

PERFLUORINATED ALKYLATED SUBSTANCES (PFAS) IN THE NORDIC ENVIRONMENT

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Table of contents

Table of contents.....	3
Preface.....	6
Summary	7
Sammendrag	8
1. Frame of the study	9
2. Background information	11
2.1. Applications and product information	13
3. Samples for PFAS screening in the Nordic environment.....	14
3.1. Sample selection: Criteria and priorities	14
3.2. Sample collection.....	16
3.2.1. Finland	16
3.2.2. Norway	17
3.2.3. Sweden.....	17
3.2.4. Denmark.....	17
3.2.5. Iceland.....	18
3.2.6. Faroe Islands	18
3.3. Analysis and quantification	18
3.3.1. Preparation of sediment and sludge samples	19
3.3.2. Preparation of water samples.....	19
3.3.3. Preparation of biota samples.....	20
3.3.4. Quantification of abiota samples	21
3.3.5. Quantification of biota samples	22
3.4. Quality control and method comparison.....	23
3.4.1. Sampling protocol.....	24
3.4.2. Limit of detection/ limit of quantification	25
3.4.3. Laboratory and field blanks	25
3.4.4. Performance tests (parallel samples)	27
3.4.5. Laboratory intercomparison.....	28
3.4.6. Data handling and comparison	29
4. Results.....	30
4.1. Levels and distribution	32
4.1.1. Abiotic samples	32
4.1.2. Biota.....	35
5. Discussion and recommendations.....	40
5.1. Source elucidation	40
5.2. Sample specific patterns and fate estimation.....	43
5.2.1. Potential sources	43
5.2.2. Seawater, fresh water and rain water samples	44
5.2.3. Sediment	44
5.2.4. Biota	45
5.3. Spatial distribution.....	47
5.3.1. Seawater.....	47

5.3.2 Sewage sludge	48
5.3.3. Sediment	49
5.3.4. Biota.....	50
5.4. Comparison with literature data.....	52
5.4.1. Water.....	52
5.4.2. Sediment	53
5.4.3. Sewage sludge	54
5.4.4. Biota.....	54
5.5. Level comparison with conventional “legacy” persistent organic pollutants.....	55
5.5.1. Concentration comparison in Seawater	56
5.5.2. Concentration comparison in Fresh water	56
5.5.3. Concentration comparison in rain water.....	56
5.5.4. Concentration comparison in sediments.....	56
5.5.5. Concentration comparison in sewage effluent.....	57
5.5.6. Concentration comparison in sewage sludge.....	57
5.5.7. Concentration comparison in landfill effluent.....	57
5.5.8. Concentration comparison in marine mammals	57
5.5.9. Concentration comparison in marine fish.....	57
5.5.10. Concentration comparison in fresh water fish	59
5.5.11. Concentration comparison in seabirds.....	59
5.6. Toxicity and ecotoxicity	59
5.7. Sources and environmental implications	61
5.8. Consequences and recommended actions.....	61
6. Conclusions and suggestions	62
7. Acknowledgements.....	63
8. Literature.....	65
Appendix 1: Sample characteristics.....	70
Appendix 2: Sampling manual.....	81
Appendix 3: Concentration list	95
Appendix 4: Sampling locations.....	103
Appendix 5: Abbreviations list	105

Preface

During the past decade, the identification of a new relevant group of environmental pollutants (i.e., perfluorinated alkylated substances = PFAS) has opened a new chapter within the various disciplines of environmental sciences. A relatively rapid development within the field of instrumental trace analysis, in combination with increased public environmental awareness has led to new concepts in detection, evaluation and remediation of potentially hazardous chemicals in the environment.

However, the group of perfluorinated alkylated substances (PFAS), recently marked as already ubiquitously distributed around our globe, demands new evaluation tools with regard to the technical detection as well as risk evaluation. The unique physico-chemical properties of the substance group are still a considerable challenge for environmental scientists as well as for regulatory authorities.

- 1.) The trace analysis of these compounds in environmental samples requires new highly sophisticated analytical instruments, such as high-performance liquid chromatography coupled to mass selective detectors in order to allow sufficient sensitive detections in the environment. Currently, these analytical methods, which are still under development, are suitable for research and method development but in most cases, not sufficiently validated for long-term monitoring in environmental compartments.
- 2.) PFAS residues are virtually both lipophobic and hydrophobic. In addition, these compounds express strong surface-active properties and usually adsorb strongly on natural surfaces. Thus, risk assessment tools, highly useful for conventional persistent organic pollutants (POPs), like the octanol-water partitioning coefficient (K_{ow}) etc., are not suitable for evaluation of the environmental fate of PFAS residues.
- 3.) Due to the strong C-F binding in the PFAS molecule, most of these compounds are extremely persistent, virtually indestructible and are, thus, expected to prevail in the environment.

International regulatory authorities are currently discussing adequate measures to control and reduce the presence of PFAS related residues in the environment. The here presented report contribute to the world-wide efforts to evaluate and put in place suitable effective measures to reduce environmental hazards posed by PFOS and other relevant PFAS related chemicals.

The project team

Summary

The here presented screening study on occurrence, distribution and fate of perfluorinated alkylated substances (PFAS) and related chemicals in the Nordic environment revealed an ubiquitous distribution of perfluorinated contaminants. Six Nordic countries participated in the screening study (Denmark, Faroe Islands, Finland, Iceland, Norway and Sweden). Compound specific distribution patterns in the different sample types confirmed that the physico-chemical properties in combination with release patterns and bioaccumulation potential are important and selective parameters for PFAS contamination.

High concentrations of PFAS related residues in sewage sludge and landfill effluents confirmed that these sample types are important primary anthropogenic sources for releases into the environment. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) dominated in sewage sludge samples. Landfill effluent was highest contaminated of all aqueous samples. PFOA was dominating in landfill effluents. Lake water, seawater and rainwater (precipitation) samples were relatively low contaminated. However, measurable amounts of PFAS were found in all samples. The Nordic biota samples showed signals of species dependent distribution and levels. Highest PFAS levels were found in top predating Danish harbour seal (*Phoca vitulina*) samples with PFOS as predominant PFAS contaminant. However, in Faroe Island pilot whales (*Globicephala melas*), PFOSA and PFOS were dominating with up to 364 ng/g wet weight. Also Finnish and Norwegian pike samples (*Esox lucius*) are highly contaminated with PFOS (PFOS = 551 ng/g ww) demonstrating that also the freshwater ecosystem is contaminated with PFAS related chemicals. The patterns found in biota point towards both country specific release patterns and species depended up-take/ accumulation properties. The fact that PFOS and PFOSA were also detected in anadromous Arctic char in the Faroe Islands indicates that long-range transport in air and/or precipitation is occurring.

Thus, PFAS related chemicals are widely distributed in the Nordic environment. The presence of this type of compounds is generally confirmed for all environmental compartments. It is therefore recommended to include the relevant PFAS-related chemicals in environmental monitoring and consider further measures to reduce the burden of PFAS to the Nordic environment.

Sammendrag

En første nordisk "screening"-undersøkelse om perfluorerte alkylerte stoffer (PFAS) med fokus på skjebne og fordeling av stoffene i miljøet, ble gjennomført med finansiell støtte av Nordisk ministerrådet (NMR). Seks nordiske land deltok i undersøkelsen (Danmark, Finland, Færøyene, Island, Norge og Sverige).

Komponent-spesifikke fordelingsmønstre i de ulike prøvetypene bekrefter at kjemiske egenskaper, i kombinasjon med utslippsmønster og akkumuleringspotensial er svært viktige parametre for opptak og spredning av PFAS i miljøet.

Høye nivåer av PFAS i kloakk og sigevannsprøver peker på at dette er viktige menneskeskapt primære kilder for utslipp og spredning av PFAS i det nordiske miljø. Perfluoroktansulfonat (PFOS) og perfluoroktansyre (PFOA) dominerer i kloakkprøvene fra alle seks nordiske land. I sigevannsprøvene (tatt fra lokaliteter i to nordiske land: Norge og Finland) dominerer PFOA. Sigevannsprøvene er betydelig høyere belastet med PFAS enn kloakkprøvene (opp til SUM PFAS = 1537 ng/g ww). Sammenlignet med kloakk og sigevann er PFAS nivåene i ferskvann (Mjøsa), saltvann og regnvann relativt lave. Men tilstedeværelsen av PFOS og PFOSA i anadrom røye fra Færøyene er en indikasjon for at atmosfærisk langtransport og nedbør er viktige kilder for PFAS i miljøet.

Indikasjoner for artspesifikke anrikningsmønstre ble funnet i det biologiske materialet (16 ulike marine og ferskvann arter). Relativ høye PFAS-konsentrasjoner er påvist i marine og ferskvanns topp-predatorer. Høyest PFAS-belastning ble funnet i steinkobbe (*Phoca vitulina*) lever fra Danmark (PFOS = 551 ng/g ww), men også i grindhval (*Globicephala melas*) fra Færøyene var PFAS nivåene høyt (PWFAR09: PFOSA = 364 ng/g ww). PFOS dominerte i selene, mens PFOSA var høyest konsentrert i grindhval-lever.

I ferskvannsfisk ble det funnet høye konsentrasjoner av PFAS i gjedde (*Esox lucius*). Konsentrasjoner i ferskvannsfisk var sammenlignbart med nivåene detektert i marine topp-predatorer (PFOS = 551 ng/g ww). Også i lever fra gjedde var PFOS den dominerende PFAS komponenten.

Basert på resultatene fremlagt i denne rapporten kan det konkluderes at PFAS også finnes i betydelige konsentrasjoner i det nordiske miljø. I alle prøvetyper som er analysert ble det funnet PFAS. Det anbefales derfor å inkludere PFAS i nasjonale overvåkingsprogrammer vurdere ytterligere tiltak som kan redusere belastningen fra PFAS i miljøet.

1. Frame of the study

A first screening project on the fate of perfluorinated alkylated substances (PFAS) in the Nordic environment was initiated by a project group with representatives of National Environmental Research Institute of Denmark, Finnish Environment Institute, Environment and Food Agency of Iceland, Food, Veterinary and Environmental Agency of the Faroe Islands, Norwegian Pollution Control Authority and Swedish Environmental Protection Agency. The project was financed and supported by the Nordic Council of Ministers through the Nordic Chemicals Group and the Nordic Monitoring and Data Group as well as the participating institutions.

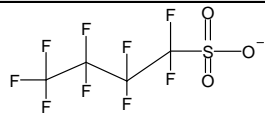
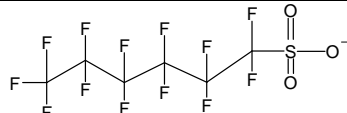
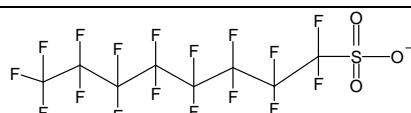
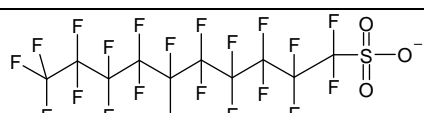
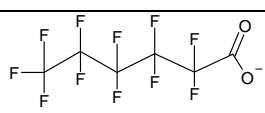
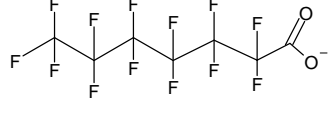
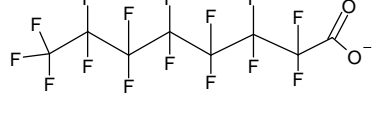
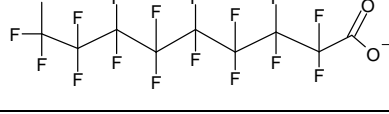
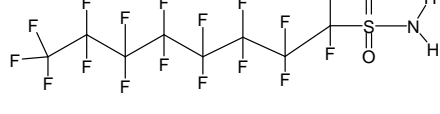
The respective participating Nordic countries organized sample selection, collection and transport based on a sample protocol and manuals provided by the analytical laboratories. Sample preparation, trace analysis and quantification were performed jointly by the Norwegian Institute for Air Research (NILU, Kjeller, Norway) and the Institute for Applied Environmental Research (ITM, Stockholm, Sweden). For this first screening, six PFAS related chemicals with potential for accumulation in the environment were chosen. In addition, the analytical laboratories voluntarily added two PFAS compounds (PFBS and PFDS,) to the list of target chemicals (table 1).

The selected PFAS related compounds were chosen due to the following priority criteria:

- Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the two compounds best documented of all PFAS related compounds so far with regard to environmental hazards. PFOS and PFOA, thus, are the major motivation for the presented screening project.
- Perfluorooctane sulfonamide (PFOSA) is suspected to be a major precursor of PFOS in the environment.
- Perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluorodecane sulfonate (PFDS) are expected to be found in the environment due to their similar structure compared with PFOS. However only sparse information about environmental properties and toxicity is available yet. In addition, PFBS is announced as successor for PFOS-related products.
- Perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA) and perfluorononanoic acid (PFNA) are expected to be present in the environment due to their resemblance with PFOA. However, only sparse information about environmental properties and toxicity is available yet.

For most of the substances included, indications existed already for their occurrence in the environment. The expected results will allow assessing the existing level of contamination (spatial distribution monitoring) and indicating regional differences. This spatial screening programme will enable the determination of the representativeness of the monitoring sites with regard to spatial variability in contaminant concentrations and will give valuable information about the ubiquity of PFAS distribution in the Nordic countries.

Table 1: Selected PFAS related chemicals chosen for the presented Nordic screening programme.

Acronym	Name	CAS-number	Structure
PFBS	Perfluorobutane sulfonate	29420-49-3	
PFHxS	Perfluorohexane sulfonate	432-50-7	
PFOS	Perfluorooctane sulfonate	2795-39-3	
PFDS	Perfluorodecane sulfonate	67906-42-7	
PFHxA	Perfluorohexanoic acid	307-24-4	
PFHpA	Perfluoroheptanoic acid	375-85-9	
PFOA	Perfluorooctanoic acid	335-67-1	
PFNA	Perfluorononanoic acid	375-95-1	
PFOSA	Perfluorooctane sulfonamide	4151-50-2	

2. Background information

Within the past 50 years, industrial application as well as consumer uses of perfluorinated alkylated substances (PFAS) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), as well as their related products have increased tremendously.

Perfluorinated compounds are commonly produced by electrochemical fluorination (ECF). As starting reaction for the production of PFOS related chemicals, the 3M corporation has introduced the fluorination of 1-octanesulfonyl fluoride to perfluorooctanesulfonyl fluoride (POSF), described in figure 1 (Anonymous, 1999).

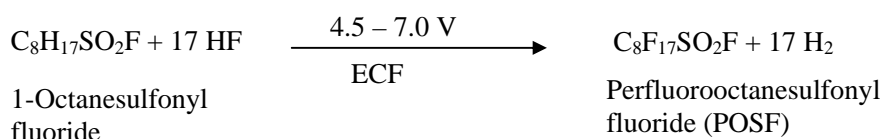


Figure 1: Industrial formation of PFAS related chemicals via ECF (Anonymous, 1999).

Perfluorooctanesulfonyl fluoride (POSF) is thereafter used as starting chemical for a huge variety of different products within the PFAS group used in a vast array of products and applications. ECF produced PFAS related substances usually are containing a sulfonyl- or carboxylic group in their molecular structure.

During the past decades, consumers in western countries embraced these chemical products as important chemical tools for all types of household related processes (e.g., cooking, clothing, furniture, etc.) as described in a comprehensive report (Hekster et al. 2002). The chemicals of the PFAS group are characterized by carbon chains with variable lengths, to which fluorine atoms are covalently bonded. The strong C-F bond is yielding ultimately in virtually indestructible chemicals that until recently were thought to be completely biologically inert and, thus, not bioavailable for biochemical processes.

Since the late 1990s, increasing numbers of published scientific studies, pinpointing the potential environmental hazards posed by this type of chemicals, have brought PFAS related chemicals in the focus of international public environmental concern. Besides being an important industrial group of compounds, PFAS related residues are today considered as highly toxic, extraordinarily persistent chemicals that pervasively contaminate human blood and wildlife all over the world. In contrast to well-documented persistent organic pollutants like polychlorinated biphenyls (PCB), chlorinated-*p*-dibenzodioxins and furans (PCDD/F), governments and scientists are today especially concerned that the most pervasive and toxic members of the PFAS group will never degrade in the environment.

Already in 2000, the U.S. Environmental Protection Agency (EPA) banned PFOS from the US market. Shortly thereafter, the manufacturer 3M also stopped voluntarily the production of PFOA. Currently, PFOA is also evaluated for regulatory actions by U.S.- EPA.

The production of sulfonyl-based fluorochemicals has recently been estimated around 6.5 million pounds world-wide only for the year 2000 (U.S. Environmental Protection Agency 2000). For PFOS only, a global production volume of 831 metric tons are estimated for the year 2000 (Anonymous 2002). Current environmental studies confirmed that PFAS are shown to be globally distributed, environmentally persistent and bioaccumulative (van de Vijer et al. 2003, Kannan et al. 2001 a,b, 2002 a,b, Giesy and Kannan 2001, Martin et al. 2004) with implication also for human exposure (Olsen et al. 2003, Taniyasu et al. 2003, Levitt & Liss 1986).

