8	18.7±44.6	2.6±173.2	9.0±31.1	20.5±62.6	4.3±97.0
[$^{13}C_5$]-PFHxA	13.0±15.5	48.7±19.6	14.7±13.7	43.7±13.3	9.8±1.8	24.2±9.3	33.8±12.5	17.4±14.1
[$^{13}C_4$]-PFHpA	78.3±2.2	87.4±14.5	78.9±13.4	96.2±15.5	46.6±24.7	51.7±8.9	62.6±24.0	62.2±13.1
[$^{13}C_4$]-PFOA	42.6±9.3	49.6±8.9	28.1±13.1	31.7±12.1	30.5±27.7	35.7±5.9	34.3±39.6	51.2±6.8
[$^{13}C_5$]-PFNA	61.6±5.0	91.6±13.3	55.8±17.8	86.9±14.3	69.1±11.8	52.3±7.9	35.0±36.5	0.0±68.3
[$^{13}C_2$]-PFDA	65.1±4.9	101.1±9.3	60.1±10.6	82.1±14.0	71.4±9.2	45.7±10.2	36.3±26.8	76.0±12.9
[$^{13}C_2$]-PFUnDA	79.0±11.0	112.2±14.0	85.6±20.8	99.8±14.5	71.9±14.0	43.4±9.7	38.5±19.8	119.4±8.9
[$^{13}C_2$]-PFDoDA	65.9±11.5	126.1±8.1	103.8±20.2	76.9±15.2	80.5±10.5	43.4±10.8	40.4±13.3	125.6±9.3
[$^{18}O_2$]-PFHxS	39.3±10.7	59.0±16.0	38.3±15.6	72.6±12.7	22.5±15.1	42.4±5.7	35.0±47.2	24.3±14.8
[$^{13}C_4$]-PFOS	104.3±11.7	115.6±14.8	93.8±17.1	118.8±19.8	101.7±18.2	74.7±15.3	75.5±26.0	109.0±8.4
[$^{2}H_3$]-MeFOSA	82.2±8.6	119.5±13.4	37.6±96.9	83.5±15.5	70.7±4.3	42.0±11.6	36.3±23.3	59.5±76.7

Sample analysis results

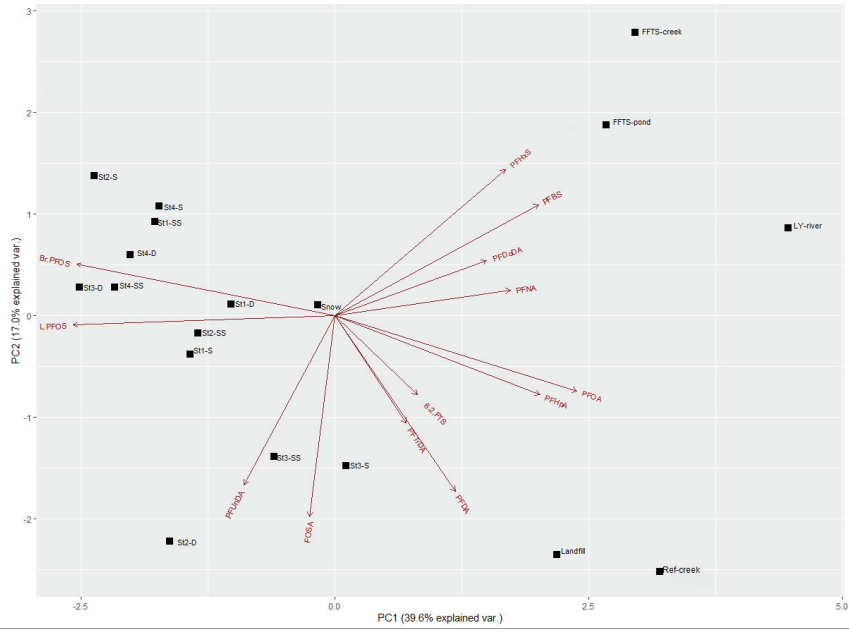


Figure S5. PCA biplots of PCA for PFAS profiles of the various samples (i.e. % of $\sum_{14}$PFAS) with PC1 and 2 explaining more than 56% of the variation.

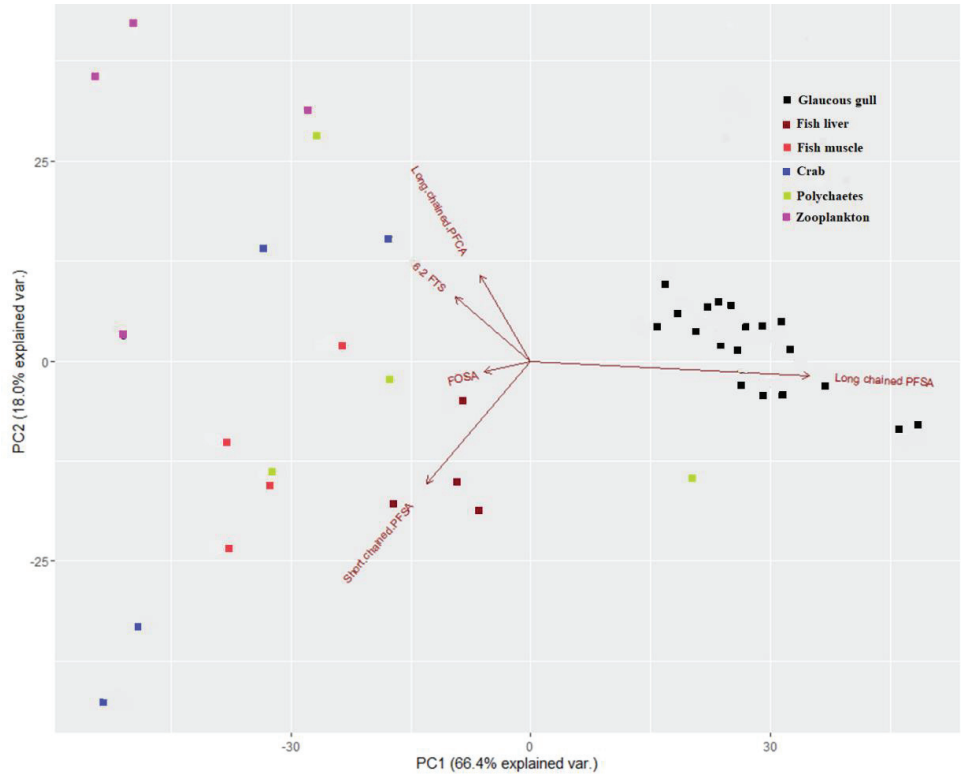


Figure S6. PCA biplots of PCA for PFAS profiles of the biota samples collected from the Adventfjord and the Isfjord, near the Svalbard Airport. (i.e. % of ∑14PFAS) with PC1 and 2 explaining more than 84% of the variation.s (Levels <LOQ were treated as zero in this figure). Short-chained PFCA: PFHxA and PFHpA; long-chained PFCA: C8-C14; Short-chained PFSA: PFBS and PFHxS; Long-chained PFSA: PFOS.

Sample analysis results

Table S13. PFAS concentrations in seawater and fresh water (ng L^{-1}± standard error of the mean) collected in the vicinity of Longyearbyen (Svalbard).

Sample	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	∑PFOS	6:2 FTS	FOSA	$\sum_{14}$PFAS
St1-surface(n=2)	nd	nd	0.19±0.03	(0.035)	nd	(0.11)	nd	nd	nd	nd	(0.38)	4.37±1.31	(0.54)	(0.03)	5.12±0.97
St1-subsurface (n=2)	nd	nd	0.14±0.09	(0.035)	nd	(0.11)	nd	nd	nd	(0.055)	(0.38)	6.41±2.09	(0.54)	nd	7.71±1.87
St1-deep (n=2)	(0.13)	(0.17)	0.19±0.14	(0.035)	nd	(0.11)	nd	nd	nd	(0.055)	0.61±0.23	5.16±3.92	(0.54)	(0.03)	6.98±2.87
St2-surface(n=2)	(0.13)	(0.17)	0.17±0.01	(0.035)	nd	(0.11)	nd	nd	nd	nd	(0.38)	9.16±3.23	nd	nd	10.06±1.17
St2-subsurface (n=2)	nd	(0.17)	0.28±0.04	(0.035)	(0.04)	(0.11)	nd	nd	nd	nd	0.61±0.24	6.51±1.65	nd	(0.03)	7.59±0.45
St2-deep (n=2)	(0.13)	(0.17)	0.17±0.01	(0.035)	(0.04)	0.35±0.24	nd	nd	nd	(0.055)	(0.38)	4.92± 0.52	nd	(0.03)	6.20±2.6
St3-surface (n=4)	0.32±0.19	(0.17)	0.80±0.54	(0.035)	(0.04)	(0.11)	nd	nd	nd	(0.055)	(0.38)	4.02±1.68	(0.54)	(0.03)	4.45±0.59
St3-subsurface(n=4)	(0.13)	(0.17)	0.22±0.02	(0.035)	(0.04)	(0.11)	nd	nd	nd	nd	(0.38)	4.37±3.51	(0.54)	(0.03)	6.11±0.63
St3-deep (n=2)	(0.13)	(0.17)	0.21±0.02	(0.035)	nd	0.25±0.09	nd	nd	nd	nd	(0.38)	8.61±1.45	nd	(0.03)	9.75±1.87
St4-surface (n=2)	nd	(0.17)	0.12±0.09	(0.035)	nd	(0.11)	nd	nd	nd	(0.055)	(0.38)	4.41±2.10	nd	nd	5.27±1.77
St4-subsurface (n=2)	(0.13)	nd	0.16±0.01	(0.035)	nd	(0.11)	nd	nd	nd	(0.055)	(0.38)	5.13±1.77	nd	(0.03)	5.97±1.19
St4-deep (n=2)	nd	nd	0.13±0.11	(0.035)	(0.04)	(0.11)	nd	nd	nd	(0.055)	(0.38)	7.90±4.02	nd	nd	8.64±2.94
Ref-creek (n=2)	0.38±0.01	0.93±0.03	1.00±0.01	0.83±0.11	(0.04)	(0.11)	nd	nd	nd	(0.055)	0.38±0.06	1.58±0.20	<LOQ	(0.03)	5.86±0.1
LY (n=2)	0.67±0.17	0.73±0.01	0.73±0.10	(0.035)	(0.04)	(0.11)	(0.55)	nd	nd	0.32±0.01	0.69±0.32	2.48±0.80	<LOQ	nd	7.054±2
Snow (n=2)	0.290±0.003	<LOQ	0.360±0.007	0.220±0.001	0.087±0.001	(0.11)	(0.55)	nd	nd	0.260±0.007	1.950±0.023	14.52±0.033	<LOQ	0.140±0.001	18.70±0.04
Landfill (n=2)	67.3±2.2	30.0±0.84	141.0±3.0	41.3±1.6	3.24±0.11	12.4±0.56	0.18±0.001	(0.05)	nd	5.92±0.19	44.9±0.81	289.3±29.15	<LOQ	3.28±0.07	643.6±84
FFTS-pond (n=2)	15.9±0.40	4.97±0.08	44.4±0.27	111.0±0.37	1.21±0.05	1.07±0.03	(0.55)	nd	nd	3.18±0.01	63.91±0.44	115.8±1.31	4.47±1.02	0.16±0.002	365.4±8.00
FFTS-creek (n=2)	10.4±0.43	3.63±0.13	6.73±0.04	0.78±0.02	(0.04)	(0.11)	(0.55)	nd	nd	1.90±0.02	13.19±0.74	19.09±0.87	1.46±0.08	(0.03)	57.4±4.0