Under the joint leadership of UK and USA, the OECD co-operation on the Investigation of Existing Chemicals group performed a first risk assessment on PFOS and its salts in 2002 concluding that PFOS is persistent, bioaccumulative and toxic to mammalian species (Anonymous 2002). There are species differences in the elimination half-life of PFOS; the half-life is 100 days in rats, 200 days in monkeys, and years in humans. The toxicity profile of PFOS is similar among rats and monkeys. Repeated exposure results in hepatotoxicity and mortality (Anonymous 2002).

Also the Swedish Chemicals Inspectorate performed a preliminary national study on the risk evaluation status and possible national risk mitigation strategies in Sweden and other European countries on PFOS and its salts (Cederberg et al. 2004). The document reports on the strategy of the UK Department for Environment; Food and Rural Affairs (DEFRA) and the UK Environment Agency to develop a risk evaluation manual on PFOS and its potential to degrade under natural conditions (Brook et al. 2004). Based on this study, in UK the main application areas of PFOS and related compounds are as follows:

Impregnation/ waterproofing of textiles and fur products: 49 % (195 tons in 2001)

Impregnation/ waterproofing of paper related products : 15 % (60 tons in 2001)

Outdoor activities: 18% (70t in 2001)

Flame retardants: 16% (65t in 2001)

Others: 2.5% (10 tons in 2001)

The European Union plan to adopt the resolutions according to the UK lead work on risk evaluation on PFOS and related compounds.

Also in the Netherlands a first evaluation of environmental risk posed by PFOS and related compounds revealed that 60 –105 tons/y (2002) are released through various products (Hekster et al. 2002).

Already in the 1980s, the acute toxicity of perfluorooctanoic acid (PFOA) and nonadecafluoro-*n*-decanoic acid (NDFDA) was evaluated in male Fischer rats (Olsen & Andersen 1983) and human B cells (Levitt & Liss 1986). In both studies toxic potency for PFOA and NDFDA was reported. Some of the toxic effects found for NDFDA were remarkably similar to those known for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). It was assumed that the acute toxicity of NDFDA might be due to the ability to interfere with fatty acid metabolism. Thus, further studies of its toxicity have been recommended as valuable in understanding toxicological mechanisms of action of TCDDs as well.

Due to the well-documented environmental concerns related to PFAS, the 3M Corporation (St Paul, MN, USA) decided to discontinue its product line for most of the PFOS related products with the effective end of production occurring already around November 2001. In addition US-EPA has initiated regulation actions with respect to PFOS-related chemicals. However, the EPA's initial actions and 3M's phase out apply only to PFOS and its derivatives. Telomer-based PFAS (e.g. fluorotelomer alcohols) will continue to be produced and no disruption of supplies will or has been experienced so far. These telomer-based PFAS related compounds are chemical products of a telomerisation process where tetrafluoroethylene (TFE) as "building blocks" is used resulting in fluorinated alcohols with varying alkyl-chain length and usually one non-fluorinated carbon atom behind the hydroxylated final carbon atom.

US-EPA is currently assessing other perfluorinated chemicals like PFOA and related chemicals such as telomer products (Fluorotelomer alcohols: FTOH) with regard to possible environmental hazards and respective regulatory actions.

Currently, international research is concentrating on assessing the mechanisms of PFOS toxicity, identifying the full range of impacts in order to get a comprehensive understanding of contamination levels in the environment incl. people and wildlife.

Most of the selected PFAS compounds chosen for the presented screening exercise, are neither water nor lipid soluble, except for PFOSA, which is found to be surprisingly lipophilic and, thus, is expected to accumulate in the course of the food webs. Thus, relatively high levels were found in all biota samples.

2.1. Applications and product information

A first survey of the product and application information available in the respective Nordic countries revealed that the excess of actual data is still difficult and often impossible for PFAS related compounds.

Norway is currently working on a material flow analysis. The preliminary estimates shows that fire fighting foams cover more than half the total PFOS-related substances and other PFAS used in the country. In protective coating and textiles the amounts is less than half of the total. In floorwax/polish and electronic industries the amounts are approximately 100-200 kg. The total amount for PFAS used in Norway is estimated with approximately 23 – 26 tons. However, there may be considerable uncertainties in these estimates (personal com., Ola Glesne).

The total sales of PFOS based chemicals to the Swedish market in 1999 was 38 tons (3M, personal com.) most of which was used in textile and leather treatment and as industrial surfactant.

3. Samples for PFAS screening in the Nordic environment

Based on recently raised concerns about possible environmental impact of perfluorinated residues in pristine environments including Northern regions, the NTEM “Nordic Chemicals Group” of the Nordic Council of ministers has initiated a first screening on the presence and distribution of selected perfluorinated alkylated substances (PFAS) in the Nordic environment.

3.1. Sample selection: Criteria and priorities

Based on already available scientific information on distribution and concentration levels, the NTEM “Nordic Chemistry group” in co-operation with the analytical laboratories in charge, the Norwegian Institute for Air Research (NILU, Kjeller, Norway) and the Institute for Applied Environmental Research (ITM, Stockholm, Sweden) selected a priority list of 6 compounds of the PFAS group (see table 1). In addition, the analytical laboratories have voluntarily added two priority compounds:

Perfluorobutane sulfonate (PFBS): This compound is announced as official successor for the PFOS related products by the manufacturers. According to the manufacturers, PFBS is not accumulating in biota. In accordance with this postulation, no PFBS traces were confirmed in biota samples yet.

Furthermore, **perfluorodecane sulfonate (PFDS)** has been included in the PFAS screening of biological samples.

A comprehensive selection of sample types spanning from seawater and precipitation towards marine mammals, as representatives for top predators, have been selected by NTEM, the working group of the Nordic council of Ministers.

Sampling locations are presented in two separate maps for sites where biota and abiotic samples were collected (see appendix 4).

For the abiotic environment, 7 sample types have been analysed and for the biotic environment, 16 species have been selected, representing freshwater and marine environments (table 2). Exclusively liver samples were analysed except for the fulmars from the Faroe Islands where eggs samples were pooled. The sample characteristics for the material provided by the 6 participating Nordic countries can be found in appendix 1.

Table 2: Sample types selected for the first Nordic PFAS screening.

	Finland	Sweden	Norway	Danmark	Iceland	Faroe Island	SUM samples
ABIOTA							
Seawater	4	0	0	3	1	3	11
Rainwater	2	3	0	0	0	0	5
Landfill effluent	1	0	5	0	0	0	6
Sewage effluent	2	0	2	0	0	1	5
Sediment	3	3	3	0	1	3	13
Sewage sludge	4	3	2	3	2	1	15
Lake water	0	0	4	0	0	0	4
BIOTA							
Flounder	0	0	0	4	0	0	4
Eelpout	0	0	0	1	0	0	1
Herring	0	0	0	1	0	0	1
Harbour seal	0	0	0	5	0	0	5
Grey seal	0	3	0	0	0	0	3
Pike	8	0	1	0	0	0	9
Sculpin	0	0	0	0	1	2	3
Dab	0	0	0	0	1	2	3
Cod	0	8	0	0	0	1	9
Arctic char	0	0	0	0	0	2	2
Trout	0	0	1	0	0	0	1
Pilot whale	0	0	0	0	0	4	4
Fulmar	0	0	0	0	0	2	2
Long-rough dab	0	0	0	0	2	0	2
Minke whale	0	0	0	0	5	0	5
Burbot	0	0	1	0	0	0	1
Perch	0	4	1	0	0	0	5
SUM per country	24	24	20	17	13	21	119

The following marine and freshwater species were analysed for PFAS residues:

Marine fish:

Flounder (*Platichthys flesus*)
 Eelpout (*Zoarces viviparus*)
 Herring (*Clupea harengus*)
 Shorthorn Sculpin (*Myoxocephalus scorpius*)
 Dab (*Limanda limanda*)
 Long-rough dab (*Hippoglossoides platessoides*)
 Atlantic cod (*Gadus morhua*)

Freshwater fish:

Pike (*Esox lucius*)
 Trout (*Salmo trutta*)
 Arctic char (*Salvelinus alpinus*)
 Perch (*Perca fluviatilis*)
 Burbot (*Lota lota*)

Marine mammals:

Harbour seal (*Phoca vitulina*)
 Grey seal (*Halichoerus grypus*)
 Pilot whale (*Globicephala melas*)
 Minke whale (*Balaenoptera acutorostrata*)

Marine birds:

Fulmar (*Fulmarus glacialis*)

A total of 119 samples have been analysed covering a large and challenging variety of matrices. In addition, 13 abiotic and 3 biota samples have been collected as parallel samples in order to provide information about method robustness and variability (table 3).

Table 3: Parallel samples for method performance tests collected in all six participating Nordic countries*

Sample type	Noway		Finland		Sweden		Danmark		Faroe Islands		Iceland		SUM parallels
	samples	parallels	samples	parallels	samples	parallels	samples	parallels	samples	parallel	samples	parallels	
Seawater							SWDAN02	2			SWICE01	4	6
Rainwater					RWSWE01	2							2
Lake water	LWNOR04	2											2
Landfill effluent	LFNOR05	2	LFFIN07	3									5
Sewage effluent	SEHOR11	2	SEFIN09	2									4
Sediment			SDFIN10	3							SDICE02	5	8
Sewage sludge			SSFIN14	3							SSICE03 + 04	4	7
Fresh water fish					PESWE3	2			ACFAR06	2			4
Marine fish											LDICE01	3	3
Sum samples	3	6	2	5	2	4	1	2	1	2	4	16	41

* Sample characteristics can be found in appendix 1

3.2. Sample collection

As a guideline for appropriate sampling, the laboratories in charge provided a sampling manual for the sampling personnel in the Nordic countries participating in the screening exercise (Appendix 2). Detailed procedures for sampling, storage and transport were given. Sampling protocols for all sample types were implemented in the sampling manual.

Detailed information on the sampling locations are provided by the respective participating countries (see also appendix 1):

3.2.1. Finland

Abiotic samples:

The waste water (sewage) treatment plants of Espoo, Helsinki and Porvoo are the biggest plants in Finland taking care of both industrial and municipal waste waters. The treatment systems are of the most modern quality and technique in Finland. In the plants there are treated the following amounts of waste water given in peq -values: Espoo = 235 000 person equivalent (peq), Helsinki = 815 000 peq, Porvoo = 170 000 peq.

The landfill effluent studied was collected from the very large Waste Treatment Centre in Espoo, s.c. Ämmässuo landfill.

The solid wastes are collected from the city areas of Helsinki, Espoo, Vantaa, Kauniainen and Kirkkonummi having the population over one million. The amount of waste received in 2002 was calculated to 670 000 tons.

Biota:

All Finnish pike samples were caught in the coastal water near the main urban city area of Helsinki (old City bay) about 200-500 m from the coastline. The area has

influences of polluted waters and sediment deposits since industrial PFA-substances were introduced into use.

3.2.2. Norway

Abiotic samples:

The sampling of landfill effluents was performed on the vicinity of 5 landfill locations situated close to the Kristiansandfjord and the Oslofjord area. The landfill sites were selected in co-operation with the Norwegian State Pollution Control Authorities (SFT). Local-co-operation partners and scientists from the Norwegian Centre for Soil and Environmental Research (Jordforsk) suggested priority sites and the scientists of the institute prepared the sampling equipment. Samples were collected during the period July - October 2003. The rest of the abiotic samples were all collected in Lake Mjøsa or at sewage treatment plants with effluents to the lake (Appendix 1).

Biota:

All freshwater fish samples were collected from the Norwegian Lake Mjøsa close to sewage treatment plants or potential source locations by scientists of the Norwegian Institute for Water Research (NIVA).

3.2.3. Sweden

Abiotic samples:

Rain water samples were collected from the Råö research station. Sampling periods: RWSWE01: 02.10.2003 –11.11.2003, RWSWE02: 11.11.2003 – 03.12.2003., RWSWE03: 03.12.2003-15.12.2003. The freshwater sediment samples were collected from potential accumulation sites upstream and downstream the municipality of Kristianstad. Representative sewage sludge samples were collected over an entire week with representative daily sampling and unification after one week (week 39, 2003). Sewage was collected from the Sewage treatment plants (STP) Kistianstad Centrala ARV, Köpinge ARV and Tollarp (supposedly household waste water only).

Biota:

Freshwater fish (Perch) was collected close to the freshwater sediment sites at the potential accumulation site in the vicinity of the STP Kristianstad. Pooled samples containing in average 10 livers were provided. Atlantic cod were collected from one near shore site and one off-shore site (Hanöbukten, Hoburgen). Grey seal samples stem from three different locations from the Swedish Baltic coast (Gästrikland, Uppland, Sörmland)

3.2.4. Denmark

Abiotic samples:

Aqueous and solid abiotic samples were collected in the vicinity of potential sources. Sewage sludge samples were chosen from large sewage treatment plants from the cities of Roskilde (Sewage treatment plant (STP) Bjergmarken), Odense (STP Stige) and Copenhagen (STP Lynetten). Seawater samples were collected in coastal areas close to the city of Rinkøbing. Sampling sites for sweater sampling close to the seage

effluent of Copenhagen (STP Lynetten), Odense (S1: Sedenstrand) were chosen. As reference site, the station 60 (st.60) situated relatively remote to effluent influences was also sampled.

Biota:

All biota samples were collected in the vicinity of potential primary PFAS sources. Flounders were caught in the coastal water close to the capitol Copenhagen. Eelpout and herring were collected in the inner part of the Roskilde fjord. The harbour seal samples were collected close to settlements (Limfjord, Hesselø, Samsø and Øresund).

3.2.5. Iceland

Abiotic samples:

Sediment and seawater samples were collected close to the landfill site Gufunes. Sewage sludge was sampled from the two STPs Klettagardar and Ananaust.

Biota:

The Icelandic Minke whale samples were collected during a research expedition in the period August/ September 2003 in the North Atlantic waters (appendix 1). All marine fish samples were collected close to city of Reykjavik (capitol of Iceland). Long-rough dab, dab and sculpin samples were collected in the harbour areas of Reykjavik, close to potential PFAS sources (e.g.,Gufunes landfill).

3.2.6. Faroe Islands

Abiotic samples:

Seawater, Sewage effluent, Sediment and Sewage sludge was collected from sites close to potential PFAS sources. Seawater samples were collected from the harbour area of Torshavn city (the capitol of the Faroe Islands). Two sediment samples were collected in the Torshavn harbour area and nearby Kaldbaksfjord. Sewage sludge was sampled from the STP Sersjantvikin in Torshavn.

Biota:

Pilot whales were caught near shore at Sandagerdi in September 2002. The Arctic char samples stem from a landlocked population in a freshwater lake (á Mýranar). The fulmar eggs were collected from a bird cliff at Vidareidi. The Atlantic cod, sculpin and dab samples were collected in coastal waters close to settlements (Kaldbak, Kirkjubö and Torshavn)

3.3. Analysis and quantification

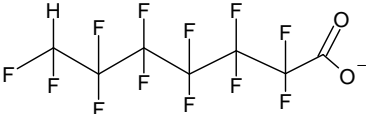
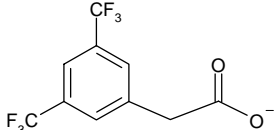
All samples were sent by the national institution responsible for sampling directly to the analytical laboratories responsible according to the procedure described in the sampling manual (Appendix 2). The abiotic samples (sea water, precipitation, sediment, sewage sludge, landfill effluent, sewage effluent and freshwater) were sent for analysis to the laboratories of the Norwegian Institute for Air Research (NILU, Kjeller, Norway), whereas the biological samples (16 species) were analysed by the Institute for Applied Environmental Research (ITM, Stockholm, Sweden).

3.3.1. Preparation of sediment and sludge samples

All samples were stored at 6 °C prior to sample preparation. No water content in sediment and sludge samples was determined. According to the supplement to the sampling manual (Appendix 2), the sewage and sediment samples should be sent to the laboratory in pre-ried or desiccated conditions. However, not all samples have been sent as required. Therefore, the samples were partly dried by filtering using a water-jet vacuum pump prior to analyses to ensure comparable sample conditions. Thereafter, quantification was based on a wet weight basis including the remaining water in the solid samples. Sediment and sludge samples were extracted using accelerated solvent extraction (ASE, Dionex, Sunnyvale, CA).

A stainless steel (11 ml volume) ASE cell was used for extraction. About 2 g rinsed and pre-cleaned sea sand (rinsed with methanol, then 200 °C for 4 h) was filled in bottom of the cell. Thereafter, approx. 5 g sample was transferred into ASE cell. Finally, the ASE extraction cell was completely filled with sea sand. Prior to extraction, 50 µl internal standard (ISTD) was added according to the standard listed in table 4.

Table 4: Internal and recovery standards used for PFAS quantification in aqueous samples, sediment and sludge

Internal quantification standard (ISTD)	Recovery standard (RSTD)
0.1 ng/µl 7H-perfluoroheptanoic acid (7H-PFHpA) in methanol	0.2 ng/µl 3,5-bis(trifluoromethyl)phenyl acetic acid in methanol
	

Accelerated solvent extraction (ASE) was performed three times with methanol (17 min/cycle, 150 °C, 2000 psi). The three extracts were combined in a Turbovap container (Zymark, Hopkinton, MA, USA) and concentrated with a Turbovap evaporator to approx. 500µL. Final concentration to 200µL took place under gentle nitrogen stream (N₂, 5.0 quality, Hydrogas, Porsgrunn, Norway).