Table S14. PFAS concentrations in sediment samples (μg kg^{-1} d.w. ± standard error of the mean) collected in the marine environment and a leachate channel of a landfill in the vicinity of Longyearbyen (Svalbard)

PFAS	Station 1		Station 2		Station 3		Station 4		Landfill	
	n	Mean±SE	n	Mean±SE	n	Mean±SE	n	Mean±SE	n	Mean±SE
PFHxA	3/3	0.0158±0.0010	2/3	0.0098±0.0051	0/3	nd	1/3	0.0029±0.0029	3/3	0.339±0.010
PFHpA	2/3	0.0098±0.0049	0/3	nd	2/3	0.0133±0.006	1/3	0.0058±0.0057	2/3	0.169±0.009
PFOA	3/3	0.0383±0.0023	3/3	0.0285±0.0004	3/3	0.036±0.0015	3/3	0.0274	3/3	1.203±0.028
PFNA	3/3	0.0678±0.0048	3/3	0.0417±0.0027	3/3	0.0340±0.0023	1/3	0.0087±0.0087	3/3	1.80±0.024
PFDA	3/3	0.0204±0.004	3/3	0.0176±0.0005	3/3	0.0237±0.003	2/3	0.0092±0.0045	3/3	0.860±0.017
PFUnDA	3/3	0.0445±0.0013	3/3	0.0354±0.0032	3/3	0.0292±0.0023	3/3	0.0250±0.0037	3/3	25.5±0.486
PFDoDA	3/3	0.0148±0.0005	3/3	0.0177±0.0011	3/3	0.0296±0.0036	3/3	0.0136±0.0010	3/3	0.693±0.016
PFTrDA	3/3	0.0208±0.0007	3/3	0.0226±0.0026	3/3	0.0337±07.004	3/3	0.0162±0.0021	3/3	4.22±0.111
PFTeDA	3/3	0.0145±0.0004	3/3	0.0178±0.0018	3/3	0.0356±0.0056	3/3	0.0129±0.0004	3/3	0.045±0.023
PFBS	3/3	0.0198±0.0046	2/3	0.0124±0.0075	0/3	nd	1/3	0.0069±0.0068	3/3	0.081±0.012
PFHxS	3/3	0.0398±0.0012	3/3	0.0446±0.0041	3/3	0.0245±0.0026	3/3	0.0229±0.0038	3/3	0.461±0.010
Br-PFOS	3/3	0.0441±0.0001	3/3	0.0341±0.0064	0/3	nd	0/3	nd	3/3	2.59±0.230
L-PFOS	3/3	0.2510±0.0323	3/3	0.1780±0.0007	3/3	0.0491±0.0033	1/3	0.0119±0.0119	3/3	42.8±1.77
6:2 FTSA	3/3	3.99±3.89	0/3	nd	1/3	0.208±0.360	0/3	nd	0/3	nd
FOSA	3/3	0.0128±0.0001	3/3	0.0129±0.0002	3/3	0.0135±0.0001	0/3	nd	3/3	0.782±0.010
∑14PFAS		4.61±3.92		0.474±0.013		0.530±0.181		0.1634±0.0279		81.6±2.13

Table S15. Sediment/water partition coefficients (log K_d in dm^3 kg^{-1}). derived from sediment and water samples taken at the same station. assuming local equilibrium.

PFAS	Landfill sediment (n=3)	Marine sediment (n=12)
PFHxA	0.68±0.03	-
PFHpA	0.85±0.03	-
PFOA	0.94±0.001	-
PFNA	1.6±0.05	-
PFDA	2.4±0.74	-
PFUnDA	3.3±1.4	2.4±1.7
PFBS	0.52±0.32	-
PFHxS	1.0±0.01	-
PFOS	2.0±0.60	1.4±1.2
FOSA	2.7±1.5	-

Table S16. PFAS levels in zooplankton samples from the stations St1-4 in Adventfjorden (µg kg^{-1} ww± standard error of the mean).

PFAS	Station 1		Station 2		Station 3		Station 4	
	n	Mean±SE	n	Mean±SE	n	Mean±SE	n	Mean±SE
PFHxA	0/3	nd	0/3	nd	0/3	nd	0/3	nd
PFHpA	0/3	nd	0/3	nd	0/3	nd	0/3	nd
PFOA	3/3	0.0292±0.0039	3/3	0.0270±0.0016	3/3	0.0274±0.0027	3/3	0.0238±0.0050
PFNA	1/3	0.0067±0.0066	1/3	0.0071±0.0071	2/3	0.0155±0.0077	0/3	nd
PFDA	2/3	0.0133±0.0066	3/3	0.0219±0.007	3/3	0.0201±0.0014	3/3	0.0198±0.0001
PFUnDA	3/3	0.0450±0.0045	3/3	0.0367±0.0016	3/3	0.0375±0.0024	3/3	0.0421±0.0008
PFDoDA	3/3	0.0204±0.0023	3/3	0.0181±0.005	3/3	0.0161±0.0001	3/3	0.0175±0.00001
PFTrDA	3/3	0.0274±0.0033	3/3	0.0226±0.0017	3/3	0.0202±0.0013	3/3	0.0269±0.0018
PFTeDA	0/3	nd	0/3	nd	0/3	nd	0/3	nd
PFBS	0/3	nd	1/3	0.0078±0.0078	2/3	0.7356±0.7088	1/3	0.0093±0.0093
PFHxS	0/3	nd	0/3	nd	2/3	0.0131±0.0131	0/3	nd
Br-PFOS	0/3	nd	0/3	nd	2/3	0.0093±0.0083	1/3	0.0156±0.0156
L-PFOS	0/3	nd	1/3	0.0046±0.0046	1/3	0.0146±0.0145	1/3	0.2270±0.02270
6:2 FTS	1/3	0.1895±0.328	3/3	1.87±0.832	3/3	0.6009±0.3392	2/3	0.1667±+.0833
FOSA	2/3	0.0107±0.0054	3/3	0.0146±0.0005	3/3	0.0150±0.0007	0/3	nd
$\sum_{14}$PFAS	-	0.3421±0.1886	-	2.03±0.82	-	1.525±1.397	-	0.5486±0.3044

Table S17. PFAS levels in polychaete samples from marine sediments stations St1-4 in Adventfjorden (μg kg^{-1} ww± standard error of the mean).

PFAS	Station 1		Station 2		Station 2		Station 2	
	n	Mean±SE	n	Mean±SE	n	Mean±SE	n	Mean±SE
PFHxA	0/3	nd	0/3	nd	0/3	nd	0/3	nd
PFHpA	0/3	nd	0/3	nd	1/3	0.1176±0.1176	0/3	nd
PFOA	0/3	nd	0/3	0.0665±0.0283	2/3	0.1602±0.0870	3/3	0.1430±0.0218
PFNA	2/3	0.0677±0.0340	2/3	0.0432±0.0176	2/3	0.0738±0.0368	1/3	0.0307±0.0307
PFDA	3/3	0.0401±0.0029	3/3	0.020±0.0079	2/3	0.0396±0.0200	3/3	0.0457±0.0086
PFUnDA	3/3	0.0745±0.005	3/3	0.0429±0.0178	3/3	0.0903±0.0136	3/3	0.0698±0.0096
PFDoDA	2/3	0.0195±0.0098	2/3	0.0231±0.0100	3/3	0.0420±0.0063	3/3	0.040±0.004
PFTrDA	3/3	0.1750±0.0430	3/3	0.1230±0.0520	3/3	0.1190±0.0118	3/3	0.150±0.026
PFTeDA	3/3	0.0319±0.0052	3/3	0.0144±0.0053	3/3	0.0507±0.0134	3/3	0.049±0.009
PFBS	3/3	0.1543±0.0323	0/3	nd	1/3	0.0621±0.0621	1/3	0.075±0.075
PFHxS	3/3	0.917±0.1247	3/3	0.2056±0.0295	3/3	1.01±0.253	0/3	nd
Br-PFOS	1/3	0.2323±0.2323	1/3	0.0134±0.0133	0/3	nd	1/3	0.0534±0.0534
L-PFOS	3/3	4.54±1.04	2/3	0.2630±0.1315	1/3	2.08±2.08	1/3	0.414±0.414
6:2 FTS	3/3	0.5971±0.2592	0/3	0.0675±0.0675	3/3	0.581±0.378	3/3	nd
FOSA	3/3	0.1922±0.0636	3/3	0.0259±0.0259	3/3	0.1110±0.0128	3/3	0.047
$\sum_{14}$PFAS	-	7.043	-	0.909±0.1394	-	4.54±2.55	-	1.12±0.053

Table S18. Concentrations of PFAS (μg kg^{-1} ww) in crab samples collected from four stations in the vicinity of Longyearbyen (Svalbard).