Subsequently, 50 µL of recovery standard (see table 4) and 250 µL 4mM ammonium acetate buffer (in deionised water) was added. The closed sample vials were treated for 10 minutes in an ultrasonic bath. In order to remove precipitation, the samples were filtrated using a Microcon YM-3 centrifugal filter device (Millipore Corp., Billerica, MA) at 14 000 rounds per minutes (rpm) for 45 min. finally, aliquots of the sample extract were transferred into autoinjector vials for quantification with high-performance liquid chromatography coupled to mass spectrometric detection.

3.3.2. Preparation of water samples

About 500 ml of the collected water samples were used for PFAS analysis. Approx. 0.5 vol.-% formic acid (HCOOH, 2.5 ml for 500 ml water) was added to prevent uncontrolled microbiological degradation processes. As a first sample preparation

step, the water samples were filtered (using a water-jet vacuum pump) through a glass fibre filter (GFF: 142 mm, PALL Life Sciences, New York, USA, cat. no. 61635). GFF and aqueous sample are, thereafter separately prepared for analysis.

The GFF was folded into an 11 mL ASE-extraction cell. 50 µl ISTD (table 4) was added and extraction is performed according to the ASE method described earlier for sediment and sludge samples.

For water analysis, 80 mg ammonium acetate (approx. 2mM) and 50 µl ISTD was added. Finally the sample bottle (PET or PP) containing the water samples was weighed prior to solid phase extraction (SPE) using an analytical balance.

For solid phase extraction (SPE), HLB Plus SPE cartridges (0.25 g, Waters co-operation) were used. Prior to extraction, the SPE system was rinsed with approx. 20 ml methanol. The cartridge was thereafter conditioned using about 10 ml Milli-Q water. The water samples were extracted through the SPE cartridge with approx. 2 drops/sec. After sample extraction, the empty bottle (still containing small amounts of residual water) was again weighed. The weight difference is used as sample amount for concentration calculation.

Prior to elution, the SPE cartridge was rinsed with 2 mL methanol/water (40/60). PFAS elution is performed with 8 mL methanol. The methanol extract was, thus, concentrated to 200 µl by a combination of Turbovap and nitrogen concentration (see method description for sludge and sediment sample preparation) and 200 µl of a 4 mM solution of ammonium acetate in water was added.

Both filter and aqueous sample extracts were finally spiked with 50 µl RSTD, filtered if necessary as described for sediment and sludge extracts (in case of precipitation) and transferred to autoinjector vials for subsequent HPLC/MS analysis and quantification

3.3.3. Preparation of biota samples

As appropriate target tissue in all fish and marine mammal samples, liver was chosen. All samples were collected according to the sampling manual provided (appendix 2). The collected samples were thereafter send to the analytical laboratory (ITM) for quantification. The tissue samples were thoroughly homogenized before preparation of aliquots for analysis. Liver samples in excess of a total of 40 g were homogenized using a Braun turbo mixer (Braun, Kronberg, Germany). This procedure was also used for the preparation of pooled samples from individual samples delivered to the laboratory. Aliquots were then further homogenized in high-purity lab water (one part sample, 5 parts MilliQ-water; MilliQ, Millipore Corp.) using an Ultra-Turrax homogenizer. From this homogenate aliquots of 1ml were taken to analysis and for replicates as well as for matrix spikes.

The extraction method was based on ion pairing as described firstly by Ylinen et al. (1985) and further elaborated by Hansen et al. (2001) An aliquot of 1 mL of the homogenate was transferred to a polypropylene (PP) tube, mixed with 2 mL of 0.25 M sodium carbonate buffer, and 1 mL of 0.5 M tetrabutylammonium solution (TBA, adjusted with NaOH to pH 10). The resulting mixture was vortex mixed for 20 seconds. 5 mL methyl tertiary butyl ether (MTBE) was added and the tube gently turned for 20 minutes. The MTBE was quantitatively transferred to a second PP-tube and another 5 mL MTBE portion added to the first tube and the procedure repeated.

The combined MTBE extract was then gently evaporated until dryness using dry nitrogen (5.0 quality) and exactly 500 µL methanol added. All extracts were finally filtered through a 0.46 µm PP-filter prior to subsequent LC/MS determination.

3.3.4. Quantification of abiota samples

An Agilent high performance liquid chromatography system (HPLC, 1100 series, Agilent, Palo Alto, CA) in combination with a time-of-flight high resolution mass spectrometer (LC-TOF: Waters-Micromass, Manchester, UK) was used for quantification.

For analysis, 20 µl sample extract in methanol/water (1:1, v:v, 2 mM ammonium acetate) were injected. An ACE C₁₈ reversed phase HPLC column (ACT, Aberdeen, UK; 150 x 2.1 mm, 3 µm particle size) was used for PFAS separation in abiotic samples.

For HPLC separation the following parameters were chosen:

Flow rate of the mobile phase: 200 µl/min;

Buffer: 2 mM ammonium acetate (NH₄OAC) in both methanol (A) and water (B).

Gradient of the mobile phase: 0-1 min 50 % A; 1-6 min linear increase to 85 % A, 6-12 min isocratic 85 % A, 12-13 min linear change to 99 % A, 13-20 min isocratic 99 % A. Equilibration time 9 min.

The compounds of interest are transferred into the TOF high-resolution mass spectrometer. PFAS were quantified with electrospray ionisation (ESI) in negative ion mode (cone voltage -35 V; cone gas 10 l/hr; desolv. gas 400 l/hr; nebulizer max). Full scan mass detection in the range of m/z 200 – 720.

The following masses (Table 5) were used for PFAS quantification in abiotic samples collected from Nordic environments (water, sediment and sludge):

Table 5: Quantification masses (m/z) for the determination of selected PFAS in abiotic samples. Mass tolerance was typically 0.1 mass units.

Comp.	PFOSA	PFOS	PFHxS	PFBS	PFNA	PFOA	PFHxA	RSTD	ISTD
m/z	498.0	499.0	399.0	299.0	419.0	369.0	269.0	227.0	281.0

Please note, the selected analytes differ between biota and abiotic samples (e.g., PFHpA, PFDCs was not analysed in abiota whereas PFBS was only analysed in abiota).

Representative mass traces for LC-TOF and LC-MS-MS quantification in environmental samples (landfill effluent and grey seal liver) are presented in figure 2 (a and b).

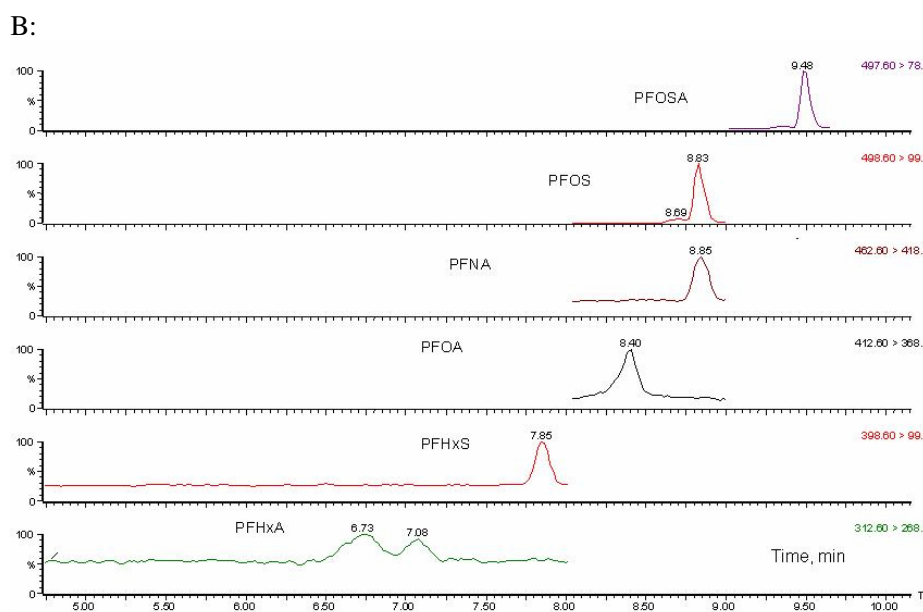
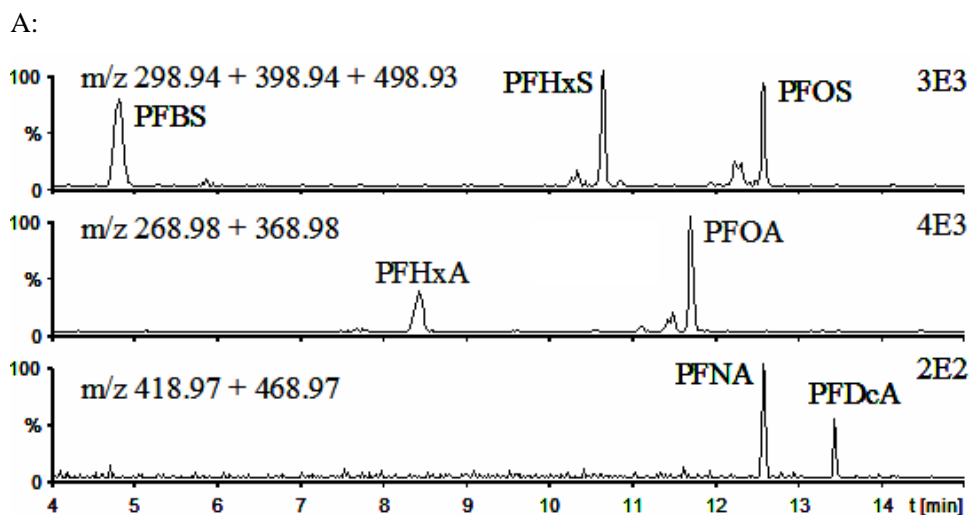


Figure 2: A.) Typical LC/MS-TOF mass traces for a landfill effluent sample.

B.) Typical LC/MS-MS chromatogram for a grey seal sample

Due to the different physico-chemical properties of the target compounds, especially for ionic compounds (sulfonates and acids) in sewage sludge, the method developed for PFOSA in sewage sludge is still considered as semi-quantitative but evaluated as sufficient for the here presented screening.

3.3.5. Quantification of biota samples

Identification and quantification was done by retention time using authentic reference compounds and selected reaction monitoring (Figure 2b: SRM-MS/MS, Micromass Quattro II, Altrincham, U.K.) with argon as a reaction gas and monitoring the transitions listed in table 6. The MS/MS instrumental conditions were identical to those described by Giesy and Kannan (2001). The detection limit was calculated from a low level spiked and extracted sample and was considered to be equal to three times the area noise level in each transition in the region of the target compound.

Table 6. Monitored MS/MS transitions

Analyte	Abbrev.	Precursor ion	Product ion
Perfluorohexanoic acid	PFHxA	313	269
Perfluoroheptanoic acid	PFHpA	363	319
Perfluorooctanoic acid	PFOA	413	369
Perfluorononanoic acid	PFNA	463	419
Perfluorohexane sulfonate	PFHxS	399	99
Perfluorooctane sulfonate	PFOS	499	99
Perfluorodecane sulfonate	PFDS	599	99
Perfluorooctane sulfonamide	PFOSA	498	78

The LC system consisted of a C18 - column (2.1 mm x 50mm x 5µm, Hypurity C18, ThermoHypersil, U.K.) with methanol/water as the eluent and 10mM ammonium acetate as modifier. The eluent was delivered at a flow of 0.2 ml/min by a Waters Alliance 2690 pump (Waters Corp., Milford, MA, U.S.A.) with a gradient program starting at 40% methanol increased to 95% at 5 min, kept for 15 min and then returned to 40% at 20 min. Total run time was 35 min., including time for conditioning of the column. All calculations were done using multilevel calibration curves of respective matrix extracts spiked with external standard mixtures and using corrections for recovery of the different analytes. Generally, at least two spike levels were included for each new matrix and/or batch. Method blanks consisting of extracted MilliQ-water (Millipore, Billerica, MA, USA) were included with each batch and one field blank consisting of triolein was also analysed.

3.4. Quality control and method comparison

Adequate quality control measures and documentation were introduced covering the entire analytical chain: sampling procedures, storage, transport, sample preparation and, ultimately analysis and quantification. For an appropriate sampling procedure with the aim to minimise contamination risk and document possible artefacts during sampling and transport, sampling protocol was developed in close co-operation between the analytical laboratories and the screening project's steering project.

3.4.1. Sampling protocol

Annex 1: Sampling protocol for sea-/river-/lake-water samples

Sample name:	Sample material:
---------------------	-------------------------

<i>Sampling</i>		Comments
Date and time:		
Site (description, preferably with latitude/longitude data):		
Approx. sampling depth (distance from surface):		
Approx. distance from bottom/shore:		
Sample volume:		
Water temperature:		
Transport temperature after sampling:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by NILU

Figure 3: Sampling protocol sheet for the collection of sea-, river and lake water samples for the Nordic PFAS screening project.

The sampling protocol (Appendix 2, sampling manual) was developed with the overall aim to address two major needs:

- 1.) Guidance for the personnel, responsible for sampling to avoid contamination.
- 2.) Ensure a complete documentation of the sampling procedure, quality of the sample and environmental circumstances during the sampling period.

Sampling protocols for seven major sample types were developed and distributed to the participating institutions. A typical sampling sheet is presented in figure 3,

the complete selection can be found in appendix 2 (sampling manual incl. supplementary information).

3.4.2. Limit of detection/ limit of quantification

Limit of detection (LOD) and limit of quantification (LOQ) are considered as two priority parameters, describing the quality of a quantitative analytical method. According to IUPAC (McNaught and Wilkinson 1997, Thomsen et al. 2003), the **LOD**, expressed as the concentration, c_L , or the quantity, q_L , is derived from the smallest measure, x_L , that can be detected with reasonable certainty for a given analytical procedure. The value of x_L is given by the equation: $x_L = \bar{x}_{bi} + k s_{bi}$

where \bar{x}_{bi} is the mean of the blank measures, s_{bi} is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired.

For abiotic and biotic samples $k = 3$ (3 x signal/noise) was chosen for the present screening study.

According to guidelines developed by the “US great Lakes monitoring programme”, the limit of quantification is defined as the lowest concentration of an analyte that produces a signal/response that is sufficiently greater than the signal/response of lab reagent blanks to enable reliable detection (and thus quantification) during routine laboratory operating conditions. The analyte response at the **limit of quantification (LOQ)** should be at least 5 times the response compared to the blank response (www.epa.gov/glnpo/monitoring/data_proj/glenda/codes/r_lim_tp.pdf).

During the present screening exercise, for PFAS analysis in abiotic samples the LOQ was set 5 x compound level in the highest field blank for the respective sample type. For PFAS determination in biota, the LOQ was defined as 3 x compound level in the highest field blank for the respective sample type.

LOD and LOQ determination was performed in accordance to the guidelines given in the above described documents.

3.4.3. Laboratory and field blanks

Laboratory and field blank analysis was an essential part of the quality control program. For all sample types relatively low laboratory and field blank levels have been determined except for PFOA where elevated concentration levels were found indicating possible contamination during transport and sample preparation (table 7 and 8).

Table 7: Laboratory and field blank determination for aqueous samples

Sample ID	Sample matrix	Blank	Total concentration in water samples (ng/l, water phase)							Recovery (%)
			PFOSA	PFBS	PFHxS	PFOS	PFHxA	PFOA	PFNA	
LAWABL01	Milli Q water	Lab-blank (Water)	0.00	0.00	0.00	0.03	0.00	0.26	0.00	73
LAWABL02	Milli Q water	Lab-blank (Water)	0.00	0.00	0.00	0.04	0.00	0.27	0.00	76
WABLFIN01	Ion free water	water (Finland)	0.00	0.00	0.00	0.04	0.00	0.24	0.00	62
WABLNOR01	Ion-exchange water	Water (Norway)	0.00	0.00	0.00	0.01	0.00	0.25	0.00	67
WABLDAN01	Milli Q water	Water (Denmark)	0.00	0.00	0.00	0.04	0.00	0.44	0.00	65
WABLICE01		Water (Iceland)	0.00	0.00	0.00	0.05	0.00	0.59	0.00	85
WABLFAR01		Water (Faroe Iceland)	0.00	0.00	0.00	0.02	0.00	0.25	0.00	73
LOD water (instrumental signal-to-noise 3:1)			0.01	0.03	0.01	0.02	0.06	0.06	0.05	
LOQ water (5 times highest field blank)			0.05	0.03	0.07	0.25	0.15	3.00	0.10	

The recovery rates for the abiota blank samples (table 7 and 8) was calculated for the internal standard (ISTD: 7H-PFHpA) against the recovery standard (RSTD: 3,5-bis(trifluoromethyl)phenyl acetic acid =100%) assuming representative behaviour of the ISTD compared to the unknown PFAS target analytes (see table 14).

The method limit of quantification (LOQ) was set as 5 x highest field blank levels determined (table 8) or, if no blank levels were present, as 5 x background noise in the chromatogram.

For biota standard spiked extracted matrix experiments have been performed to determine the respective recovery rates for all target analytes.

The detection limit was calculated from a low level spiked and extracted sample and was considered to be equal to three times the area noise level in each transition in the region of the target compound. The concentrations of target analytes were in the following range: low level spiked = 3-8ng/g; high level spiked = 30-80 ng/g.

Table 8: Laboratory and field blank determination for sediment and sewage sludge samples [ng/g ww].

Sample ID	Sample matrix	Blank	PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFNA	Recovery (%)
LASEBLFAR01	Sea-sand	Sediment/sludge (Faroe Islands)	0	0	0	0	16	0	66
LASEBLFAR02	Sea-sand	Sediment/sludge (Faroe Islands)	0	0	0	0	15	0	78
SEBLNOR01	Silica + water	Sediment (Norway)	3	0	5	0	59	0	90
SEBLICE01	Silica	Sediment (Iceland)	4	0	10	0	67	0	53
SSBLSWE01	Silica + tap water	Sludge (Sweden)	0	2	7	0	60	0	77
LOD (instrumental signal-to-noise 3:1)			1	0	2	5	6	5	
LOQ (5 times highest field blank)			18	7	50	10	200	10	

- = not analysed.

The Finnish participants sent one field blank sample of triolein (standardised lipid: C₅₇H₁₀₄O₆; CAS-nr. 122-32-7) to ITM. No target analytes were detected in this sample. The field blank was analysed in parallel with the Finnish pike samples with high recovery (50-80%) for all target analytes.

Analytical method blanks (MilliQ water) have accompanied each series and instrument blanks (MeOH) were included with each instrument series. Limit of detection levels are calculated as instrument detection limit at 100% recovery (table 9). The method LOD describes the lowest detection range depending on sample matrix (see 3.4.2).

For the PFAS analysis in biota, the recovery rates were found to be highly matrix dependent. The recovery ranges are listed in Table 10. Recovery is corrected for by quantifying each sample using a spiked and extracted sample from each series and matrix type.

Table 9: Limit of detection (instrument and method) for the target PFAS compounds in biota [ng/g].

Compound	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFOSA	PFDS
<i>LOD type</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>	<i>Instrument LOD</i>
LOD [ng/g ww]	0.5	0.3	0.4	0.4	0.4	0.5	0.1	1.4
<i>LOD Type</i>	<i>Metod LOD</i>	<i>Metod LOD</i>	<i>Metod LOD</i>	<i>Metod LOD</i>	<i>Metod LOD</i>	<i>Metod LOD</i>	<i>Metod LOD</i>	<i>Metod LOD</i>
LOD [ng/g ww]	0.5-1.3	0.3-0.4	0.4-1.4	0.6-1	0.6-1	0.6-1	0.8	1.4-1.8

Table 10: Recovery ranges for PFAS in biota [%]

PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFOSA	PFDS
67 - 105	72 - 111	70 - 90	40 - 72	43 - 82	55 - 78	26 - 36	22 - 78

Repeated injection of selected biota samples revealed the low variation in the quantification method for PFAS quantification in biota using LC-MS/MS techniques (table 11).

Table 11: Repeated PFOS quantification for Swedish and Finnish biota samples

Sample	Day 1	Day 2
COSWE06	9.1	10.9
COSWE07	8.1	9.0
COSWE08	8.7	9.0
COSWE09	20	24.5
COSWE10	6.4	8.4
COSWE06	6.4	11.0
PIFIN01	594	551
PIFIN02	220	204
PIFIN03	227	211
PIFIN04	258	240
PIFIN05	284	263
PIFIN06	273	253
PIFIN07	530	492

3.4.4. Performance tests (parallel samples)

As a part of an accompanying quality control programme abiotic samples (seawater, precipitation (rainwater), landfill effluent, sewage effluent, sediment and sewage sludge samples) as well as biota (long-rough dab, Arctic char and perch) have been collected in parallel to document the representativeness of sampling methods as well as analytical method variability and robustness of sample preparation (table 3). From 6 countries 6 different sample types (16 samples) were collected in parallel (2- 5 parallel samples respectively). The complete dataset can be found in appendix 3 (concentration lists).

Depending on sample type, sample numbers and absolute concentration the relative deviation varied between 3 % and 22 % for the method used for abiotic compounds. The variability in the parallel sampling test documents that the method repeatability is sufficient for the present screening exercise. In addition, sample types and amounts showed to be sufficiently representative for the screening exercise.

3.4.5. Laboratory intercomparison

For a first method intercomparison and as an integrated part of the quality control program, a standard solution (in methanol) was prepared for parallel quantification of PFAS compounds using the respective trace-analytical methods developed by the two participating Nordic laboratories. The results are summarised in table 13.

Table 12: Method intercomparison between the NILU and the ITM method used for PFAS determination and quantification (see method description).

Concentration of the standard solution in methanol = Theoretical values

		PFOSA	PFBS	PFHxS*	PFOS	PFHxA	PFOA	PFNA	PFDA
Theoretical values	Conc. ng/mL	121	85.7	5.8	35.9	22.9	12.5	83.2	21.6
NILU	Relative deviation	89.9	82.3	8.18	31.1	28.3	13.7	91.7	21.9
		26%	4%	41%	13%	24%	10%	10%	1%
ITM	Relative deviation	178	75	9	36	32	16	107	32
		47%	12%	55%	0%	40%	28%	29%	48%

**please note, PFHxS is present as contamination in the PFOS standard mixture. Therefore, the theoretical value for PFHxS is probably underestimated.*

For both methods deviations from the expected concentration value up to 55% have been found (table 12) demonstrating the results of the analytical methods used in this studies are considered acceptable compared with well-established and fully evaluated monitoring methods. However, a more comprehensive method comparison is needed to fully evaluate the analytical methods. The overall results of this first method intercomparison showed a good quality of the analytical and quantification methods sufficient for the here performed screening exercise with regard to accuracy and comparability of the method.

Thus, for future quality control and assurance tests, sample preparation methods as well as matrix related method intercomparison will be considered as additional necessary step in direction of a fully evaluated and quality assured trace analytical method.

Table 13. Differences between the NILU and ITM PFAS quantification method.

Topic	Laboratory	
	NILU	ITM
<i>Standard calibration</i>	Internal and external quantification standard calibration	External matrix spike standard for calibration
Recovery	Internal recovery standard	Spiked extracted matrix
Instrumentation	LC-TOF (ESI)	LC-quadrupole MS (ESI)
Identification/quantification	High resolution single m/z quantification	SRM-MS/MS transition

As already outlined before, both methods are developed following different concepts with regard to sample preparation, analysis and quantification. The major differences are identified for the final LC/MS analysis and quantification (Table 13).

Merknad: =

3.4.6. Data handling and comparison

Compound- specific comparison of PFAS related residues in the various sample types is performed using median values instead of arithmetic mean since concentration distribution is not assumed to be normal distributed.

4. Results

The here presented data sets represent the first attempt to evaluate the distribution of PFAS related compounds in the Nordic environment. Institutions from 6 Nordic nations participated in the here presented screening exercise. A comprehensive selection of 23 different sample types representing abiotic and biotic environments were selected for the study (table 2).

Table 14A: Nomenclature for the selected abiotic samples within the Nordic PFAS Screening.

Sample type	Abbreviation	Country	Abbreviation	Sample Number
Sediment	SD	Finland	FIN	10-12
Sediment	SD	Faroe islands	FAR	5-7
Sediment	SD	Norway	NOR	12-14
Sediment	SD	Sweden	SWE	4-6
Sediment	SD	Iceland	ICE	2 (a-e)
Sewage sludge	SS	Finland	FIN	13, 14 (a-c) – 16
Sewage sludge	SS	Norway	NOR	15-16
Sewage sludge	SS	Denmark	DAN	4-6
Sewage sludge	SS	Iceland	ICE	3 (a-b) – 4(a-b)
Sewage Sludge	SS	Sweden	SWE	7-9
Sewage sludge	SS	Faroe islands	FAR	8
Seawater	SW	Finland	FIN	1-4
Seawater	SW	Denmark	DAN	1-2(a-b)-3
Seawater	SW	Iceland	ICE	1(a-d)
Seawater	SW	Faroe islands	FAR	1-3
Rain water	RW	Finland	FIN	5-6
Rain water	RW	Sweden	SWE	1(a-b)-3
Lake water	LW	Norway	NOR	1-4(a-b)
Sewage effluent	SE	Finland	FIN	8-9(a-b)
Sewage effluent	SE	Norway	NOR	10-11(a-b)
Sewage effluent	SE	Faroe	FAR	4

		islands		
Landfill effluent	LE	Finland	FIN	7(a-c)
Landfill effluent	LE	Norway	NOR	5(a-b)-9

Sampling, sample handling, transport, sample preparation and quantification were performed along a detailed quality control program including sampling manual and standardised laboratory procedures ensuring the best possible data quality for the analysed Nordic samples. The nomenclature, chosen for the samples selected within the here presented Nordic screening exercise for perfluorinated organic contaminants (PFAS) is listed in table 14A and B.

According to the above given table 14A, the sample number is composed by the abbreviations of sample type, countries name and the sample number. Thus, the 4th seawater sample from Finland is named **SWFIN04**. Please note parallel samples are distinguished with letters (a-e).

Table 14B: Nomenclature for the selected biotic samples within the Nordic PFAS screening.

Sample type	Abbreviation	Country	Abbreviation	Sample Number
Pike	PI	Finland	FIN	1-8
Pike	PI	Norway	NOR	3
Perch	PE	Sweden	SWE	1-3(a-b, 4
Perch	PE	Norway	NOR	4
Burbot	BU	Norway	NOR	1
Atlantic cod	CO	Sweden	SWE	5-12
Atlantic cod	CO	Faroe islands	FAR	5
Grey seal	GS	Sweden	SWE	14-16
Harbour seal	HS	Denmark	DAN	7-11
Trout	TR	Norway	NOR	2
Flounder	FL	Denmark	DAN	1-4
Eelpout	EP	Denmark	DAN	5
Herring	HE	Denmark	DAN	6
Long-rough dab	LD	Iceland	ICE	1(a-c)-2
Shorthorn sculpin	SC	Iceland	ICE	3
Shorthorn sculpin	SC	Faroe Islands	FAR	1-2
Dab	DA	Iceland	ICE	4
Dab	DA	Faroe islands	FAR	3-4
Minke whale	MW	Iceland	ICE	5-9
Arctic char	AC	Faroe islands	FAR	6(a-b)-7
Pilot whale	PW	Faroe islands	FAR	8-11
Fulmar	FU	Faroe islands	FAR	12-13

According to the above given table 14B, the sample number is composed by the abbreviations of sample type, countries name and the sample number. Thus, the 4th pike sample from Finland is named **PIFIN04**.

Blank samples are additionally abbreviated with “BL”. Thus, the first field blank for Swedish sewage sludge is named **SSBLSWE01** (see table 8).

4.1. Levels and distribution

A comprehensive sample set consisting of 119 environmental samples:

- 11 seawater samples from 4 Nordic countries
- 5 rainwater samples from 2 Nordic countries
- 6 landfill effluent samples from 2 Nordic countries
- 5 sewage effluent samples from 3 countries
- 15 sewage sludge samples from 6 Nordic countries
- 13 sediment samples from 5 Nordic countries
- 4 Lake water samples from 1 Nordic country
- 23 marine fish samples from 5 Nordic countries
- 18 freshwater fish samples from 4 Nordic countries
- 17 marine mammal samples from 4 Nordic countries
- 2 pooled seabird egg samples from 1 Nordic country.

represents the basis for the here presented first investigation on the fate and distribution of PFAS related residues in the Nordic environment (table 2).

Although a large number of samples is represented, the large variety of sample types collected in each country and the small number of individual samples representing the respective sample type restrict the assessment of general trends and spatial distribution. The differences between sampling locations and sample types within a Nordic country may be as large as between the respective countries. These variations are not considered in the here presented screening study. Thus, the results presented herein, should only be considered and discussed as indications and hints for further in-depth scientific studies.

4.1.1. Abiotic samples

The abiotic subset of samples consisted of 59 samples ranging from seawater to sewage sludge and sediments (table 2). For a better comparison the abiotic sample set is divided into two sub-groups: abiotic solid samples and aqueous samples.

Solid abiotic samples

The highest levels in solid abiotic sample material for PFAS related residues were found for sewage sludge samples (SSSWE09, PFOS = 2644 pg/g ww). Considerable concentration differences were found for the various sample types (figure 4).

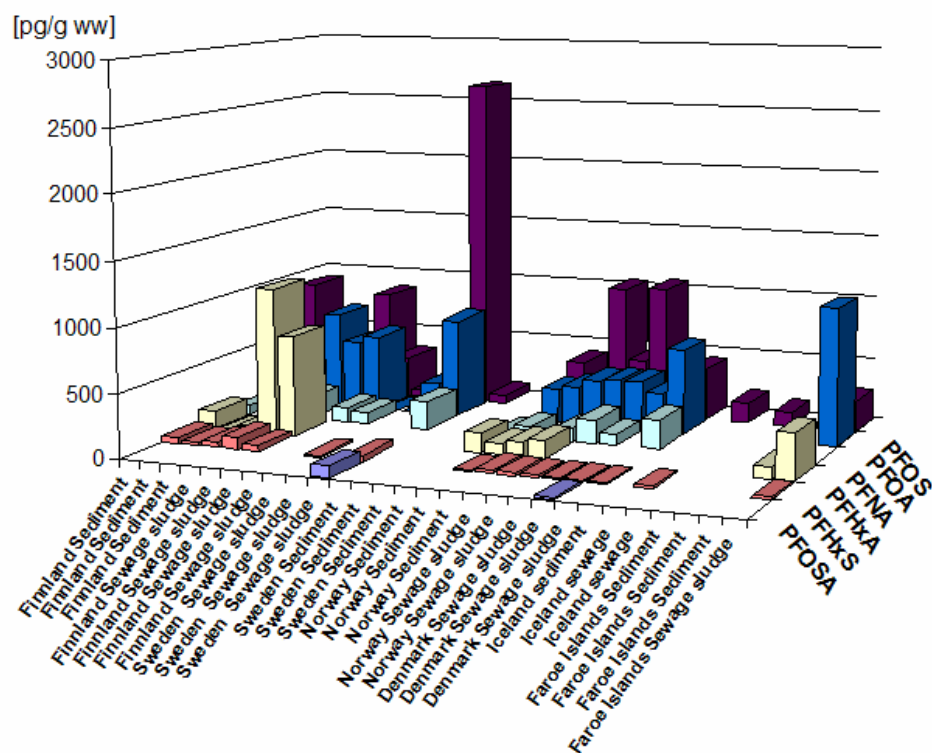


Figure 5: Compound specific levels for PFAS residues in solid abiotic samples: Sediment and sewage sludge. Concentration levels are given in pg/g ww (for more sampling details see appendices).

PFOS and PFOA are the predominant PFAS residues in solid abiotic samples. However, in the Finnish sewage sludge samples (see appendix 3: SSFIN13 and SSFIN14) also PFHxA is contributing significantly to the PFAS burden. No detectable PFAS residues were found in the Swedish freshwater sediment samples except for one sample where PFOS was found (SDSWE04: PFOS = 69 ng/g ww). In the only Icelandic sediment sample all PFAS were below limit of quantification (LOQ).

Aqueous samples

For the here presented screening study five different types of aqueous sample types were chosen: Seawater, lake water, rain water, sewage effluent and landfill effluent (table 2). Remarkable concentration differences were found for the different sample types (Figure 5). Highest levels were found for Norwegian landfill effluent samples (LFNOR06 ; SUM PFAS = 1537 ng/L, LFNOR08; SUM PFAS = 1162 ng/L). The Finnish landfill effluent samples were collected in parallel and reflect again the good repeatability of the analytical method (see chapter about quality control). Sewage effluent had considerable lower concentration levels (SUM PFAS, SENOR11 = 59 ng/L and SEFIN08 = 105 ng/L). Lowest concentrations were found for lake water and seawater samples (Figure 5) and rainwater levels ranging between sewage effluent and lake water concentrations. In all aqueous samples regardless sample type PFOA represented the predominant PFAS compound (except for the highest contaminated Landfill effluent sample LFNOR06 where PFHxA was the predominant PFAS related residue). PFOS, the most prominent PFAS residue in solid abiotic samples, is not as

dominant in the aqueous samples. However in Finnish landfill effluent samples PFOS is found in the same concentration range as PFHxA.