PFAS	Station 1 (n=5)			Station2 (n=5)			Station 3 (n=1)	Station 4 (n=7)		
	n	Mean±SEM	Median	n	Mean±SEM	Median	St3_Crab	n	Mean±SEM	Median
PFHxA	0/5	nd	nd	0/5	nd	nd	nd	0/7	nd	nd
PFHpA	0/5	nd	nd	0/5	nd	nd	nd	0/7	nd	nd
PFOA	5/5	0.018	0.018	5/5	0.026±0.007	0.018	0.018	7/7	0.040±0.009	0.037
PFNA	3/5	0.033±0.013	0.049	3/5	0.027±0.012	0.023	nd	4/7	0.043±0.019	0.039
PFDA	5/5	0.055±0.007	0.051	5/5	0.030±0.006	0.030	0.033	7/7	0.043±0.007	0.049
PFUnDA	5/5	0.218±0.052	0.204	5/5	0.120±0.026	0.108	0.116	7/7	0.133±0.025	0.146
PFTrDA	5/5	0.255±0.195	0.180	5/5	0.144±0.024	0.133	0.121	7/7	0.122±0.023	0.132
PFTeDA	5/5	0.062±0.022	0.051	5/5	0.035±0.002	0.035	0.030	7/7	0.041±0.006	0.044
PFBS	1/5	0.309±0.691	nd	1/5	4.50±1.87	6.16	1.92	1/7	nd	nd
PFHxS	0/5	nd	nd	0/5	0.144±0.144	nd	nd	0/7	nd	nd
Br-PFOS	2/5	0.033±0.029	nd	2/5	nd	nd	0.034	3/7	0.013±0.008	nd
L-PFOS	4/5	0.276±0.115	0.215	4/5	0.191±0.012	0.195	0.158	7/7	0.312±0.063	0.350
6:2 FTS	2/5	0.66±0.43	nd	2/5	(0.08)	nd	(0.08)	3/7	(0.08)	nd
FOSA	5/5	0.248±0.044	0.210	5/5	0.269±0.022	0.280	0.314	7/7	0.256±0.049	0.235
$\sum_{14}$PFAS	-	1.56±0.491	1.054	-	5.629±1.95	6.943	3.02	-	1.02±0.152	0.956

Table S19. Concentrations of PFAS (μg kg^{-1}; w/w) in muscle of fish collected in the marine in the marine environment in the vicinity of Longyearbyen (Svalbard)

PFAS*	Station 1			Station 2			Station 3			Station 4		
	n	Mean±SEM	median	n	Mean±SEM	median	n	Mean±SEM	median	n	Mean±SEM	median
PFOA	5/5	0.021±0.006	0.016	3/3	0.037±0.005	0.034	11/11	0.027±0.003	0.027	8/8	0.021±0.002	0.021
PFNA	5/5	0.046±0.008	0.047	3/3	0.055±0.002	0.055	11/11	0.049±0.005	0.047	8/8	0.037±0.006	0.040
PFDA	5/5	0.028±0.003	0.030	3/3	0.028±0.001	0.028	11/11	0.028±0.002	0.029	8/8	0.021±0.002	0.020
PFUnDA	5/5	0.085±0.025	0.087	3/3	0.056±0.005	0.054	11/11	0.062±0.007	0.066	8/8	0.043±0.008	0.033
PFDoDA	5/5	0.025±0.004	0.024	3/3	0.020±0.001	0.020	11/11	0.021±0.001	0.020	8/8	0.016±0.001	0.016
PFTrDA	5/5	0.063±0.021	0.048	3/3	0.033±0.003	0.035	11/11	0.040±0.003	0.042	8/8	0.029±0.003	0.029
PFTeDA	5/5	0.020±0.002	0.018	3/3	0.015±0.0001	0.016	11/11	0.019±0.001	0.018	8/8	0.015±0.001	0.016
PFHxS	5/5	0.48±0.17	0.360	3/3	0.010±0.006	0.099	11/11	0.215±0.033	0.204	7/8	0.0192±0.068	0.147
Br-PFOS	5/5	0.018±0.005	0.015	3/3	0.013±0.005	0.010	10/11	0.017±0.002	0.018	8/8	0.017±0.001	0.018
L-PFOS	5/5	0.149±0.044	0.123	3/3	0.140±0.027	0.160	8/11	0.071±0.018	0.066	8/8	0.087±0.017	0.075
FOSA	5/5	0.212±0.124	0.121	3/3	0.140±0.034	0.112	8/11	0.148±0.063	0.096	8/8	0.045±0.003	0.044
$\sum_{14}$PFAS	-	1.14±0.19	1.244	-	0.640±0.068	0.586	-	0.696±0.068	0.686	-	0.524±0.09	0.475

* PFHxA, PFHpA, 6:2 FTS, PFBS were not detected in any muscle sample.

Table S20. Concentrations of PFAS (μg kg^{-1}; w/w) in liver of fish collected in the marine in the marine environment in the vicinity of Longyearbyen (Svalbard)

PFAS*	Station 1			Station 2			Station 3			Station 4		
	n	Mean±SEM	median	n	Mean±SEM	median	n	Mean±SEM	median	n	Mean±SEM	median
PFHxA	0/5	nd	nd	0/7	nd	0	3/12	0.134±0.090	0.000	0/4	nd	nd
PFHpA	0/5	nd	nd	0/7	nd	0	0/12	nd	0.000	0/4	nd	nd
PFOA	2/5	0.247±0.216	0.000	3/7	0.06±0.030	0	4/12	0.025±0.013	0.000	3/4	0.136±0.053	0.153
PFNA	5/5	0.385±0.142	0.341	7/7	0.138±0.027	0.129667274	12/12	0.241±0.035	0.212	3/4	0.410±0.143	0.486
PFDA	4/5	0.223±0.129	0.128	6/7	0.049±0.010	0.05016601	12/12	0.116±0.014	0.126	3/4	0.174±0.085	0.177
PFUnDA	5/5	0.661±0.246	0.564	7/7	0.164±0.019	0.17319068	12/12	0.357±0.059	0.329	4/4	0.538±0.136	0.583
PFDoDA	5/5	0.179±0.072	0.161	7/7	0.040±0.006	0.037419633	12/12	0.069±0.008	0.068	4/4	0.150±0.032	0.157
PFTrDA	5/5	0.554±0.161	0.557	7/7	0.140±0.028	0.140520246	12/12	0.237±0.053	0.171	4/4	0.495±0.140	0.519
PFTeDA	5/5	0.118±0.062	0.058	6/7	0.022±0.006	0.022609377	11/12	0.0167±0.004	0.041	4/4	0.145±0.058	0.122
PFBS	0/5	nd	0.000	2/7	0.027±0.020	0	0/12	nd	0.000	1/4	0.066±0.065	0.000
PFHxS	4/5	3.02±1.85	1.298	6/7	0.672±0.250	0.367317029	10/12	1.693±0.397	1.587	2/4	0.445±0.280	0.310
Br-PFOS	4/5	0.127±0.054	0.122	6/7	0.103±0.021	0.115676717	12/12	0.154±0.028	0.112	2/4	0.157±0.092	0.137
L-PFOS	4/5	2.812±1.12	2.166	7/7	0.993±0.310	0.574313066	12/12	2.105±0.661	1.416	3/4	2.046±0.792	2.359
6:2 FTS	0/5	nd	0.000	0/7	nd	0	0/12	nd	0.000	nd	nd	0.000
FOSA	4/5	0.234±0.10	0.151	7/7	0.216±0.0739	0.138292607	12/12	0.255±0.089	0.145	4/4	0.447±0.213	0.298
$\sum_{14}$PFAS	-	8.56±3.94	4.318	-	2.624±0.327	2.29086767	-	5.467±0.845	5.300	-	5.2±1.5	6.460

Table S21. Bioaccumulation factors (BAF. L kg^{-1}) for PFAS on Svalbard

PFAS	Log $BAF_{fish\ muscle}$±SE	Log $BAF_{fish\ liver}$±SE
PFOA	2.09±0.103	2.87±0.210
PFNA	2.96±0.141	3.71±0.249
PFDA	3.19±0.161	3.78±0.357
PFUnDA	2.61±0.110	3.41±0.221
PFHxS	2.72±0.140	3.44±0.196
L-PFOS	1.52±0.148	2.61±0.143

Table S22. Concentrations of PFAS µg kg^{-1} (wet weight) detected in glaucous gull collected in Svalbard (n denotes number of samples detected of total number sampled).

PFAS	**n**	**Mean±SEM**	**Range**	**Median**
PFHxA	nd	nd	nd	nd
PFHpA	2/20	0.006±0.005	nd-0.093	nd
PFOA	13/20	0.101±0.025	nd-0.326	0.093
PFNA	20/20	3.16±0.375	0.796-6.55	3.038
PFDA	20/20	1.95±0.190	0.743-3.61	2.060
PFUnDA	20/20	4.38±0.556	1.40-11.9	4.484
PFDoDA	20/20	0.710±0.078	0.320-1.78	0.685
PFTrDA	20/20	1.55±0.351	0.477-7.94	1.165
PFTeDA	20/20	0.182±0.015	0.009-0.306	0.189
PFBS	nd	nd	nd	nd
PFHxS	19/20	1.75±0.720	nd-15.22	1.054
Br-PFOS	20/20	3.62±2.50	0.156-51.1	0.878
L-PFOS	20/20	51.4±18.0	12.4-382	28.986
6:2 FTS	19/20	nd	nd	nd
FOSA	nd	0.035±0.006	nd-0.122	0.032
$\sum_{14}$PFAS	-	68.9±22.3	16.98-479	44.728

Table S23 Relative distribution (mean±SEM) of the sum [∑] branched PFOS isomer (Br-PFOS) versus linear PFOS (L-PFOS) in abiotic and biotic samples in the Longyearbyen

Sample	Br-PFOS % of sum ΣPFOS	L-PFOS % of ΣPFOS	SEM
Snow	23.4	76.6	0.71
Ref-creek	30.0	70.0	0.41
FFTS-creek	31.2	68.8	0.78
FFTS-pond	39.8	60.2	0.78
Landfil leachate	27.1	72.9	0.91
LY-river	26.3	73.7	0.91
St-1-Seawater	27.9	72.1	0.82
St-2-Seawater	26.3	73.7	1
St-3-Seawater	27.0	73.0	0.65
St-4-Seawater	29.6	70.4	0.47
Marine sediment	20.5	79.5	0.7
Lansdfill sediment	6.7	93.3	0.1
Zooplankton	21.9	78.0	2.2
Polychaetes	15.4	84.6	2.3
Crab	8.7	91.3	3.2
Fish muscle	13.5	86.5	1.3
Fish liver	18.7	81.3	2.34
Glaucous gull	12.8	87.1	3.3

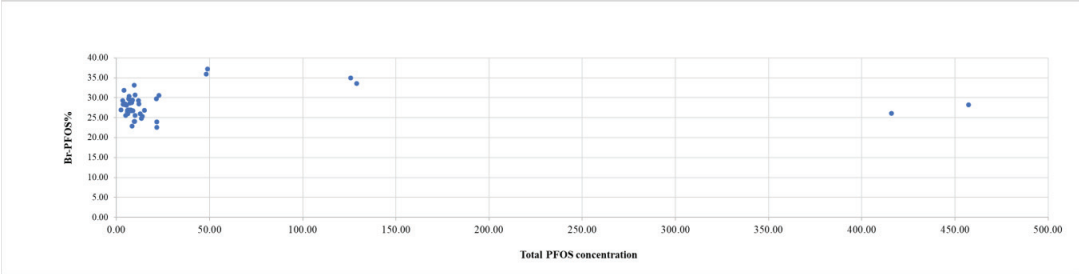


Figure S7. Sum [∑] branched PFOS isomer percentages (Br-PFOS%) versus PFOS total concentration