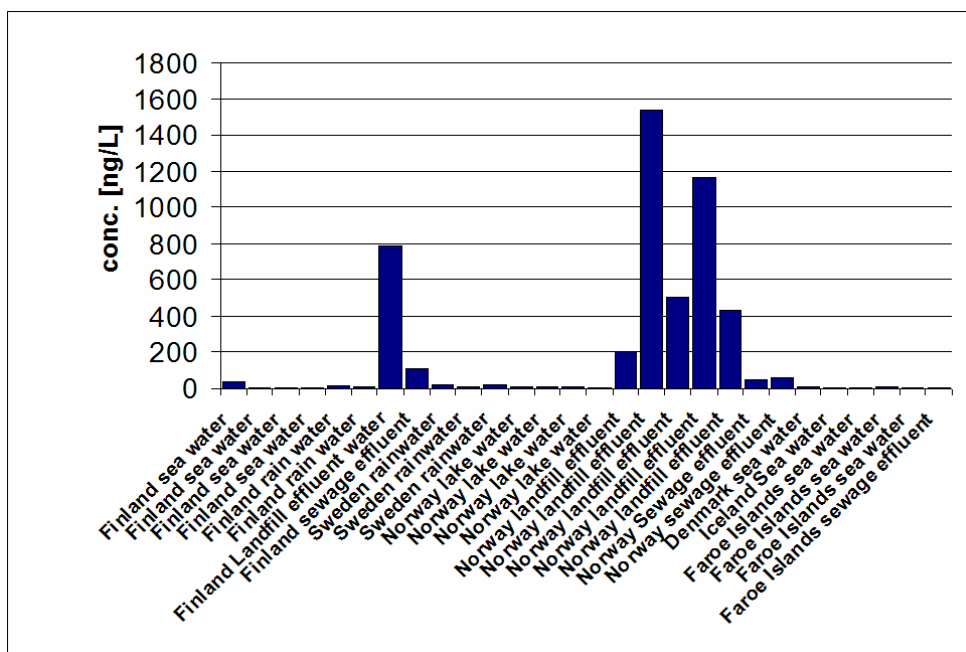


Figure 6: SUM PFAS concentration for aqueous abiotic samples: Seawater, rain water, lake water, landfill effluents and sewage effluents. Concentrations are given in SUM PFAS = ng/L. $SUM\ PFAS = PFOSA + PFBS + PFHxS + PFOS + PFHxA + PFOA + PFNA$.

For more information on the sample characteristics see appendices 1 and 3.

4.1.2. Biota

For comparison, the biota samples collected for the Nordic PFAS screening are presented as four sub-groups: Freshwater fish, marine fish, seabirds and marine mammals. A total of 60 biota samples are collected whereof 23 are marine fish samples, 18 freshwater fish, 17 marine mammals and 2 marine bird samples (table 2). The comprehensive selection of biota samples represents various biological and environmental endpoints. Thus, differences in levels and pattern distribution are expected to be related to trophic level, food habit, habitat, age, sex etc (biological information as well as other sample characteristics are summarised in appendix 1).

Freshwater fish

In all freshwater fish (liver), PFOS is the predominant PFAS representative (figure 7) followed by PFOSA regardless trophic level except for one sample (PINOR03; PFOS = 24 ng/g ww, PFOSA = 60 ng/g ww) where PFOSA is the most prominent compound. Pike represents the freshwater top predators and, thus, shows the highest PFAS contamination in the analysed freshwater biota. The highest PFAS levels were found in Finnish Pike samples (PIFIN01, PFOS = 551 ng/g ww, PFOSA = 141 ng/g ww). PFOS and PFOSA represent in all samples more than 90% of the PFAS burden.

Although the Swedish perch samples represent a lower trophic level as pike, the PFOS levels are not significantly lower than found for Pike. However, the PFOSA contribution is significantly minor compared to pike pointing towards food chain specific uptake or differences in transformation processes (Figure 7).

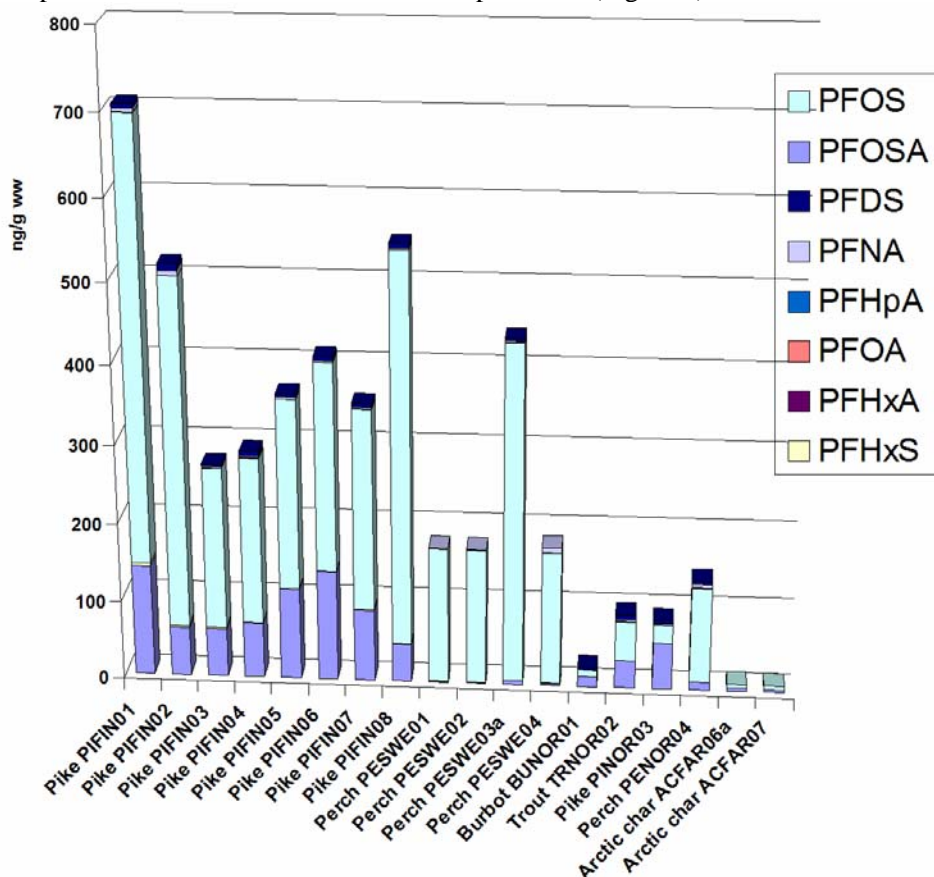


Figure 7: Compound specific level distribution for PFAS residues in freshwater fish liver: Pike (Fin=8, NO =1), perch (SWE=4, NO=1.), trout (No=1), landlocked Arctic char (FAR = 2) and burbot (NO=1). Concentrations are given in ng/g ww. For more information on the sample characteristics see appendices.

Norwegian and Swedish perch showed comparable PFAS concentration and patterns. However the contamination level in the one Norwegian pike sample is considerably lower as found for the Finnish pikes. In addition, PFOS is not the dominating PFAS residue (but PFOSA) in the Norwegian Pike sample as already mentioned before. In addition, the fact that PFOS and PFOSA were also detected in anadromous Arctic char in the Faroe Islands indicate that long-range transport in air and/or precipitation is occurring.

Marine fish

The PFAS distribution in marine fish species (liver samples) is characterised by a surprisingly high variability reflecting differences in food chain, food habits and

transformation strategies. Also for marine fish species, PFOS represents in most cases the predominant representative of the PFAS contamination (figure 8). However, in Sculpins, PFOSA is the found as the highest PFAS contaminant. Also for the Atlantic cod sample from the Faroe islands PFOSA is higher concentrated than found for the Swedish cod samples (Figure 8). The highest PFAS levels were found for a Swedish cod (COSWE12; PFOS = 62 ng/g ww) and a Danish Eelpout (EPDAN05; PFOS = 60 ng/g ww). Danish Eelpout and Herring contained also measurable amounts of minor PFAS contributors like PFHxA and PFOA. In Long-rough dab and sculpin from Iceland PFHxA is even one of the dominating PFAS contributors. However, PFHxA is not prevalent in the Icelandic dab sample. The marine fish samples from the Faroe Islands are the lowest contaminated samples measured with regard to PFAS. Country specific application pattern can, thus, not be excluded as important reason for pattern distribution and concentration levels.

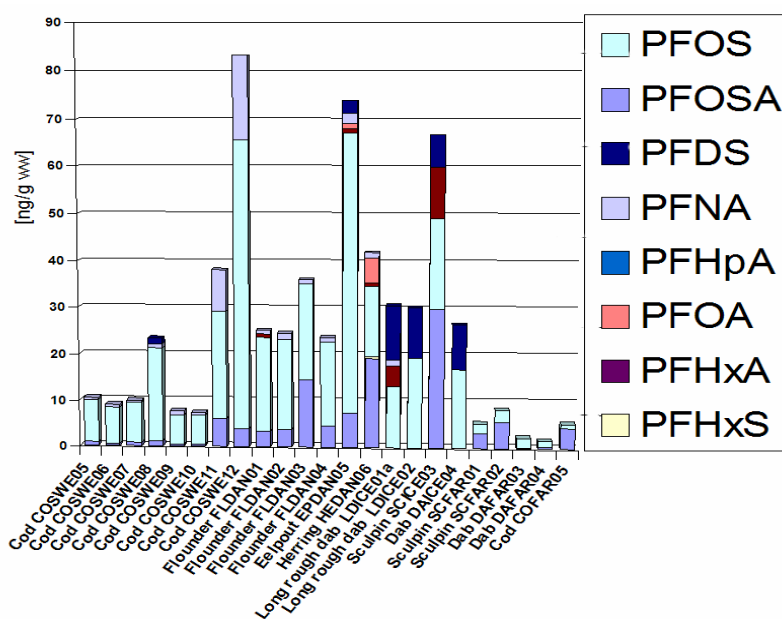


Figure 8 Compound specific level distribution for PFAS residues in marine fish liver [ng/ ww]. PFAS was determined in Atlantic cod (SWE=8, FAR=1), Herring (DAN=1), Flounders (DAN = 4), Eelpout (DAN =1), Long-rough dab (ICE = 2), Sculpin (ICE=1, FAR=2), Dab (ICE=1, FAR =2).

Nevertheless, marine fish species are significantly minor contaminated compared with the previously described freshwater samples indicating a certain correlation to the primary source distance. Please not that Perfluorodecane sulfone (PFDS) levels are surprisingly high in all Icelandic marine fish samples.

Marine mammals

The 17 marine mammal samples (liver samples) selected for the here presented PFAS screening represents the top predators of the marine environment. Marine mammals are considerably higher contaminated as the marine and fresh water fish samples previously described. However, Icelandic minke whales are characterised by a relatively low PFAS contamination compared with the pilot whales from the Faroe Islands (figure 9) indicating a correlation to the position in the food chain and food

habits. Swedish and Danish grey seals are highest contaminated with PFAS residues. The highest PFOS values were found in Danish Harbour seal samples (HSDAN10; PFOS = 977 ng/g ww). Usually PFOS is the dominating PFAS residue also in marine mammals. However in Pilot whales from the Faroe Islands, PFOSA is equally contributing to the PFAS burden in two cases even exceeding the PFOS levels considerably (PWFAR08; PFOSA = 218 ng/g ww and PWFAR09; PFOSA = 364 ng/g ww).

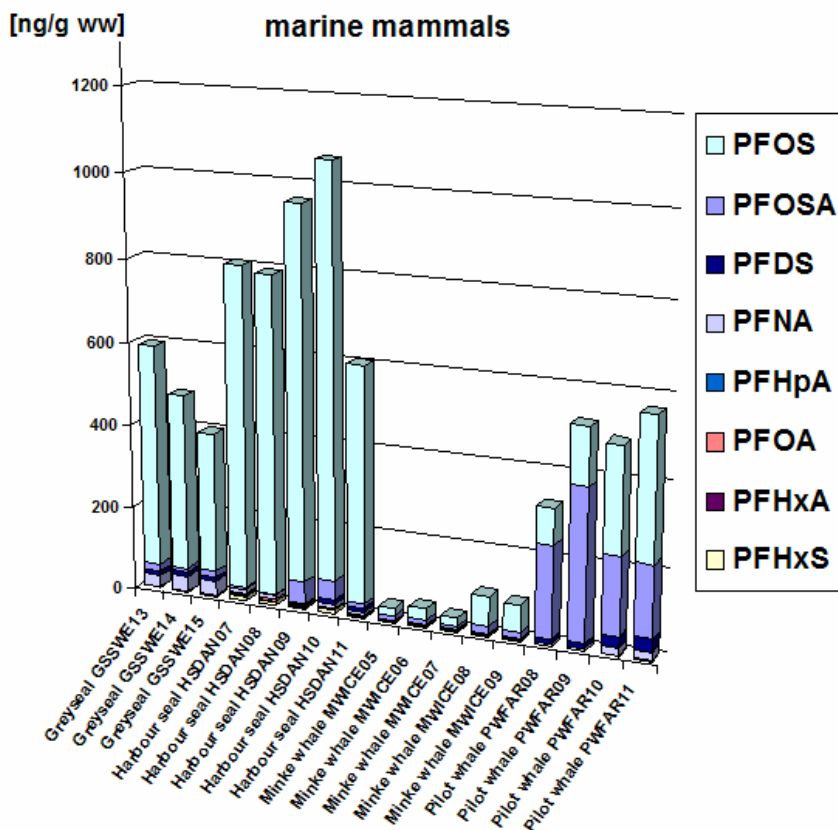


Figure 9: Compound specific level distribution for PFAS residues in marine mammals (livers): Harbour seals (Denmark), grey seals (Sweden), minke whales (Iceland) and pilot whales (Faroe Islands).

In all marine mammal samples, PFDS, a perfluorinated residue with a long-alkylated chain, is found in considerable amounts indicating bioaccumulation potential for this type of PFAS contaminants. Also hexanoic compounds (PFHxS and PFHxA) are found in measurable concentrations in all sample types (highest in harbour seals).

Marine birds

Two Fulmar samples (pooled eggs) were collected as pooled samples at the Faroe Islands. The PFAS levels were found in the sample concentration range as for marine fish species (Figure 10). Although PFOS is also for Fulmars the predominant PFAS residue, PFOSA is not as dominant as found for the other biota samples. In Fulmars, PFNA is the second highest PFAS contaminant. Nevertheless, PFOS stands for about 95 % of the PFAS contamination in the Fulmar samples from the Faroe

Islands.

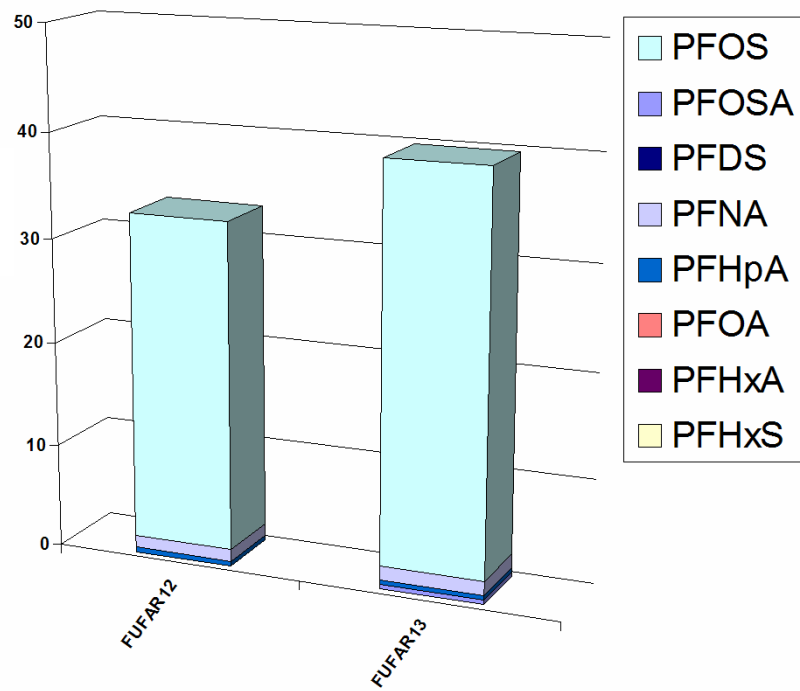


Figure 10: Compound specific level distribution for PFAS residues in pooled Fulmar egg samples from the Faroe Islands [ng/g ww].

5. Discussion and recommendations

The first Nordic screening on fate and distribution of PFAS related residues in environmental samples confirmed that PFAS residues are widely present in the Nordic environment. The first overview indicates that sewage sludge and landfill effluents are contributing as important anthropogenic sources for the release of PFAS into the environment. Large amounts of PFAS related contaminants are, thereafter, deposited in sediment. Whether remobilisation from the sediments into the adjacent water column and the food web also is an important contribution remains still unknown at present. However, significant amounts of PFAS related chemicals mostly dominated by PFOS are accumulating in the marine and freshwater food web into the top predating organisms reaching surprisingly high concentration levels.

5.1. Source elucidation

Already during preparation of the presented Nordic PFAS screening, sewage and landfill was identified as major anthropogenic sources based on general literature survey. Thus, sewage sludge, sewage effluent and landfill effluent was collected to document the concentration burden in this specific sample types representing primary environmental releases (figure 11-13).

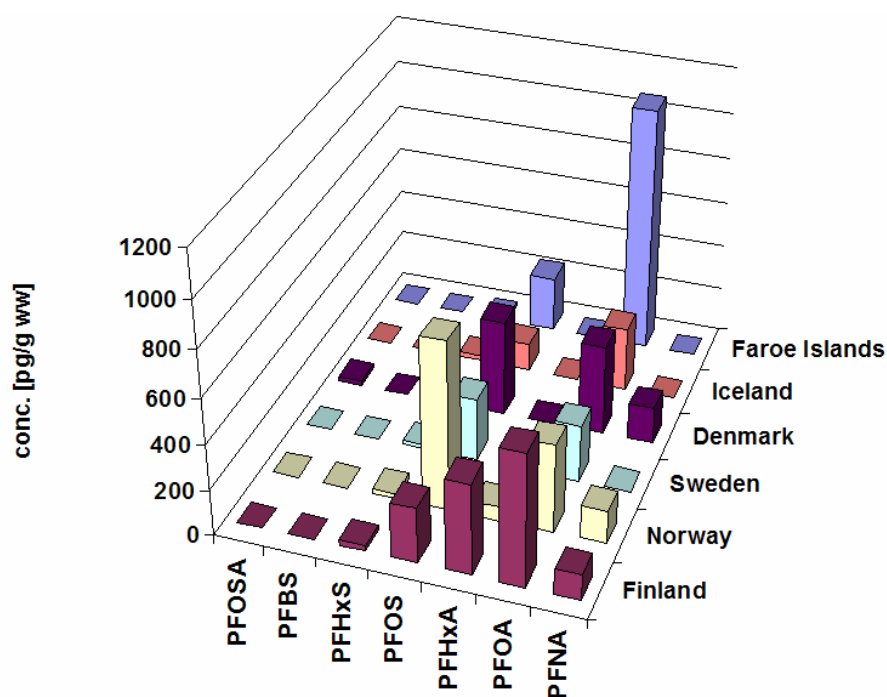


Figure 11a: Median distribution [pg/g ww] compounds in Nordic sewage sludge samples.

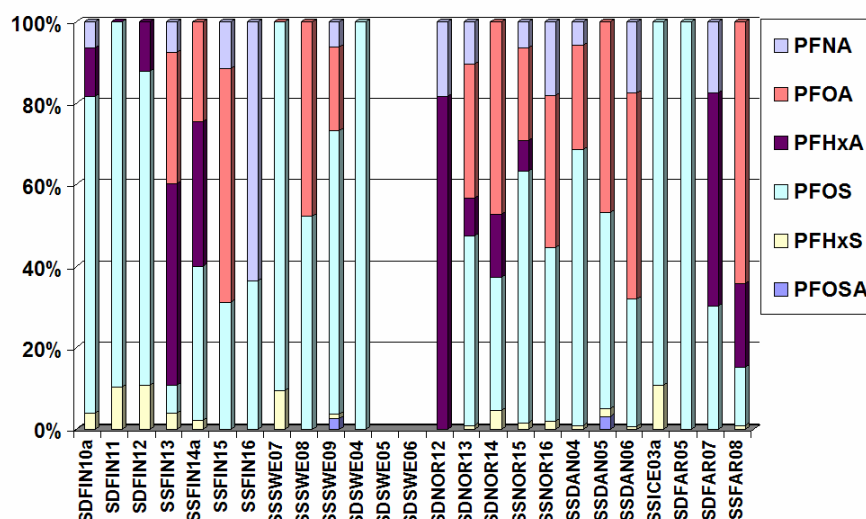


Figure 11b: Percentage distribution of PFAS related residues in Nordic abiotic solid samples (SS = sewage sludge and SD = sediment).

A first comparison of PFAS contamination in sewage sludge collected in 6 different Nordic countries revealed significant pattern differences. In general PFOS was the predominant PFAS residue in sewage sludge (figure 11a-b). On the other hand, PFOA, is the predominant PFAS residue in some Finish, Danish and Faroe Island sewage sludge samples (SSFIN15, SSDAN06, SSFAR08). In few samples (SSFIN13, SDNOR12, SDFAR07) even PFHxA is dominating the PFAS pattern. These strong local variations in the PFAS distribution and levels indicate different sources or considerable temporal fluctuation in the release patterns.

Highest individual PFAS concentrations were found for a Swedish sludge sample (SUM PFAS SSSWE09 = 3793 pg/g ww, figure 4). The detected differences in pattern distribution point towards an application specific release pattern from anthropogenic sewage sludge sources into the environment with country specific influences. The PFAS distribution in sewage effluent samples reflect in general the concentrations found in sewage sludge from the different Nordic countries (Figure 12).

However, the median concentrations in the three sewage effluent sample sets are surprisingly homogeneous distributed (Figure 12). In both Norwegian and Finnish effluent samples, PFOA is the predominant PFAS constituent whereas PFHxA is equally concentrated as PFOS in the Finnish sewage effluent sample. The sewage effluent sample from the Faroe island is considerably lower contaminated. The obvious shift in PFAS predominance from sewage sludge to sewage effluent (especially pronounced for the samples from the Faroe islands) indicated that also the physico-chemical properties are important in the distribution and release of PFAS from primary sources like sewage sludge. PFOA and PFHxA are more soluble in aqueous samples than PFOS. Therefore, PFOA and PFHxA are distributed via the water phase whereas PFOS is assumed to be introduced into the environment mainly via biosolids adsorbed on surfaces. PFBS, the perfluorinated chemical promoted currently as successor for PFOS related products is found in significant amounts in all aqueous samples.

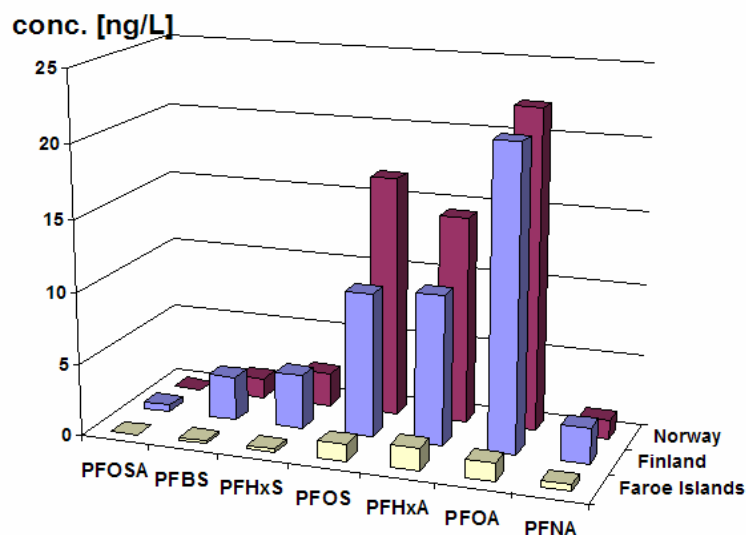


Figure 12: Median distribution [ng/L] compounds in sewage effluent

Landfill effluents are identified as additional possible anthropogenic sources (figure 13).

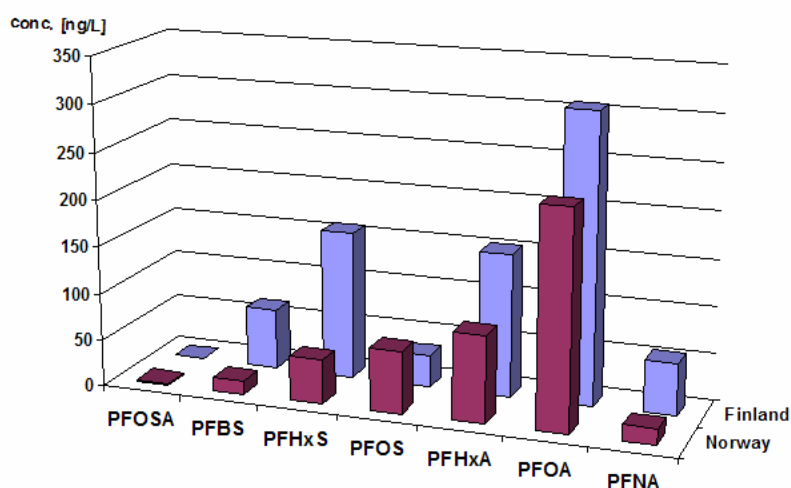


Figure 13: Median PFAS distribution [ng/L] in Nordic landfill effluent

The concentration levels found for the two sample sets of landfill effluent are considerably higher than the levels previously discussed for sewage effluents (around 10 x higher, see figure 12) confirming the significant contribution of landfill effluent water as major anthropogenic source for PFAS in Nordic countries. PFHxS, PFHxA and PFOA are dominating the Finnish landfill effluent sample. In the Norwegian samples, PFOS, PFHxA and PFOA are dominating. PFOA is the predominant PFAS constituent in all landfill effluent.

5.2. Sample specific patterns and fate estimation

The distribution of PFAS related residues in environmental samples is ruled by a combination of chemical, physical and biological processes including physico-chemical properties of the chemical, the physical environment (temperature, adsorption, storage medium, light-conditions) and biological accumulation and transformation processes.

5.2.1. Potential sources

Sewage sludge, sewage effluent and landfill effluents are identified as potential primary sources for the release of PFAS residues into the Nordic environment due to the high levels of PFAS related compounds detected in these sample types (figure 5 and 6).

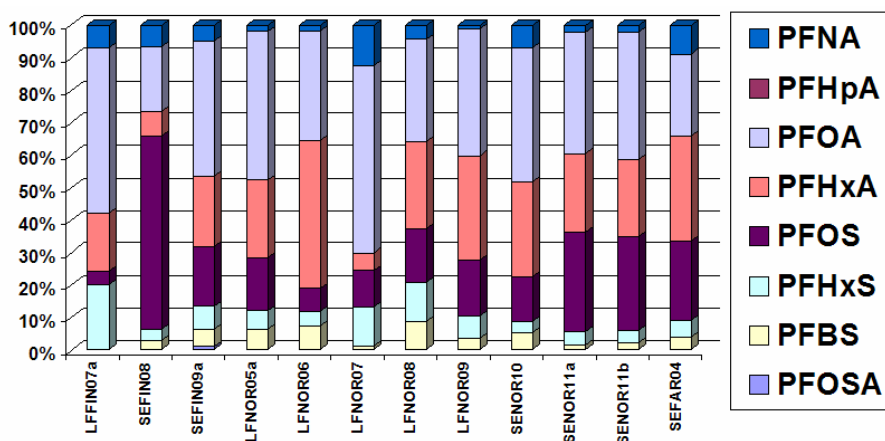


Figure 14: Relative pattern distribution of PFAS residues in Nordic sewage effluent and landfill effluent samples.

Based on the available data, the release pattern seems mainly governed by physico-chemical properties of the target compounds in combination with application patterns characteristic for the respective Nordic country.

The PFAS patterns in sewage sludge (figure 11b), sewage effluent and landfill effluents are mainly ruled by PFOA, PFOS and PFHxA (figure 14). Sewage sludge from Finland is dominated by PFOA whereas Swedish sewage is dominated by PFOS. Norwegian sewage effluent samples are dominated by PFOA and PFOS. Sewage effluents from Finland do not reflect the characteristic patterns found for the respective sewage sludge samples indicating a strong “day-to-day” fluctuation in the release patterns and amounts.

Relative high concentration levels were found in marine mammals, which usually express strong migration behaviour. In addition, the concentration ranges reported on a global basis (Giesy et al. 2001) in combination with the here presented data set indicate that already now many PFAS related residues (PFOS, PFOSA) must be considered as ubiquitously distributed throughout the globe and thus, long-range transport (e.g., ocean currents, atmosphere) is expected to be a major source for PFAS contamination in remote places such as the Arctic regions.

5.2.2. Seawater, fresh water and rain water samples

Adjacent water bodies serve as direct recipients of the sewage and landfill related environmental release. However, except for one seawater sample (SWFIN01), the water samples (seawater, lake water, precipitation) do not reflect the primary release pattern identified for the previously described sewage and landfill samples (figure 14 and figure 15). The PFAS pattern in all Swedish and Finnish precipitation samples (rainwater) are governed by PFOA (Figure 15).

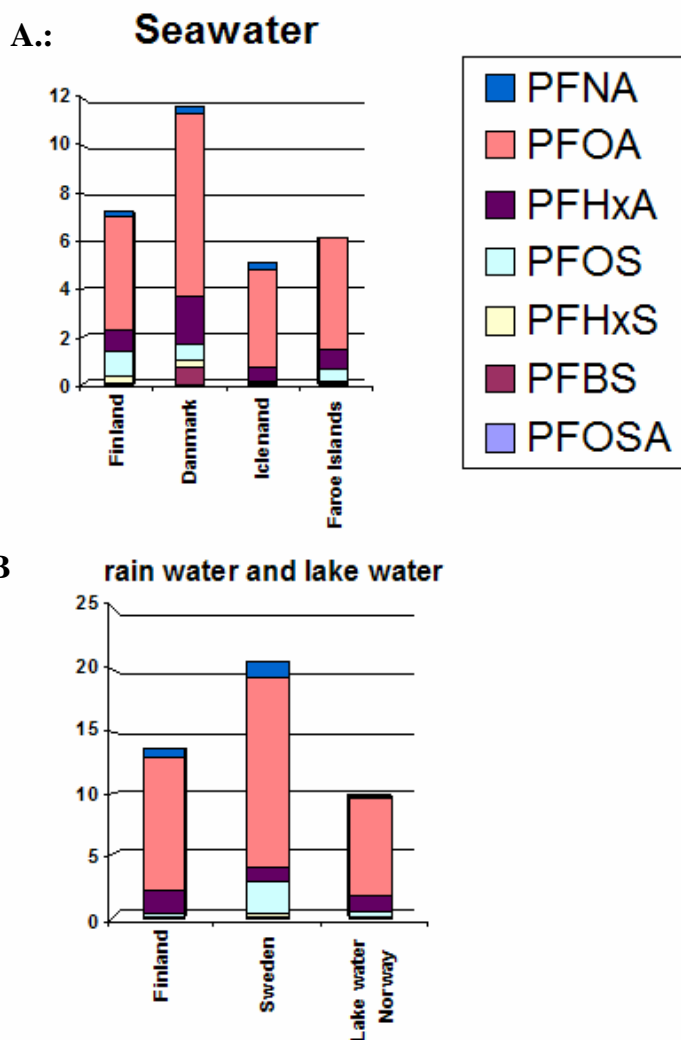


Figure 15: A: Median concentrations for seawater; B: rain (Sweden) and lake water/fresh water samples (Finland, Norway). Concentration are given in ng/L.

Whereas no clear pattern distinction between lake water, rain water and seawater could be established regardless location (where the samples have been collected).

5.2.3. Sediment

The median distribution (Figure 16) showed that the PFAS levels in sediment are different in the respective Nordic countries. PFOS is only dominating in the Finnish

sediment samples. In the Norwegian samples, PFOA is the predominant PFAS residue, whereas the lowest levels were found in sediments from Sweden with PFOS as the predominant PFAS constituent. Low PFAS levels were also found in Faroe Island sediments with PFOS and PFHxA as dominating compound.

PFOS was identified as important PFAS related pollutant in sediments representing in all samples the predominant or the second most concentrated PFAS contaminant in all sediments analysed.

Whether these distinct differences are a result of the differences in sediment composition or a result of country specific release patterns remains unknown and should be investigated in more detail.

Median distribution: Sediments

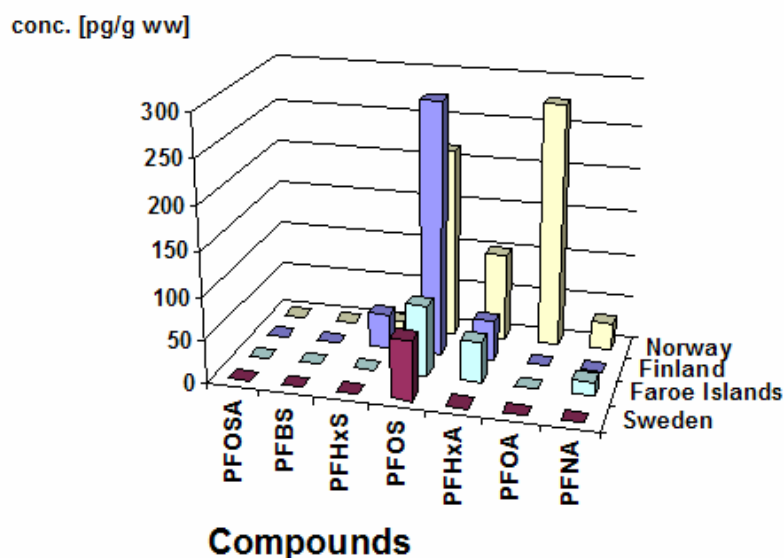


Figure 16: Median PFAS concentrations in Nordic sediment samples.

5.2.4. Biota

A complex combination of trophic level, up-take via the food web, passive accumulation processes as well as bioconcentration is assumed to rule the PFAS patterns in the Nordic biota samples.