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Doctoral theses in Biology
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Year	Name	Degree	Title
1974	Tor-Henning Iversen	Dr. philos Botany	The roles of statholiths, auxin transport, and auxin metabolism in root gravitropism
1978	Tore Slagsvold	Dr. philos Zoology	Breeding events of birds in relation to spring temperature and environmental phenology
1978	Egil Sakshaug	Dr. philos Botany	The influence of environmental factors on the chemical composition of cultivated and natural populations of marine phytoplankton
1980	Arnfinn Langeland	Dr. philos Zoology	Interaction between fish and zooplankton populations and their effects on the material utilization in a freshwater lake
1980	Helge Reinertsen	Dr. philos Botany	The effect of lake fertilization on the dynamics and stability of a limnetic ecosystem with special reference to the phytoplankton
1982	Gunn Mari Olsen	Dr. scient Botany	Gravitropism in roots of *Pisum sativum* and *Arabidopsis thaliana*
1982	Dag Dolmen	Dr. philos Zoology	Life aspects of two sympartic species of newts (*Triturus, Amphibia*) in Norway, with special emphasis on their ecological niche segregation
1984	Eivin Røskaft	Dr. philos Zoology	Sociobiological studies of the rook *Corvus frugilegus*
1984	Anne Margrethe Cameron	Dr. scient Botany	Effects of alcohol inhalation on levels of circulating testosterone, follicle stimulating hormone and luteinzing hormone in male mature rats
1984	Asbjørn Magne Nilsen	Dr. scient Botany	Alveolar macrophages from expectorates – Biological monitoring of workers exposed to occupational air pollution. An evaluation of the AM-test
1985	Jarle Mork	Dr. philos Zoology	Biochemical genetic studies in fish
1985	John Solem	Dr. philos Zoology	Taxonomy, distribution and ecology of caddisflies (*Trichoptera*) in the Dovrefjell mountains
1985	Randi E. Reinertsen	Dr. philos Zoology	Energy strategies in the cold: Metabolic and thermoregulatory adaptations in small northern birds
1986	Bernt-Erik Sæther	Dr. philos Zoology	Ecological and evolutionary basis for variation in reproductive traits of some vertebrates: A comparative approach
1986	Torleif Holthe	Dr. philos Zoology	Evolution, systematics, nomenclature, and zoogeography in the polychaete orders *Oweniimorpha* and *Terebellomorpha*, with special reference to the Arctic and Scandinavian fauna
1987	Helene Lampe	Dr. scient Zoology	The function of bird song in mate attraction and territorial defence, and the importance of song repertoires
1987	Olav Hogstad	Dr. philos Zoology	Winter survival strategies of the Willow tit *Parus montanus*
1987	Jarle Inge Holten	Dr. philos Botany	Autecological investigations along a coust-inland transect at Nord-Møre, Central Norway

1987	Rita Kumar	Dr. scient Botany	Somaclonal variation in plants regenerated from cell cultures of *Nicotiana sanderae* and *Chrysanthemum morifolium*
1987	Bjørn Åge Tømmerås	Dr. scient Zoology	Olfaction in bark beetle communities: Interspecific interactions in regulation of colonization density, predator - prey relationship and host attraction
1988	Hans Christian Pedersen	Dr. philos Zoology	Reproductive behaviour in willow ptarmigan with special emphasis on territoriality and parental care
1988	Tor G. Heggberget	Dr. philos Zoology	Reproduction in Atlantic Salmon (*Salmo salar*): Aspects of spawning, incubation, early life history and population structure
1988	Marianne V. Nielsen	Dr. scient Zoology	The effects of selected environmental factors on carbon allocation/growth of larval and juvenile mussels (*Mytilus edulis*)
1988	Ole Kristian Berg	Dr. scient Zoology	The formation of landlocked Atlantic salmon (*Salmo salar* L.)
1989	John W. Jensen	Dr. philos Zoology	Crustacean plankton and fish during the first decade of the manmade Nesjø reservoir, with special emphasis on the effects of gill nets and salmonid growth
1989	Helga J. Vivås	Dr. scient Zoology	Theoretical models of activity pattern and optimal foraging: Predictions for the Moose *Alces alces*
1989	Reidar Andersen	Dr. scient Zoology	Interactions between a generalist herbivore, the moose *Alces alces*, and its winter food resources: a study of behavioural variation
1989	Kurt Ingar Draget	Dr. scient Botany	Alginate gel media for plant tissue culture
1990	Bengt Finstad	Dr. scient Zoology	Osmotic and ionic regulation in Atlantic salmon, rainbow trout and Arctic charr: Effect of temperature, salinity and season
1990	Hege Johannesen	Dr. scient Zoology	Respiration and temperature regulation in birds with special emphasis on the oxygen extraction by the lung
1990	Åse Krøkje	Dr. scient Botany	The mutagenic load from air pollution at two work-places with PAH-exposure measured with Ames Salmonella/microsome test
1990	Arne Johan Jensen	Dr. philos Zoology	Effects of water temperature on early life history, juvenile growth and prespawning migrations of Atlantic salmon (*Salmo salar*) and brown trout (*Salmo trutta*): A summary of studies in Norwegian streams
1990	Tor Jørgen Almaas	Dr. scient Zoology	Pheromone reception in moths: Response characteristics of olfactory receptor neurons to intra- and interspecific chemical cues
1990	Magne Husby	Dr. scient Zoology	Breeding strategies in birds: Experiments with the Magpie *Pica pica*
1991	Tor Kvam	Dr. scient Zoology	Population biology of the European lynx (*Lynx lynx*) in Norway
1991	Jan Henning L'Abêe Lund	Dr. philos Zoology	Reproductive biology in freshwater fish, brown trout *Salmo trutta* and roach *Rutilus rutilus* in particular
1991	Asbjørn Moen	Dr. philos Botany	The plant cover of the boreal uplands of Central Norway. I. Vegetation ecology of Sølendet nature reserve; haymaking fens and birch woodlands
1991	Else Marie Løbersli	Dr. scient Botany	Soil acidification and metal uptake in plants
1991	Trond Nordtug	Dr. scient Zoology	Reflectometric studies of photomechanical adaptation in superposition eyes of arthropods
1991	Thyra Solem	Dr. scient Botany	Age, origin and development of blanket mires in Central Norway

1991	Odd Terje Sandlund	Dr. philos Zoology	The dynamics of habitat use in the salmonid genera *Coregonus* and *Salvelinus*: Ontogenic niche shifts and polymorphism
1991	Nina Jonsson	Dr. philos Zoology	Aspects of migration and spawning in salmonids
1991	Atle Bones	Dr. scient Botany	Compartmentation and molecular properties of thioglucoside glucohydrolase (myrosinase)
1992	Torgrim Breiehagen	Dr. scient Zoology	Mating behaviour and evolutionary aspects of the breeding system of two bird species: the Temminck's stint and the Pied flycatcher
1992	Anne Kjersti Bakken	Dr. scient Botany	The influence of photoperiod on nitrate assimilation and nitrogen status in timothy (*Phleum pratense* L.)
1992	Tycho Anker-Nilssen	Dr. scient Zoology	Food supply as a determinant of reproduction and population development in Norwegian Puffins *Fratercula arctica*
1992	Bjørn Munro Jenssen	Dr. philos Zoology	Thermoregulation in aquatic birds in air and water: With special emphasis on the effects of crude oil, chemically treated oil and cleaning on the thermal balance of ducks
1992	Arne Vollan Aarset	Dr. philos Zoology	The ecophysiology of under-ice fauna: Osmotic regulation, low temperature tolerance and metabolism in polar crustaceans.
1993	Geir Slupphaug	Dr. scient Botany	Regulation and expression of uracil-DNA glycosylase and O^6-methylguanine-DNA methyltransferase in mammalian cells
1993	Tor Fredrik Næsje	Dr. scient Zoology	Habitat shifts in coregonids.
1993	Yngvar Asbjørn Olsen	Dr. scient Zoology	Cortisol dynamics in Atlantic salmon, *Salmo salar* L.: Basal and stressor-induced variations in plasma levels and some secondary effects.
1993	Bård Pedersen	Dr. scient Botany	Theoretical studies of life history evolution in modular and clonal organisms
1993	Ole Petter Thangstad	Dr. scient Botany	Molecular studies of myrosinase in Brassicaceae
1993	Thrine L. M. Heggberget	Dr. scient Zoology	Reproductive strategy and feeding ecology of the Eurasian otter *Lutra lutra*.
1993	Kjetil Bevanger	Dr. scient Zoology	Avian interactions with utility structures, a biological approach.
1993	Kåre Haugan	Dr. scient Botany	Mutations in the replication control gene trfA of the broad host-range plasmid RK2
1994	Peder Fiske	Dr. scient Zoology	Sexual selection in the lekking great snipe (*Gallinago media*): Male mating success and female behaviour at the lek
1994	Kjell Inge Reitan	Dr. scient Botany	Nutritional effects of algae in first-feeding of marine fish larvae
1994	Nils Røv	Dr. scient Zoology	Breeding distribution, population status and regulation of breeding numbers in the northeast-Atlantic Great Cormorant *Phalacrocorax carbo carbo*
1994	Annette-Susanne Hoepfner	Dr. scient Botany	Tissue culture techniques in propagation and breeding of Red Raspberry (*Rubus idaeus* L.)
1994	Inga Elise Bruteig	Dr. scient Botany	Distribution, ecology and biomonitoring studies of epiphytic lichens on conifers
1994	Geir Johnsen	Dr. scient Botany	Light harvesting and utilization in marine phytoplankton: Species-specific and photoadaptive responses