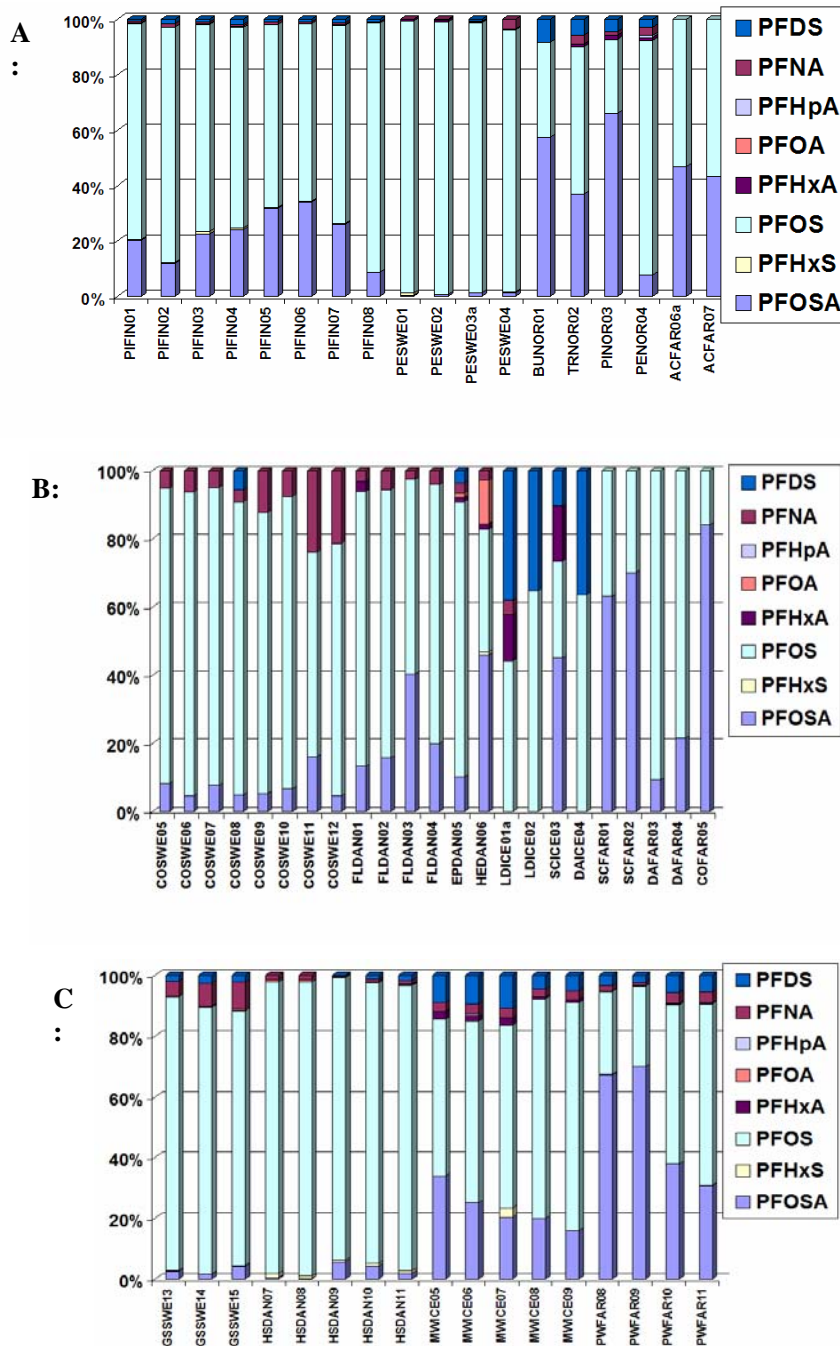


Figure 17: Relative pattern distribution for PFAS residues in freshwater fish (A), marine fish (B) and marine mammals (C).

For samples codes see page 33-34

PFAS pattern in the various biota samples reflect the biological status of the species and not so much the sample location/ country. A first pattern analysis revealed that species representing high trophic levels (top predators) are mainly dominated by

PFOSA and PFOS (figure 17a-c). Danish harbour seals and Swedish grey seals are dominated by PFOS whereas PFOSA is predominant in Pilote whales from the Faroe Islands. Also Finnish pike samples are strongly influenced by PFOS. Marine and freshwater fish species representing lower trophic levels seem not as strongly influenced by PFOS and PFOSA as top predated species.

PFOS and PFOSA are present in the fresh water pike and perch in almost as high concentrations as in the marine mammals. These high burdens are probably due to primary source in the vicinity of the sampling site. However, the diversity of PFAS found in the marine fish and mammals seems to be higher than in the fresh water fish reflecting a stronger influence of possible secondary sources like long-range transport (atmosphere and ocean currents) as well as migration patterns of marine species (predators and prey species).

5.3. Spatial distribution

A first attempt to find indications for country specific distribution pattern is undertaken. Only for sample types collected and analysed from more than 3 Nordic countries a comparison of the results has been performed. However, statistically the available data set is by far not sufficient to reveal significant and statistically confirmed spatial trends. Thus, the here presented tendencies and patterns should only be considered as indications and used as basis for later in-depth trend studies.

5.3.1. Seawater

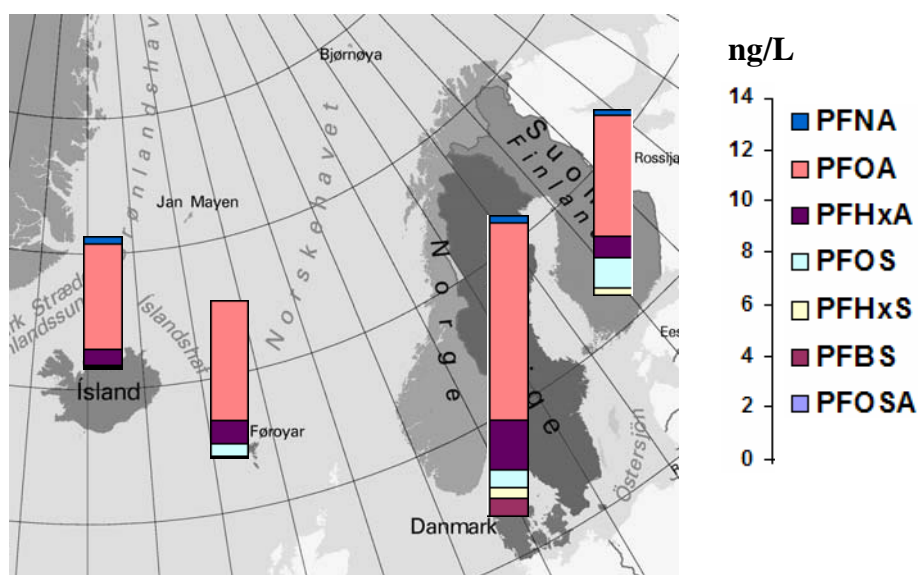


Figure 18: Spatial distribution of PFAS residues (ng/L median concentrations) in seawater from Nordic countries.

Please note, the placement of the histograms in the map does not reflect any information on sampling location.

In general, the PFAS median values for seawater samples collected in Iceland, Farøer Islands, Denmark and Finland reflect a similar PFAS distribution pattern (Figure 18).

PFOA is dominating all seawater samples analysed (up to 70% of the PFAS burden) usually followed by PFHxA. However, in the Finnish samples, PFOS is slightly higher concentrated than PFHxA. The overall concentrations for PFAS are highest in Finland and Denmark indicating a certain influence of the population density. However, The concentration differences between the countries with smaller populations (Iceland, Faroe Islands) and larger populations (Denmark, Finland) are surprisingly small (around factor 2). Thus, the contribution of PFAS burdens from long-range transport may be considered and investigated as import source in future investigations.

However, sampling specific circumstances (e.g., distance to potential sources, sea currents, tidal conditions etc.) may contribute to the small differences between PFAS levels found in seawater.

5.3.2 Sewage sludge

For many comprehensively investigated anthropogenic pollutants, sewage sludge is considered as a significant primary release source. Therefore, also for the here presented study, sewage sludge was considered as an important sample type and, thus, collected in all six participating countries. A direct correlation between population size contributing to the sewage treatment plant (person equivalents) or specific sewage treatment procedures with the PFAS pattern found in sewage samples was not established in the here presented study. However, indications reflecting possible country specific application and release patterns are obvious (figure 19). The concentrations found in sewage sludge are relatively high amounting up to the lower micro-gram per gram (wet weight) range.

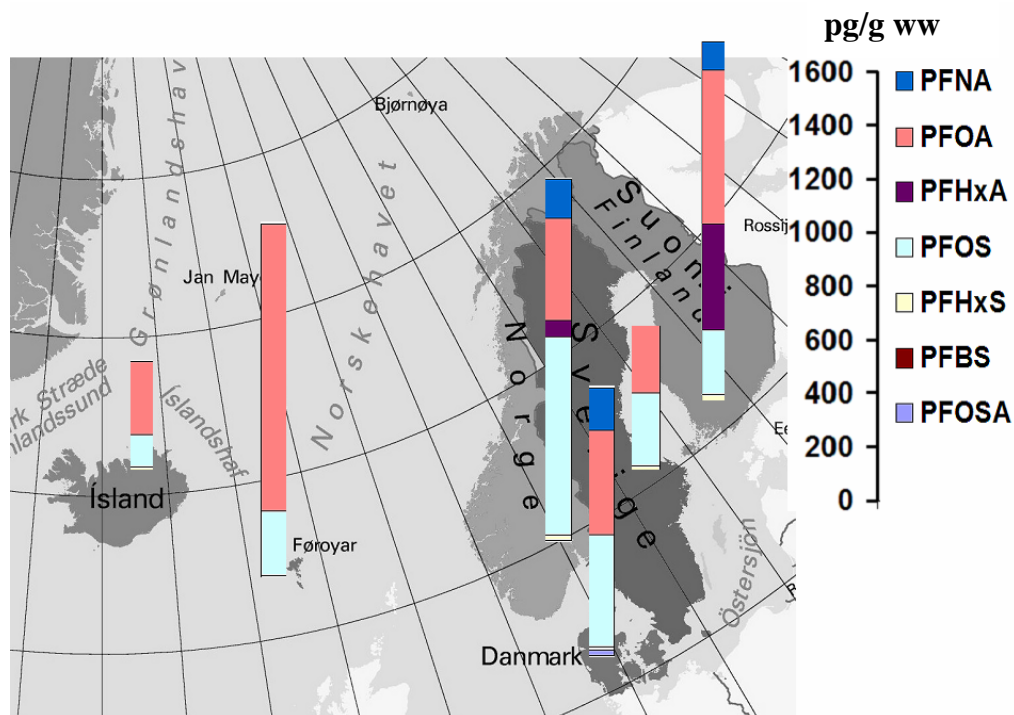


Figure 19: Spatial distribution of PFAS residues (pg/g ww median concentrations) in sewage sludge from Nordic countries.

Please note, the placement of the histograms in the map does not reflect any information on sampling location

In the median distribution presented in figure 20, usually PFOA and PFOS were the predominant PFAS residues released through sewage sludge in all Nordic countries. However, whereas PFOA dominated in sewage samples from less populated countries (Iceland, Faroe Islands), PFOS was more prevalent in sewage from Denmark, Norway and Sweden). The PFAS burden of sewage from Finland, on the other hand, showed a somewhat different pattern. PFHxA is identified as second high concentrated PFAS residue in those samples indicating different release patterns (Figure 19). PFNA was also found insignificant amounts in Norwegian, Danish and Finnish Sewage (up to 10% of the PFAS burden).

When comparing concentration ranges for PFOS, relatively similar concentration ranges were confirmed for Nordic countries with large population numbers (Norway, Sweden, Denmark and Finland). For Iceland and the Faroe Islands very low levels were found (table 15).

Table 15: Concentration ranges for sum PFOS in Nordic sewage sludge samples

Country	Number of sampling locations	Concentrations [pg/g ww]
Norway	2	449 - 1023
Denmark	3	316 -1041
Sweden	3	167 – 2644
Finland	3	35 - 925
Iceland	2	< LOQ - 220
Faroe Islands	1	241

5.3.3. Sediment

Sediment samples were collected from five Nordic countries. In the Icelandic sample no PFAS were detected and only in one Swedish sample PFOS was at a quantifiable level. PFAS levels found in Norwegian Freshwater sediments were surprisingly high with up to 637 pg/g ww (sum PFAS median concentrations) for these sediment samples (figure 20).

However, a spatial comparison of PFAS levels in sediment samples is difficult since in general sediment composition, sedimentation rate, depth of the water column, etc. play as significant role in the up-take rates and residence time of persistent contaminants in those environmental compartments.

In sediments from the Faroe Islands, Sweden and Finland, PFOS is the predominant PFAS residue followed by PFHxA. In Swedish samples, even PFOS only was detected. The Norwegian and Swedish sediment samples were collected from freshwater lakes. The Norwegian sediments were collected from the largest freshwater lake in Norway, lake Mjøsa. The Swedish samples showed exclusively PFOS as dominating residue. The Norwegian sediments, however, are dominated by PFOA, with considerable contributions of PFOS and PFHxA. Also PFNA was founding at significant levels. It can be assumed that, hydrological conditions (tidal patterns, currents), sediment composition, sedimentation rates etc. are significantly different in freshwater sediments compared to the ocean-borne sediments from the

Baltic Sea (Finland), and the Atlantic Ocean (Faroe Islands and Iceland). Thus, no ocean current long-range transport contributes to and no tidal currents dilutes the PFAS burden deposited in the fresh water sediments from Lake Mjøsa (Norway) and the Swedish sites, whereas ocean-borne transport can be assumed contributing significantly to the PFAS patterns and burden in sediments from Finland and the Faroe Islands.

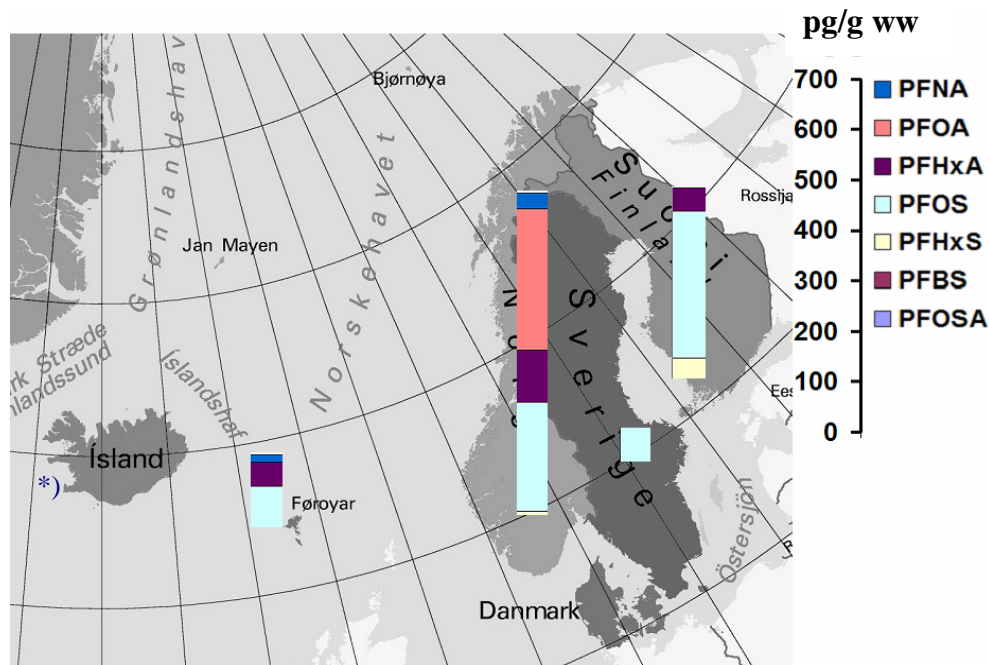


Figure 20 Spatial distribution of PFAS residues in sediment (pg/g ww median concentrations) from Nordic countries.

*) In the Icelandic sediment samples analysed, very low amounts of PFAS were found (see appendix 3).

Please note, the placement of the histograms in the map does not reflect any information on sampling location

5.3.4. Biota

Specimens of 16 different species were collected representing marine and fresh water environments. Samples from 6 species were collected from 2 different Nordic countries. Therefore, a comprehensive spatial distribution analysis is not possible based on the biota samples collected for the here presented Nordic PFAS screening exercise. However, the restricted data available are useful as indications for level distribution of PFAS in biota which should be subject for further elucidation.

In pike collected from Norway and Finland, the total PFAS concentration and contribution of PFOS to the overall PFAS burden is different (figure 21) indicating differences in primary sources and/or feeding habits.

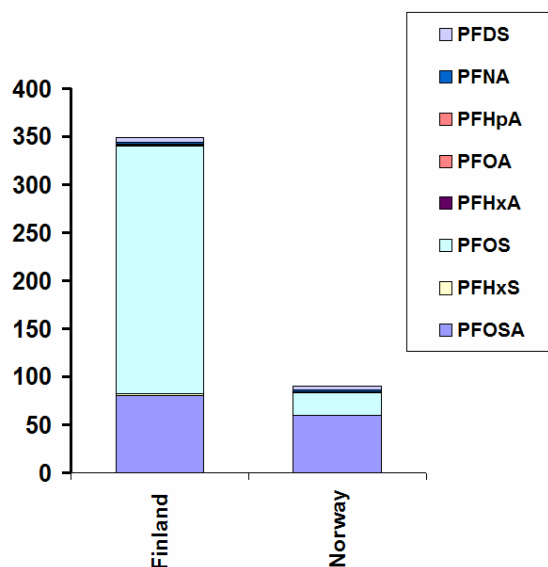


Figure 21: Median distribution of PFAS in Pike liver [ng/g ww] from Finland (n=8) and Norway (n=1).

The Finnish pike samples are higher contaminated with PFAS as the Norwegian sample. However, whereas the PFOSA levels are in a similar concentration range in pike liver from both countries, PFOS contributes with 10x higher levels to the overall PFAS burden in the Finnish pikes. The concentration levels in these freshwater fish were surprisingly high, found in the same concentration range as for top predating marine mammals (grey seal liver), indicating a considerable release of PFAS into freshwater system pointing towards different contamination sources. However, these preliminary assumptions are based on a very small data set and, thus, should only be considered as indication.