1994	Morten Bakken	Dr. scient Zoology	Infanticidal behaviour and reproductive performance in relation to competition capacity among farmed silver fox vixens, *Vulpes vulpes*
1994	Arne Moksnes	Dr. philos Zoology	Host adaptations towards brood parasitism by the Cockoo
1994	Solveig Bakken	Dr. scient Botany	Growth and nitrogen status in the moss *Dicranum majus* Sm. as influenced by nitrogen supply
1994	Torbjørn Forseth	Dr. scient Zoology	Bioenergetics in ecological and life history studies of fishes.
1995	Olav Vadstein	Dr. philos Botany	The role of heterotrophic planktonic bacteria in the cycling of phosphorus in lakes: Phosphorus requirement, competitive ability and food web interactions
1995	Hanne Christensen	Dr. scient Zoology	Determinants of Otter *Lutra lutra* distribution in Norway: Effects of harvest, polychlorinated biphenyls (PCBs), human population density and competition with mink *Mustela vision*
1995	Svein Håkon Lorentsen	Dr. scient Zoology	Reproductive effort in the Antarctic Petrel *Thalassoica antarctica*; the effect of parental body size and condition
1995	Chris Jørgen Jensen	Dr. scient Zoology	The surface electromyographic (EMG) amplitude as an estimate of upper trapezius muscle activity
1995	Martha Kold Bakkevig	Dr. scient Zoology	The impact of clothing textiles and construction in a clothing system on thermoregulatory responses, sweat accumulation and heat transport
1995	Vidar Moen	Dr. scient Zoology	Distribution patterns and adaptations to light in newly introduced populations of *Mysis relicta* and constraints on Cladoceran and Char populations
1995	Hans Haavardsholm Blom	Dr. philos Botany	A revision of the *Schistidium apocarpum* complex in Norway and Sweden
1996	Jorun Skjærmo	Dr. scient Botany	Microbial ecology of early stages of cultivated marine fish; inpact fish-bacterial interactions on growth and survival of larvae
1996	Ola Ugedal	Dr. scient Zoology	Radiocesium turnover in freshwater fishes
1996	Ingibjørg Einarsdottir	Dr. scient Zoology	Production of Atlantic salmon (*Salmo salar*) and Arctic charr (*Salvelinus alpinus*): A study of some physiological and immunological responses to rearing routines
1996	Christina M. S. Pereira	Dr. scient Zoology	Glucose metabolism in salmonids: Dietary effects and hormonal regulation
1996	Jan Fredrik Børseth	Dr. scient Zoology	The sodium energy gradients in muscle cells of *Mytilus edulis* and the effects of organic xenobiotics
1996	Gunnar Henriksen	Dr. scient Zoology	Status of Grey seal *Halichoerus grypus* and Harbour seal *Phoca vitulina* in the Barents sea region
1997	Gunvor Øie	Dr. scient Botany	Eevalution of rotifer *Brachionus plicatilis* quality in early first feeding of turbot *Scophtalmus maximus* L. larvae
1997	Håkon Holien	Dr. scient Botany	Studies of lichens in spruce forest of Central Norway. Diversity, old growth species and the relationship to site and stand parameters
1997	Ole Reitan	Dr. scient Zoology	Responses of birds to habitat disturbance due to damming
1997	Jon Arne Grøttum	Dr. scient Zoology	Physiological effects of reduced water quality on fish in aquaculture

1997	Per Gustav Thingstad	Dr. scient Zoology	Birds as indicators for studying natural and human-induced variations in the environment, with special emphasis on the suitability of the Pied Flycatcher
1997	Torgeir Nygård	Dr. scient Zoology	Temporal and spatial trends of pollutants in birds in Norway: Birds of prey and Willow Grouse used as
1997	Signe Nybø	Dr. scient Zoology	Impacts of long-range transported air pollution on birds with particular reference to the dipper *Cinclus cinclus* in southern Norway
1997	Atle Wibe	Dr. scient Zoology	Identification of conifer volatiles detected by receptor neurons in the pine weevil (*Hylobius abietis*), analysed by gas chromatography linked to electrophysiology and to mass spectrometry
1997	Rolv Lundheim	Dr. scient Zoology	Adaptive and incidental biological ice nucleators
1997	Arild Magne Landa	Dr. scient Zoology	Wolverines in Scandinavia: ecology, sheep depredation and conservation
1997	Kåre Magne Nielsen	Dr. scient Botany	An evolution of possible horizontal gene transfer from plants to sail bacteria by studies of natural transformation in *Acinetobacter calcoacetius*
1997	Jarle Tufto	Dr. scient Zoology	Gene flow and genetic drift in geographically structured populations: Ecological, population genetic, and statistical models
1997	Trygve Hesthagen	Dr. philos Zoology	Population responses of Arctic charr (*Salvelinus alpinus* (L.)) and brown trout (*Salmo trutta* L.) to acidification in Norwegian inland waters
1997	Trygve Sigholt	Dr. philos Zoology	Control of Parr-smolt transformation and seawater tolerance in farmed Atlantic Salmon (*Salmo salar*) Effects of photoperiod, temperature, gradual seawater acclimation, NaCl and betaine in the diet
1997	Jan Østnes	Dr. scient Zoology	Cold sensation in adult and neonate birds
1998	Seethaledsumy Visvalingam	Dr. scient Botany	Influence of environmental factors on myrosinases and myrosinase-binding proteins
1998	Thor Harald Ringsby	Dr. scient Zoology	Variation in space and time: The biology of a House sparrow metapopulation
1998	Erling Johan Solberg	Dr. scient Zoology	Variation in population dynamics and life history in a Norwegian moose (*Alces alces*) population: consequences of harvesting in a variable environment
1998	Sigurd Mjøen Saastad	Dr. scient Botany	Species delimitation and phylogenetic relationships between the Sphagnum recurvum complex (Bryophyta): genetic variation and phenotypic plasticity
1998	Bjarte Mortensen	Dr. scient Botany	Metabolism of volatile organic chemicals (VOCs) in a head liver S9 vial equilibration system in vitro
1998	Gunnar Austrheim	Dr. scient Botany	Plant biodiversity and land use in subalpine grasslands. – A conservation biological approach
1998	Bente Gunnveig Berg	Dr. scient Zoology	Encoding of pheromone information in two related moth species
1999	Kristian Overskaug	Dr. scient Zoology	Behavioural and morphological characteristics in Northern Tawny Owls *Strix aluco*: An intra- and interspecific comparative approach
1999	Hans Kristen Stenøien	Dr. scient Botany	Genetic studies of evolutionary processes in various populations of nonvascular plants (mosses, liverworts and hornworts)
1999	Trond Arnesen	Dr. scient Botany	Vegetation dynamics following trampling and burning in the outlying haylands at Sølendet, Central Norway

1999	Ingvar Stenberg	Dr. scient Zoology	Habitat selection, reproduction and survival in the White-backed Woodpecker *Dendrocopos leucotos*
1999	Stein Olle Johansen	Dr. scient Botany	A study of driftwood dispersal to the Nordic Seas by dendrochronology and wood anatomical analysis
1999	Trina Falck Galloway	Dr. scient Zoology	Muscle development and growth in early life stages of the Atlantic cod (*Gadus morhua* L.) and Halibut (*Hippoglossus hippoglossus* L.)
1999	Marianne Giæver	Dr. scient Zoology	Population genetic studies in three gadoid species: blue whiting (*Micromisistius poutassou*), haddock (*Melanogrammus aeglefinus*) and cod (*Gadus morhua*) in the North-East Atlantic
1999	Hans Martin Hanslin	Dr. scient Botany	The impact of environmental conditions of density dependent performance in the boreal forest bryophytes *Dicranum majus*, *Hylocomium splendens*, *Plagiochila asplenigides*, *Ptilium crista-castrensis* and *Rhytidiadelphus lokeus*
1999	Ingrid Bysveen Mjølnerød	Dr. scient Zoology	Aspects of population genetics, behaviour and performance of wild and farmed Atlantic salmon (*Salmo salar*) revealed by molecular genetic techniques
1999	Else Berit Skagen	Dr. scient Botany	The early regeneration process in protoplasts from *Brassica napus* hypocotyls cultivated under various g-forces
1999	Stein-Are Sæther	Dr. philos Zoology	Mate choice, competition for mates, and conflicts of interest in the Lekking Great Snipe
1999	Katrine Wangen Rustad	Dr. scient Zoology	Modulation of glutamatergic neurotransmission related to cognitive dysfunctions and Alzheimer's disease
1999	Per Terje Smiseth	Dr. scient Zoology	Social evolution in monogamous families:
1999	Gunnbjørn Bremset	Dr. scient Zoology	Young Atlantic salmon (*Salmo salar* L.) and Brown trout (*Salmo trutta* L.) inhabiting the deep pool habitat, with special reference to their habitat use, habitat preferences and competitive interactions
1999	Frode Ødegaard	Dr. scient Zoology	Host specificity as a parameter in estimates of arthropod species richness
1999	Sonja Andersen	Dr. scient Zoology	Expressional and functional analyses of human, secretory phospholipase A2
2000	Ingrid Salvesen	Dr. scient Botany	Microbial ecology in early stages of marine fish: Development and evaluation of methods for microbial management in intensive larviculture
2000	Ingar Jostein Øien	Dr. scient Zoology	The Cuckoo (*Cuculus canorus*) and its host: adaptions and counteradaptions in a coevolutionary arms race
2000	Pavlos Makridis	Dr. scient Botany	Methods for the microbial control of live food used for the rearing of marine fish larvae
2000	Sigbjørn Stokke	Dr. scient Zoology	Sexual segregation in the African elephant (*Loxodonta africana*)
2000	Odd A. Gulseth	Dr. philos Zoology	Seawater tolerance, migratory behaviour and growth of Charr, (*Salvelinus alpinus*), with emphasis on the high Arctic Dieset charr on Spitsbergen, Svalbard
2000	Pål A. Olsvik	Dr. scient Zoology	Biochemical impacts of Cd, Cu and Zn on brown trout (*Salmo trutta*) in two mining-contaminated rivers in Central Norway
2000	Sigurd Einum	Dr. scient Zoology	Maternal effects in fish: Implications for the evolution of breeding time and egg size
2001	Jan Ove Evjemo	Dr. scient Zoology	Production and nutritional adaptation of the brine shrimp *Artemia* sp. as live food organism for larvae of marine cold water fish species

2001	Olga Hilmo	Dr. scient Botany	Lichen response to environmental changes in the managed boreal forest systems
2001	Ingebrigt Uglem	Dr. scient Zoology	Male dimorphism and reproductive biology in corkwing wrasse (*Symphodus melops* L.)
2001	Bård Gunnar Stokke	Dr. scient Zoology	Coevolutionary adaptations in avian brood parasites and their hosts
2002	Ronny Aanes	Dr. scient Zoology	Spatio-temporal dynamics in Svalbard reindeer (*Rangifer tarandus platyrhynchus*)
2002	Mariann Sandsund	Dr. scient Zoology	Exercise- and cold-induced asthma. Respiratory and thermoregulatory responses
2002	Dag-Inge Øien	Dr. scient Botany	Dynamics of plant communities and populations in boreal vegetation influenced by scything at Sølendet, Central Norway
2002	Frank Rosell	Dr. scient Zoology	The function of scent marking in beaver (*Castor fiber*)
2002	Janne Østvang	Dr. scient Botany	The Role and Regulation of Phospholipase A_2 in Monocytes During Atherosclerosis Development
2002	Terje Thun	Dr. philos Biology	Dendrochronological constructions of Norwegian conifer chronologies providing dating of historical material
2002	Birgit Hafjeld Borgen	Dr. scient Biology	Functional analysis of plant idioblasts (Myrosin cells) and their role in defense, development and growth
2002	Bård Øyvind Solberg	Dr. scient Biology	Effects of climatic change on the growth of dominating tree species along major environmental gradients
2002	Per Winge	Dr. scient Biology	The evolution of small GTP binding proteins in cellular organisms. Studies of RAC GTPases in *Arabidopsis thaliana* and the Ral GTPase from *Drosophila melanogaster*
2002	Henrik Jensen	Dr. scient Biology	Causes and consequences of individual variation in fitness-related traits in house sparrows
2003	Jens Rohloff	Dr. philos Biology	Cultivation of herbs and medicinal plants in Norway – Essential oil production and quality control
2003	Åsa Maria O. Espmark Wibe	Dr. scient Biology	Behavioural effects of environmental pollution in threespine stickleback *Gasterosteus aculeatur* L.
2003	Dagmar Hagen	Dr. scient Biology	Assisted recovery of disturbed arctic and alpine vegetation – an integrated approach
2003	Bjørn Dahle	Dr. scient Biology	Reproductive strategies in Scandinavian brown bears
2003	Cyril Lebogang Taolo	Dr. scient Biology	Population ecology, seasonal movement and habitat use of the African buffalo (*Syncerus caffer*) in Chobe National Park, Botswana
2003	Marit Stranden	Dr. scient Biology	Olfactory receptor neurones specified for the same odorants in three related Heliothine species (*Helicoverpa armigera, Helicoverpa assulta* and *Heliothis virescens*)
2003	Kristian Hassel	Dr. scient Biology	Life history characteristics and genetic variation in an expanding species, *Pogonatum dentatum*
2003	David Alexander Rae	Dr. scient Biology	Plant- and invertebrate-community responses to species interaction and microclimatic gradients in alpine and Artic environments
2003	Åsa A Borg	Dr. scient Biology	Sex roles and reproductive behaviour in gobies and guppies: a female perspective
2003	Eldar Åsgard Bendiksen	Dr. scient Biology	Environmental effects on lipid nutrition of farmed Atlantic salmon (*Salmo salar* L.) parr and smolt
2004	Torkild Bakken	Dr. scient Biology	A revision of Nereidinae (Polychaeta, Nereididae)

2004	Ingar Pareliussen	Dr. scient Biology	Natural and Experimental Tree Establishment in a Fragmented Forest, Ambohitantely Forest Reserve, Madagascar
2004	Tore Brembu	Dr. scient Biology	Genetic, molecular and functional studies of RAC GTPases and the WAVE-like regulatory protein complex in *Arabidopsis thaliana*
2004	Liv S. Nilsen	Dr. scient Biology	Coastal heath vegetation on central Norway; recent past, present state and future possibilities
2004	Hanne T. Skiri	Dr. scient Biology	Olfactory coding and olfactory learning of plant odours in heliothine moths. An anatomical, physiological and behavioural study of three related species (*Heliothis virescens, Helicoverpa armigera* and *Helicoverpa assulta*)
2004	Lene Østby	Dr. scient Biology	Cytochrome P4501A (CYP1A) induction and DNA adducts as biomarkers for organic pollution in the natural environment
2004	Emmanuel J. Gerreta	Dr. philos Biology	The Importance of Water Quality and Quantity in the Tropical Ecosystems, Tanzania
2004	Linda Dalen	Dr. scient Biology	Dynamics of Mountain Birch Treelines in the Scandes Mountain Chain, and Effects of Climate Warming
2004	Lisbeth Mehli	Dr. scient Biology	Polygalacturonase-inhibiting protein (PGIP) in cultivated strawberry (*Fragaria* x *ananassa*): characterisation and induction of the gene following fruit infection by *Botrytis cinerea*
2004	Børge Moe	Dr. scient Biology	Energy-Allocation in Avian Nestlings Facing Short-Term Food Shortage
2005	Matilde Skogen Chauton	Dr. scient Biology	Metabolic profiling and species discrimination from High-Resolution Magic Angle Spinning NMR analysis of whole-cell samples
2005	Sten Karlsson	Dr. scient Biology	Dynamics of Genetic Polymorphisms
2005	Terje Bongard	Dr. scient Biology	Life History strategies, mate choice, and parental investment among Norwegians over a 300-year period
2005	Tonette Røstelien	PhD Biology	Functional characterisation of olfactory receptor neurone types in heliothine moths
2005	Erlend Kristiansen	Dr. scient Biology	Studies on antifreeze proteins
2005	Eugen G. Sørmo	Dr. scient Biology	Organochlorine pollutants in grey seal (*Halichoerus grypus*) pups and their impact on plasma thyroid hormone and vitamin A concentrations
2005	Christian Westad	Dr. scient Biology	Motor control of the upper trapezius
2005	Lasse Mork Olsen	PhD Biology	Interactions between marine osmo- and phagotrophs in different physicochemical environments
2005	Åslaug Viken	PhD Biology	Implications of mate choice for the management of small populations
2005	Ariaya Hymete Sahle Dingle	PhD Biology	Investigation of the biological activities and chemical constituents of selected *Echinops* spp. growing in Ethiopia
2005	Anders Gravbrøt Finstad	PhD Biology	Salmonid fishes in a changing climate: The winter challenge
2005	Shimane Washington Makabu	PhD Biology	Interactions between woody plants, elephants and other browsers in the Chobe Riverfront, Botswana
2005	Kjartan Østbye	Dr. scient Biology	The European whitefish *Coregonus lavaretus* (L.) species complex: historical contingency and adaptive radiation

2006	Kari Mette Murvoll	PhD Biology	Levels and effects of persistent organic pollutans (POPs) in seabirds, Retinoids and α-tocopherol – potential biomakers of POPs in birds?
2006	Ivar Herfindal	Dr. scient Biology	Life history consequences of environmental variation along ecological gradients in northern ungulates
2006	Nils Egil Tokle	PhD Biology	Are the ubiquitous marine copepods limited by food or predation? Experimental and field-based studies with main focus on *Calanus finmarchicus*
2006	Jan Ove Gjershaug	Dr. philos Biology	Taxonomy and conservation status of some booted eagles in south-east Asia
2006	Jon Kristian Skei	Dr. scient Biology	Conservation biology and acidification problems in the breeding habitat of amphibians in Norway
2006	Johanna Järnegren	PhD Biology	*Acesta oophaga* and *Acesta excavata* – a study of hidden biodiversity
2006	Bjørn Henrik Hansen	PhD Biology	Metal-mediated oxidative stress responses in brown trout (*Salmo trutta*) from mining contaminated rivers in Central Norway
2006	Vidar Grøtan	PhD Biology	Temporal and spatial effects of climate fluctuations on population dynamics of vertebrates
2006	Jafari R Kideghesho	PhD Biology	Wildlife conservation and local land use conflicts in Western Serengeti Corridor, Tanzania
2006	Anna Maria Billing	PhD Biology	Reproductive decisions in the sex role reversed pipefish *Syngnathus typhle*: when and how to invest in reproduction
2006	Henrik Pärn	PhD Biology	Female ornaments and reproductive biology in the bluethroat
2006	Anders J. Fjellheim	PhD Biology	Selection and administration of probiotic bacteria to marine fish larvae
2006	P. Andreas Svensson	PhD Biology	Female coloration, egg carotenoids and reproductive success: gobies as a model system
2007	Sindre A. Pedersen	PhD Biology	Metal binding proteins and antifreeze proteins in the beetle *Tenebrio molitor* - a study on possible competition for the semi-essential amino acid cysteine
2007	Kasper Hancke	PhD Biology	Photosynthetic responses as a function of light and temperature: Field and laboratory studies on marine microalgae
2007	Tomas Holmern	PhD Biology	Bushmeat hunting in the western Serengeti: Implications for community-based conservation
2007	Kari Jørgensen	PhD Biology	Functional tracing of gustatory receptor neurons in the CNS and chemosensory learning in the moth *Heliothis virescens*
2007	Stig Ulland	PhD Biology	Functional Characterisation of Olfactory Receptor Neurons in the Cabbage Moth, (*Mamestra brassicae* L.) (Lepidoptera, Noctuidae). Gas Chromatography Linked to Single Cell Recordings and Mass Spectrometry
2007	Snorre Henriksen	PhD Biology	Spatial and temporal variation in herbivore resources at northern latitudes
2007	Roelof Frans May	PhD Biology	Spatial Ecology of Wolverines in Scandinavia
2007	Vedasto Gabriel Ndibalema	PhD Biology	Demographic variation, distribution and habitat use between wildebeest sub-populations in the Serengeti National Park, Tanzania
2007	Julius William Nyahongo	PhD Biology	Depredation of Livestock by wild Carnivores and Illegal Utilization of Natural Resources by Humans in the Western Serengeti, Tanzania

2007	Shombe Ntaraluka Hassan	PhD Biology	Effects of fire on large herbivores and their forage resources in Serengeti, Tanzania
2007	Per-Arvid Wold	PhD Biology	Functional development and response to dietary treatment in larval Atlantic cod *(Gadus morhua* L.) Focus on formulated diets and early weaning
2007	Anne Skjetne Mortensen	PhD Biology	Toxicogenomics of Aryl Hydrocarbon- and Estrogen Receptor Interactions in Fish: Mechanisms and Profiling of Gene Expression Patterns in Chemical Mixture Exposure Scenarios
2008	Brage Bremset Hansen	PhD Biology	The Svalbard reindeer (*Rangifer tarandus platyrhynchus*) and its food base: plant-herbivore interactions in a high-arctic ecosystem
2008	Jiska van Dijk	PhD Biology	Wolverine foraging strategies in a multiple-use landscape
2008	Flora John Magige	PhD Biology	The ecology and behaviour of the Masai Ostrich (*Struthio camelus massaicus*) in the Serengeti Ecosystem, Tanzania
2008	Bernt Rønning	PhD Biology	Sources of inter- and intra-individual variation in basal metabolic rate in the zebra finch, *Taeniopygia guttata*
2008	Sølvi Wehn	PhD Biology	Biodiversity dynamics in semi-natural mountain landscapes - A study of consequences of changed agricultural practices in Eastern Jotunheimen
2008	Trond Moxness Kortner	PhD Biology	The Role of Androgens on previtellogenic oocyte growth in Atlantic cod (*Gadus morhua*): Identification and patterns of differentially expressed genes in relation to Stereological Evaluations
2008	Katarina Mariann Jørgensen	Dr. scient Biology	The role of platelet activating factor in activation of growth arrested keratinocytes and re-epithelialisation
2008	Tommy Jørstad	PhD Biology	Statistical Modelling of Gene Expression Data
2008	Anna Kusnierczyk	PhD Biology	*Arabidopsis thaliana* Responses to Aphid Infestation
2008	Jussi Evertsen	PhD Biology	Herbivore sacoglossans with photosynthetic chloroplasts
2008	John Eilif Hermansen	PhD Biology	Mediating ecological interests between locals and globals by means of indicators. A study attributed to the asymmetry between stakeholders of tropical forest at Mt. Kilimanjaro, Tanzania
2008	Ragnhild Lyngved	PhD Biology	Somatic embryogenesis in *Cyclamen persicum.* Biological investigations and educational aspects of cloning
2008	Line Elisabeth Sundt-Hansen	PhD Biology	Cost of rapid growth in salmonid fishes
2008	Line Johansen	PhD Biology	Exploring factors underlying fluctuations in white clover populations – clonal growth, population structure and spatial distribution
2009	Astrid Jullumstrø Feuerherm	PhD Biology	Elucidation of molecular mechanisms for pro-inflammatory phospholipase A2 in chronic disease
2009	Pål Kvello	PhD Biology	Neurons forming the network involved in gustatory coding and learning in the moth *Heliothis virescens:* Physiological and morphological characterisation, and integration into a standard brain atlas
2009	Trygve Devold Kjellsen	PhD Biology	Extreme Frost Tolerance in Boreal Conifers
2009	Johan Reinert Vikan	PhD Biology	Coevolutionary interactions between common cuckoos *Cuculus canorus* and *Fringilla* finches

2009	Zsolt Volent	PhD Biology	Remote sensing of marine environment: Applied surveillance with focus on optical properties of phytoplankton, coloured organic matter and suspended matter
2009	Lester Rocha	PhD Biology	Functional responses of perennial grasses to simulated grazing and resource availability
2009	Dennis Ikanda	PhD Biology	Dimensions of a Human-lion conflict: Ecology of human predation and persecution of African lions (*Panthera leo*) in Tanzania
2010	Huy Quang Nguyen	PhD Biology	Egg characteristics and development of larval digestive function of cobia (*Rachycentron canadum*) in response to dietary treatments - Focus on formulated diets
2010	Eli Kvingedal	PhD Biology	Intraspecific competition in stream salmonids: the impact of environment and phenotype
2010	Sverre Lundemo	PhD Biology	Molecular studies of genetic structuring and demography in *Arabidopsis* from Northern Europe
2010	Iddi Mihijai Mfunda	PhD Biology	Wildlife Conservation and People's livelihoods: Lessons Learnt and Considerations for Improvements. The Case of Serengeti Ecosystem, Tanzania
2010	Anton Tinchov Antonov	PhD Biology	Why do cuckoos lay strong-shelled eggs? Tests of the puncture resistance hypothesis
2010	Anders Lyngstad	PhD Biology	Population Ecology of *Eriophorum latifolium*, a Clonal Species in Rich Fen Vegetation
2010	Hilde Færevik	PhD Biology	Impact of protective clothing on thermal and cognitive responses
2010	Ingerid Brænne Arbo	PhD Medical technology	Nutritional lifestyle changes – effects of dietary carbohydrate restriction in healthy obese and overweight humans
2010	Yngvild Vindenes	PhD Biology	Stochastic modeling of finite populations with individual heterogeneity in vital parameters
2010	Hans-Richard Brattbakk	PhD Medical technology	The effect of macronutrient composition, insulin stimulation, and genetic variation on leukocyte gene expression and possible health benefits
2011	Geir Hysing Bolstad	PhD Biology	Evolution of Signals: Genetic Architecture, Natural Selection and Adaptive Accuracy
2011	Karen de Jong	PhD Biology	Operational sex ratio and reproductive behaviour in the two-spotted goby (*Gobiusculus flavescens*)
2011	Ann-Iren Kittang	PhD Biology	*Arabidopsis thaliana* L. adaptation mechanisms to microgravity through the EMCS MULTIGEN-2 experiment on the ISS: The science of space experiment integration and adaptation to simulated microgravity
2011	Aline Magdalena Lee	PhD Biology	Stochastic modeling of mating systems and their effect on population dynamics and genetics
2011	Christopher Gravningen Sørmo	PhD Biology	Rho GTPases in Plants: Structural analysis of ROP GTPases; genetic and functional studies of MIRO GTPases in Arabidopsis thaliana
2011	Grethe Robertsen	PhD Biology	Relative performance of salmonid phenotypes across environments and competitive intensities
2011	Line-Kristin Larsen	PhD Biology	Life-history trait dynamics in experimental populations of guppy (*Poecilia reticulata*): the role of breeding regime and captive environment
2011	Maxim A. K. Teichert	PhD Biology	Regulation in Atlantic salmon (*Salmo salar*): The interaction between habitat and density

2011	Torunn Beate Hancke	PhD Biology	Use of Pulse Amplitude Modulated (PAM) Fluorescence and Bio-optics for Assessing Microalgal Photosynthesis and Physiology
2011	Sajeda Begum	PhD Biology	Brood Parasitism in Asian Cuckoos: Different Aspects of Interactions between Cuckoos and their Hosts in Bangladesh
2011	Kari J. K. Attramadal	PhD Biology	Water treatment as an approach to increase microbial control in the culture of cold water marine larvae
2011	Camilla Kalvatn Egset	PhD Biology	The Evolvability of Static Allometry: A Case Study
2011	AHM Raihan Sarker	PhD Biology	Conflict over the conservation of the Asian elephant (*Elephas maximus*) in Bangladesh
2011	Gro Dehli Villanger	PhD Biology	Effects of complex organohalogen contaminant mixtures on thyroid hormone homeostasis in selected arctic marine mammals
2011	Kari Bjørneraas	PhD Biology	Spatiotemporal variation in resource utilisation by a large herbivore, the moose
2011	John Odden	PhD Biology	The ecology of a conflict: Eurasian lynx depredation on domestic sheep
2011	Simen Pedersen	PhD Biology	Effects of native and introduced cervids on small mammals and birds
2011	Mohsen Falahati-Anbaran	PhD Biology	Evolutionary consequences of seed banks and seed dispersal in *Arabidopsis*
2012	Jakob Hønborg Hansen	PhD Biology	Shift work in the offshore vessel fleet: circadian rhythms and cognitive performance
2012	Elin Noreen	PhD Biology	Consequences of diet quality and age on life-history traits in a small passerine bird
2012	Irja Ida Ratikainen	PhD Biology	Foraging in a variable world: adaptations to stochasticity
2012	Aleksander Handå	PhD Biology	Cultivation of mussels (*Mytilus edulis):* Feed requirements, storage and integration with salmon (*Salmo salar*) farming
2012	Morten Kraabøl	PhD Biology	Reproductive and migratory challenges inflicted on migrant brown trout (*Salmo trutta* L.) in a heavily modified river
2012	Jisca Huisman	PhD Biology	Gene flow and natural selection in Atlantic salmon
2012	Maria Bergvik	PhD Biology	Lipid and astaxanthin contents and biochemical post-harvest stability in *Calanus finmarchicus*
2012	Bjarte Bye Løfaldli	PhD Biology	Functional and morphological characterization of central olfactory neurons in the model insect *Heliothis virescens*.
2012	Karen Marie Hammer	PhD Biology	Acid-base regulation and metabolite responses in shallow- and deep-living marine invertebrates during environmental hypercapnia
2012	Øystein Nordrum Wiggen	PhD Biology	Optimal performance in the cold
2012	Robert Dominikus Fyumagwa	Dr. Philos Biology	Anthropogenic and natural influence on disease prevalence at the human –livestock-wildlife interface in the Serengeti ecosystem, Tanzania
2012	Jenny Bytingsvik	PhD Biology	Organohalogenated contaminants (OHCs) in polar bear mother-cub pairs from Svalbard, Norway. Maternal transfer, exposure assessment and thyroid hormone disruptive effects in polar bear cubs
2012	Christer Moe Rolandsen	PhD Biology	The ecological significance of space use and movement patterns of moose in a variable environment

2012	Erlend Kjeldsberg Hovland	PhD Biology	Bio-optics and Ecology in *Emiliania huxleyi* Blooms: Field and Remote Sensing Studies in Norwegian Waters
2012	Lise Cats Myhre	PhD Biology	Effects of the social and physical environment on mating behaviour in a marine fish
2012	Tonje Aronsen	PhD Biology	Demographic, environmental and evolutionary aspects of sexual selection
2012	Bin Liu	PhD Biology	Molecular genetic investigation of cell separation and cell death regulation in *Arabidopsis thaliana*
2013	Jørgen Rosvold	PhD Biology	Ungulates in a dynamic and increasingly human dominated landscape – A millennia-scale perspective
2013	Pankaj Barah	PhD Biology	Integrated Systems Approaches to Study Plant Stress Responses
2013	Marit Linnerud	PhD Biology	Patterns in spatial and temporal variation in population abundances of vertebrates
2013	Xinxin Wang	PhD Biology	Integrated multi-trophic aquaculture driven by nutrient wastes released from Atlantic salmon (*Salmo salar*) farming
2013	Ingrid Ertshus Mathisen	PhD Biology	Structure, dynamics, and regeneration capacity at the sub-arctic forest-tundra ecotone of northern Norway and Kola Peninsula, NW Russia
2013	Anders Foldvik	PhD Biology	Spatial distributions and productivity in salmonid populations
2013	Anna Marie Holand	PhD Biology	Statistical methods for estimating intra- and inter-population variation in genetic diversity
2013	Anna Solvang Båtnes	PhD Biology	Light in the dark – the role of irradiance in the high Arctic marine ecosystem during polar night
2013	Sebastian Wacker	PhD Biology	The dynamics of sexual selection: effects of OSR, density and resource competition in a fish
2013	Cecilie Miljeteig	PhD Biology	Phototaxis in *Calanus finmarchicus* – light sensitivity and the influence of energy reserves and oil exposure
2013	Ane Kjersti Vie	PhD Biology	Molecular and functional characterisation of the IDA family of signalling peptides in *Arabidopsis thaliana*
2013	Marianne Nymark	PhD Biology	Light responses in the marine diatom *Phaeodactylum tricornutum*
2014	Jannik Schultner	PhD Biology	Resource Allocation under Stress - Mechanisms and Strategies in a Long-Lived Bird
2014	Craig Ryan Jackson	PhD Biology	Factors influencing African wild dog *(Lycaon pictus*) habitat selection and ranging behaviour: conservation and management implications
2014	Aravind Venkatesan	PhD Biology	Application of Semantic Web Technology to establish knowledge management and discovery in the Life Sciences
2014	Kristin Collier Valle	PhD Biology	Photoacclimation mechanisms and light responses in marine micro- and macroalgae
2014	Michael Puffer	PhD Biology	Effects of rapidly fluctuating water levels on juvenile Atlantic salmon (*Salmo salar* L.)
2014	Gundula S. Bartzke	PhD Biology	Effects of power lines on moose *(Alces alces)* habitat selection, movements and feeding activity
2014	Eirin Marie Bjørkvoll	PhD Biology	Life-history variation and stochastic population dynamics in vertebrates
2014	Håkon Holand	PhD Biology	The parasite *Syngamus trachea* in a metapopulation of house sparrows
2014	Randi Magnus Sommerfelt	PhD Biology	Molecular mechanisms of inflammation – a central role for cytosolic phospholiphase A2

2014	Espen Lie Dahl	PhD Biology	Population demographics in white-tailed eagle at an on-shore wind farm area in coastal Norway
2014	Anders Øverby	PhD Biology	Functional analysis of the action of plant isothiocyanates: cellular mechanisms and in vivo role in plants, and anticancer activity
2014	Kamal Prasad Acharya	PhD Biology	Invasive species: Genetics, characteristics and trait variation along a latitudinal gradient.
2014	Ida Beathe Øverjordet	PhD Biology	Element accumulation and oxidative stress variables in Arctic pelagic food chains: *Calanus*, little auks (*Alle alle*) and black-legged kittiwakes (*Rissa tridactyla*)
2014	Kristin Møller Gabrielsen	PhD Biology	Target tissue toxicity of the thyroid hormone system in two species of arctic mammals carrying high loads of organohalogen contaminants
2015	Gine Roll Skjervø	Dr. philos Biology	Testing behavioral ecology models with historical individual-based human demographic data from Norway
2015	Nils Erik Gustaf Forsberg	PhD Biology	Spatial and Temporal Genetic Structure in Landrace Cereals
2015	Leila Alipanah	PhD Biology	Integrated analyses of nitrogen and phosphorus deprivation in the diatoms *Phaeodactylum tricornutum* and *Seminavis robusta*
2015	Javad Najafi	PhD Biology	Molecular investigation of signaling components in sugar sensing and defense in *Arabidopsis thaliana*
2015	Bjørnar Sporsheim	PhD Biology	Quantitative confocal laser scanning microscopy: optimization of in vivo and in vitro analysis of intracellular transport
2015	Magni Olsen Kyrkjeeide	PhD Biology	Genetic variation and structure in peatmosses (*Sphagnum*)
2015	Keshuai Li	PhD Biology	Phospholipids in Atlantic cod (*Gadus morhua* L.) larvae rearing: Incorporation of DHA in live feed and larval phospholipids and the metabolic capabilities of larvae for the de novo synthesis
2015	Ingvild Fladvad Størdal	PhD Biology	The role of the copepod *Calanus finmarchicus* in affecting the fate of marine oil spills
2016	Thomas Kvalnes	PhD Biology	Evolution by natural selection in age-structured populations in fluctuating environments
2016	Øystein Leiknes	PhD Biology	The effect of nutrition on important life-history traits in the marine copepod *Calanus finmarchicus*
2016	Johan Henrik Hårdensson Berntsen	PhD Biology	Individual variation in survival: The effect of incubation temperature on the rate of physiological ageing in a small passerine bird
2016	Marianne Opsahl Olufsen	PhD Biology	Multiple environmental stressors: Biological interactions between parameters of climate change and perfluorinated alkyl substances in fish
2016	Rebekka Varne	PhD Biology	Tracing the fate of escaped cod (*Gadus morhua* L.) in a Norwegian fjord system
2016	Anette Antonsen Fenstad	PhD Biology	Pollutant Levels, Antioxidants and Potential Genotoxic Effects in Incubating Female Common Eiders (*Somateria mollissima*)
2016	Wilfred Njama Marealle	PhD Biology	Ecology, Behaviour and Conservation Status of Masai Giraffe (*Giraffa camelopardalis tippelskirchi*) in Tanzania
2016	Ingunn Nilssen	PhD Biology	Integrated Enviromental Mapping and Monitoring: A Methodological approach for end users.
2017	Konika Chawla	PhD Biology	Discovering, analysing and taking care of knowledge.

2017	Øystein Hjorthol Opedal	PhD Biology	The Evolution of Herkogamy: Pollinator Reliability, Natural Selection, and Trait Evolvability.
2017	Ane Marlene Myhre	PhD Biology	Effective size of density dependent populations in fluctuating environments
2017	Emmanuel Hosiana Masenga	PhD Biology	Behavioural Ecology of Free-ranging and Reintroduced African Wild Dog (*Lycaon pictus*) Packs in the Serengeti Ecosystem, Tanzania
2017	Xiaolong Lin	PhD Biology	Systematics and evolutionary history of *Tanytarsus* van der Wulp, 1874 (Diptera: Chironomidae)
2017	Emmanuel Clamsen Mmassy	PhD Biology	Ecology and Conservation Challenges of the Kori bustard in the Serengeti National Park
2017	Richard Daniel Lyamuya	PhD Biology	Depredation of Livestock by Wild Carnivores in the Eastern Serengeti Ecosystem, Tanzania
2017	Katrin Hoydal	PhD Biology	Levels and endocrine disruptive effects of legacy POPs and their metabolites in long-finned pilot whales of the Faroe Islands
2017	Berit Glomstad	PhD Biology	Adsorption of phenanthrene to carbon nanotubes and its influence on phenanthrene bioavailability/toxicity in aquatic organism
2017	Øystein Nordeide Kielland	PhD Biology	Sources of variation in metabolism of an aquatic ectotherm
2017	Narjes Yousefi	PhD Biology	Genetic divergence and speciation in northern peatmosses (*Sphagnum*)
2018	Signe Christensen-Dalgaard	PhD Biology	Drivers of seabird spatial ecology - implications for development of offshore wind-power in Norway
2018	Janos Urbancsok	PhD Biology	Endogenous biological effects induced by externally supplemented glucosinolate hydrolysis products (GHPs) on *Arabidopsis thaliana*
2018	Alice Mühlroth	PhD Biology	The influence of phosphate depletion on lipid metabolism of microalgae
2018	Franco Peniel Mbise	PhD Biology	Human-Carnivore Coexistence and Conflict in the Eastern Serengeti, Tanzania
2018	Stine Svalheim Markussen	PhD Biology	Causes and consequences of intersexual life history variation in a harvested herbivore population
2018	Mia Vedel Sørensen	PhD Biology	Carbon budget consequences of deciduous shrub expansion in alpine tundra ecosystems
2018	Hanna Maria Kauko	PhD Biology	Light response and acclimation of microalgae in a changing Arctic
2018	Erlend I. F. Fossen	PhD Biology	Trait evolvability: effects of thermal plasticity and genetic correlations among traits
2019	Peter Sjolte Ranke	PhD Biology	Demographic and genetic and consequences of dispersal in house sparrows
2019	Mathilde Le Moullec	PhD Biology	Spatiotemporal variation in abundance of key tundra species: from local heterogeneity to large-scale synchrony
2019	Endre Grüner Ofstad	PhD Biology	Causes and consequences of variation in resource use and social structure in ungulates
2019	Yang Jin	PhD Biology	Development of lipid metabolism in early life stage of Atlantic salmon (*Salmo salar*)
2019	Elena Albertsen	PhD Biology	Evolution of floral traits: from ecological contex to functional integration
2019	Mominul Islam Nahid	PhD Biology	Interaction between two Asian cuckoos and their hosts in Bangladesh

2019	Knut Jørgen Egelie	Phd Biology	Management of intellectual property in university-industry collaborations – public access to and control of knowledge
2019	Thomas Ray Haaland	Phd Biology	Adaptive responses to enviromental stochasticity on different evolutionary time-scales
2019	Kwaslema Malle Hariohay	Phd Biology	Human wildlife interactions in the Ruaha-Rungwa Ecosystem, Central Tanzania
2019	Mari Engvig Løseth	Phd Biology	Exposure and effects of emerging and legacy organic pollutants in white-tailed eagle (*Haliaeetis albicilla*) nestlings
2019	Joseph Mbyati Mukeka	Phd Biology	Human-Wildlife Conflicts and Compensation for Losses in Kenya: Dynamics, Characteristics and Correlates
2019	Helene Løvstrand Svarva	Phd Biology	Dendroclimatology in southern Norway: tree rings, demography and climate
2019	Nathalie Briels	Phd Biology	Exposure and effects of legacy and emerging organic pollutants in developing birds – Laboratory and field studies
2019	Anders L.Kolstad	Phd Biology	Moose browsing effects on boreal production forests – implications for ecosystems and human society
2019	Bart Peeters	Phd Biology	Population dynamics under climate change ad harvesting: Results from the high Arctic Svalbard reindeer
2019	Alex Kojo Datsomor	Phd Biology	The molecular basis of long chain polyunsaturated fatty acid (LC-PUFA) biosynthesis in Atlantic salmon (*Salmo salar L*): In vivo functions, functional redundancy and transcriptional regulation of LC-PUFA biosynthetic enzymes
2020	Ingun Næve	Phd Biology	Development of non-invasive methods using ultrasound technology in monitoring of Atlantic salmon (*Salmo Salar*) production and reproduction
2020	Rachael Morgan	Phd Biology	Physiological plasticity and evolution of thermal performance in zebrafish
2020	Mahsa Jalili	Phd Biology	Effects of different dietary ingredients on the immune responses and antioxidant status in Atlantic salmon (*Salmo salar L.):* possible nutriomics approaches
2020	Haiqing Wang	Phd Biology	Utilization of the polychaete Hediste diversicolor (O.F. Millier, 1776) in recycling waste nutrients from land-based fish farms for valueadding applications'
2020	Louis Hunninck	Phd Biology	Physiological and behavioral adaptations of impala to anthropogenic disturbances in the Serengeti ecosystems
2020	Kate Layton-Matthews	Phd Biology	Demographic consequences of rapid climate change and density dependence in migratory Arctic geese
2020	Amit Kumar Sharma	Phd Biology	Genome editing of marine algae: Technology development and use of the CRISPR/Cas9 system for studies of light harvesting complexes and regulation of phosphate homeostasis
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2020	Sindre Håvarstein Eldøy	Phd Biology	The influence of physiology, life history and environmental conditions on the marine migration patters of sea trout

2020	Vasundra Touré	Ph Biology	Improving the FAIRness of causal interactions in systems biology: data curation and standardisation to support systems modelling applications
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2020	Jørn Olav Løkken	Phd Biology	Change in vegetation composition and growth in the forest-tundra ecotone – effects of climate warming and herbivory
2020	Kristin Odden Nystuen	Phd Biology	Drivers of plant recruitment in alpine vegetation
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2021	Semona Issa	Phd Biology	Combined effects of environmental variation and pollution on zooplankton life history and population dynamics

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