The levels in Atlantic cod were found in general to be low (low ng/g ww range). The Swedish cod samples were collected in the Baltic Sea, a region where many potential primary source are expected to release PFAS related residues in the marine environment close to the natural habitats of the cod. Thus, the levels of PFAS (median values from eight samples) in the Swedish cods were about 2 times higher than in the cod liver sample from Torshavn harbour (Faroe Islands, Figure 22). Whereas PFOS was the predominant PFAS contributor to the Swedish samples, PFOSA dominated in the Cod sample from the Faroe Island indicating different sources for respective populations.

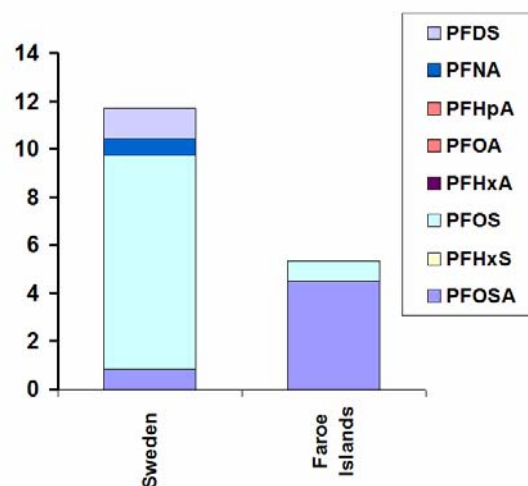


Figure 22: Median distribution of PFAS in Atlantic cod liver [ng/g ww] from the Faroe Islands (n=1) and Sweden (n=8).

In all other biological samples analysed for PFAS residues, no clear signals for county or region specific PFAS patterns and levels were identified.

5.4. Comparison with literature data

Until today only few reports are published and, thus, publicly available on the distribution of PFAS related residues in environmental sample. A first attempt is, therefore, made to compare the results of the Nordic PFAS screening with already available literature data reporting PFAS levels in comparable environmental matrices. However, due to the comprehensive analytical challenges posed by this specific group of environmental residues, the trace analytical methods available today are still in the stage of development. Thus instrumental differences in analytical methods used, method validation documented and quantification methods applied restrict a comprehensive comparison of the literature data available. Therefore, the here presented comparison should only be considered as indicative. More up-to-date international investigations (like the here presented Nordic screening exercise) are on the way, which, hopefully, will allow in future a more thorough comparison and evaluation of global distribution, fate and occurrence of PFAS related environmental contaminants.

5.4.1. Water

Several published scientific papers report on PFAS reported contaminants in aqueous samples. Three international studies from Germany, USA and Japan are identified which reported environmental concentration of PFAS residues (table 16).

Table 16: Concentration distribution of selected PFAS residues in aqueous samples [ng/L]

Matrix	Location	PFHxS	PFOS	PFOA	PFOSA	Reference
Surface water (freshwater)	Germany	-	2 – 43	LOD – 8	-	Lang et al. 2004
Tennessee upstream of fluorofactory	USA, Tennessee river	-	17 – 54	<25	-	Hansen et al. 2002
Marine surface water	Japan	<11	LOD – 59	-	-	Taniyasu et al. 2003
Nordic sea water	Nordic countries	0.08 – 4.39	<LOD – 21.7	3.53 – 8.48	<LOD - 0.07	This study
Nordic lake water	Norway	<LOD – 0.11	<LOD – 0.48	4.82 - 8.23	<LOD	This study
Nordic precipitation	Nordic countries	<LOD – 0.59	0.24 – 2.97	8.23 – 16.8	<LOD - 0.14	This study

The German and the US study reported PFAS levels in freshwater, whereas the Japanese study focused on PFAS residues in marine surface water samples. In the literature data on fresh water used for this comparison PFOS was the predominant PFAS constituent. No distinct differences between freshwater and seawater (surface) is found in the literature references. These results are different compared to the here presented Nordic data set. However, the literature values focus mainly on PFOS and no information about e.g. PFHxA is available by now. In all Nordic water samples (seawater, freshwater (lake) and precipitation), PFOA is the predominant PFAS residue followed by PFOS or PFHxA. The PFOS levels in the Nordic samples are considerably lower than reported in the three reference studies whereas PFOA values were in comparable concentration ranges as described in the literature (table 15). However, the relative high LOD for PFOA reported in the USA study (Tennessee) indicate considerable methodological limitations.

5.4.2. Sediment

Only one recent study has been identified in the literature so far reporting on PFOS and PFOA residues in sediment samples (table 16). A first comparison of these literature data with the here reported Nordic sediment data revealed that the sediment concentrations measured in the Nordic samples were considerably higher compared with the sediment samples analysed from The Netherlands. In-line with the literature data from the Netherlands PFOS is identified as dominating PFAS residue in sediment samples (table 17). However, a direct comparison of the two data sets is difficult because the Dutch sediment concentration levels are reported on dry weight basis, whereas the Nordic data set is based upon wet weight. In general, the Nordic sediment samples were higher contaminated than reported for the Dutch sediments, revealing considerable contamination potential in Nordic sediments.

Table 17: Concentration distribution of selected PFAS residues in sediment samples [ng/g]. dw = dry weight, ww = wet weight

Matrix	Location	PFHxS	PFOS	PFOA	PFOSA	Reference
Sediments/ suspended matter (dw)	The Netherlands	-	LOD – 47	LOD – 24	-	Schrap et al. (2004)
Nordic Sediment (ww)	Nordic countries	LOD – 45	LOD – 892	LOD – 312	< LOD	This study

5.4.3. Sewage sludge

Also for PFAS in sewage sludge only one relevant study (Germany) was identified for comparison with the here presented Nordic PFAS study. However, PFOS was analysed in the German study and the detection limit was extremely high (6000 ng/g dw). Thus, PFOS was not detected in any of the German samples. In the Nordic study, PFOS was the dominant PFAS related contaminant in sewage sludge, but the highest concentration found was below the detection limit of the German study, which, furthermore, is given on dry weight basis. This prevents any comparison of the two studies. In the Nordic sewage sludge samples PFOA was detected as the second dominant PFAS residue, whereas PFOSA and PFHxS were detected in levels up to 90 ng/g ww (table 18).

Table 18: Concentration distribution of selected PFAS residues in sewage sludge samples [ng/g]. dw = dry weight, ww = wet weight

Matrix	Location	PFHxS	PFOS	PFOA	PFOSA	Referene
Sewage sludge (dw)	Germany	-	<LOD (6000 ng/g dw)	-	-	Schröder (2003)
Nordic sewage sludge (ww)	Nordic countries	<LOD – 91	55 – 2644	<LOD – 1075	<LOD – 94	This study

5.4.4. Biota

Most of the PFAS data found in scientific literature were reported for various biological samples. Based on this so far reported literature survey, an ubiquitous global distribution must be assumed for PFOS and related compounds (table 19). A set of 9 relevant scientific references reporting PFAS residues in biota was identified for the here presented literature comparison. One common feature was identified for all reported biota data. PFOS was the predominant PFAS residue identified in biota regardless sample type or trophic level. A first comparison confirmed, that the highest environmental PFAS burdens were found in marine mammal samples (table 19), although highest individual PFOS values were found for single marine fish samples. Taniyasu et al. (2003) reported up to 7900 ng/g ww in a Japanese fish liver.

Also for marine mammals, mainly PFOS was reported in international studies except for a study on Baltic seals were also residues for other PFAS related compounds were found (table 19). The PFAS (e.g., PFOS, PFHxA, PFOA, PFOSA) concentrations found in the Nordic seal samples (Denmark, Sweden) are found in the same concentration range as reported from the Baltic study. In the Nordic study, all seal samples have been found to be highest contaminated with PFAS residues of all Nordic biota analysed.

Table 19: Concentration distribution of selected PFAS residues in biological samples [ng/g]. dw = dry weight, ww = wet weight.

Matrix	Location	PFHxS	PFOS	PFOA	PFOSA	Reference
Bird liver (ww)	Korea/ Japan	LOD – 34	LOD – 650	LOD – 21	LOD – 215	Kannan et al. (2002c)
Bird liver worldwide (ww)	-	-	LOD – 690	-	-	Giesy et al. (2001)
Fulmar, pooled eggs (ww)	Nordic countries	<LOD	31 – 37	<LOD	<LOD – 0.46	This study
Seal liver (ww)	Baltic Sea/ Bothnian Bay	<7.5	130 – 1100	LOD – 39	LOD – 47	Kannan et al. (2002a)
Seal/dolphin/ polar bear/ otter liver (ww)	Worldwide survey	-	LOD – 990	-	-	Giesy et al. (2001)
Dolphin liver (ww)	USA/Canada/ Mexico	-	37 – 1520	-	-	Kannan et al. (2001b)
Minke whales (ww)	Nordic countries	<LOD – 1.1	19 – 71	< LOD	7.2-19	This study
Pilot whales (ww)	Nordic countries	0.39 – 1.0	88 – 336	0.35 - 1.7	172-364	This study
Seals (ww)	Nordic countries	0.67 – 10	331 – 977	0.3-5.6	0.93–55	This study
Fish liver (ww)	worldwide	-	LOD – 170	-	-	Giesy et al. (2001)
Fish liver (ww)	The Netherlands, Western Scheldt	-	>10 – 7760	-	-	Hoff et al. (2003)
Oysters (dw)	USA	-	LOD – 1225	-	-	Kannan et al. (2002d)
Eel filet (ww)	The Netherlands	-	LOD – 143	<LOD	-	Schrap et al. (2004)
Atlantic salmon liver (ww)	Not identified	<7.5	<8	<19	<19	Kannan et al. (2002a)
Fish liver (ww)	Japan	LOD – 19	3 – 7900	-	-	Taniyasu et al. (2003)
Freshwater fish (ww)	Nordic countries	<LOD – 3.4	4.7 – 551	<LOD – 1.4	0.6 – 141	This study
Marine fish (ww)	Nordic countries	<LOD – 0.4	0.9 – 62	<LOD – 5.4	<LOD – 30	This study

The PFAS levels found in the Nordic whale samples (e.g., minke whales, pilot whales) were considerably lower contaminated as previously reported for marine mammals (dolphin liver) from Middle America (Mexico, USA).

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5.5. Level comparison with conventional “legacy” persistent organic pollutants

Persistent organic pollutants (POP) have been investigated comprehensively in all environmental contaminants throughout the past decades. Although many of the legacy POPs are banned or restricted in use on an international basis, high levels are still remaining in the environment documenting their high persistence and stability in the environment. Compounds like polychlorinated biphenyls (PCB), hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB) are still in the focus of environmental concern although banned for decades.

In order to illustrate the environmental significance of our findings in the light of the general contamination of environmental compartments with persistent organic contaminants, a first comparison with levels reported for selected conventional persistent organic pollutants (POP) from the literature is presented (table 20).

5.5.1. Concentration comparison in Seawater

PCBs belong to the most investigated POP compounds worldwide since they were detected for the first time in the 1960s. PFAS levels in the Nordic environmental samples analysed are in general found in comparable concentration ranges as reported for PCB. For seawater the levels found for sum PFAS was considerably higher than the PCB values reported for the North Sea. Also compared to γ -HCH (a still in-use pesticide) and HCB, the levels for PFAS are considerably higher in North Sea water (table 20).

5.5.2. Concentration comparison in Fresh water

The PFAS levels in fresh water (lake Mjøsa) are also higher than reported for PCBs in Russian rivers. However γ -HCH levels in freshwater are exceeding the Sum PFAS concentration reported for the Nordic countries in average 10 times. The polycyclic musk compounds Galaxolide (HHCB) and Tonalide (AHTN) are found in even higher concentrations in fresh water systems (table 20).

5.5.3. Concentration comparison in rain water

The concentration levels for PFAS found in wet deposition (rain water) is found in the same concentration range than reported for γ -HCH. However, hexachlorobenzene (HCB) was found in considerably higher levels than PFAS. In the newly reported ThemaNord report 503 "Synthetic musks in the Nordic environment", rain water samples were analysed for synthetic musks. Synthetic musks were found in the same concentration range as reported for PFAS.

5.5.4. Concentration comparison in sediments

PCBs in contaminated sediments are found in higher concentration ranges than PFAS indicating the importance of considering the different physico-chemical properties of the two compound groups for a proper environmental fate assessment. However, both γ -HCH and HCB are generally reported in concentration ranges comparable to PFAS in Nordic sediments. Synthetic musks (HHCB and AHTN) are reported in concentrations exceeding PFAS levels in several orders of magnitudes (although reported on a dry weight basis). PBDE 47 (2,2',4,4'-TeBDE) is found in considerably lower concentration ranges in Swedish Sediments than found for PFAS in the Nordic samples (table 20).

5.5.5. Concentration comparison in sewage effluent

In landfill effluent, sum PFAS levels from the here presented Nordic study exceed sum PCB concentrations from New Jersey, USA by one order of magnitude (table 20).

5.5.6. Concentration comparison in sewage sludge

Also for conventional POPs, sewage sludge is always a medium where high concentrations can be expected. PCBs levels are exceeding the levels reported for PFAS. Also synthetic musks (HHCB and AHTN) are orders of magnitude higher concentrated in sewage sludge compared with PFAS (Table 21). PBDE levels (PBDE 47) were found to be in a similar concentration range in sewage sludge as reported for PFAS.

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5.5.7. Concentration comparison in landfill effluent

In landfill effluent, PCB concentrations reported are found in a similar concentration range (New Jersey, USA) as reported for PFAS in the here presented Nordic study. However, the maximum values for PFAS are about 10 times higher than the PCB concentrations reported in US landfill effluent (waste water).

5.5.8. Concentration comparison in marine mammals

Marine mammals represent a very heterogeneous group of marine animals with regard to trophic levels, food and migration habits as well as physiology and adaptations to their environments. However, in order to provide first indication for compound group specific distribution, this generalisation is thought to be adequate. PFAS levels in marine mammals from Nordic countries (grey-/ harbour seals, pilot whales and minke whales) were found in similar concentration ranges as reported for PCBs, HCB and γ -HCH in marine mammals from Norwegian coastal waters. The concentration reported for PBDE47 is considerably lower than the PFAS levels found (Table 20).

5.5.9. Concentration comparison in marine fish

Concentration ranges reported for conventional POPs in marine fish samples are varying considerably depending on sampling location and species caught. However, in general it was found that PFAS levels in the marine fish species collected during the Nordic screening exercise are lower than reported for PCBs. On the other hand, γ -HCH and PBDE47 are usually reported in lower concentrations than PFAS. HCB is found in a similar concentration range as PFAS.

Table 20: Literature survey and comparison of PFAS residues with levels of conventional POPs in selected environment samples.

Concentration range reported										
Concentration	PFOS	PFOA	SUM PFAS (8 comp.)	Sum PCB (7 stand. comp.)	γ-HCH	HCB	HHCB	AHTN	2,2',4,4'-TeBDE	
Seawater	< LOQ - 22	< LOQ - 0.07	4.4 - 37	0.98 (+/- 0.44) ¹⁰	0.1 - 1.8 ³	0.06 (+/- 0.02) ¹⁰	-	-	-	
fresh water	< LOQ - 0.48	< LOQ	9-10	0.01 - 0.22 ¹⁷	3 - 114 ¹⁸	-	< LOQ - 500 ¹⁹	< LOQ - 300 ¹⁹	-	
rain water	0.24 - 2.97	< LOQ - 0.14	11.2 - 22	-	2-12 ¹⁸	40 - 160 ¹⁸	-	-	-	
Sediment	< LOQ - 892	< LOQ	89 - 1147	1.00-14000 (dw) ¹	100 - 1210 ¹⁰	500 - 1250 (dw) ¹	< LOQ - 2200000(dw) ¹⁹	< LOQ - 2600000(dw) ¹⁹	46 - 54 ⁸	
Sewage sludge	55 - 2644	< LOQ - 94	150 - 3793	610 - 1800 ¹⁴	< LOQ - 70 ¹⁴	-	45000 ng/g (dw) ¹⁹	42000 ng/g (dw) ¹⁹	470 ng/g(dw) ¹²	
Sewage effluent	1.2 - 62.6	< LOQ - 0.48	5 - 105.4	100 ng/g (dw) ¹²	-	-	26500 ng/g (dw) ²³	3600 ng/g (dw) ²³	-	
Landfill effluent	30.7 - 187	< LOQ - 3.28	199 - 11537	-	-	-	600-2000 ¹⁹	800-2400 ¹⁹	-	
marine mammals	19 - 977	0.9 - 364	36 - 1060	5 - 200 ¹³	-	-	-	-	-	
marine fish	0.9 - 62	< LOQ - 30	1.7 - 83.3	1640 - 3100 ¹⁰	40-1250 (lw) ⁵	190 - 2590 (lw) ⁵	-	-	16 - 33(lw) ⁹	
				4500 - 22000 (lw) ⁷	46 - 130 ¹⁰	13-30 ¹⁰	-	-	-	
				< LOQ - 3500 ¹	1 - 20 ¹	< LOQ - 25 ¹	-	1-199 ²⁰	1-5 ²	
				199 - 1329 ²	1-5 ²	1.1 - 67 ²	-	-	-	
				27-396 ⁴	-	-	-	-	3.2-27(lw) ⁹	
				-	-	-	-	-	167(lw) ⁹	
				32 ²²	0.6 ²²	3 ²²	-	-	-	
freshwater fish	4.7 - 551	0.6 - 141	8 - 707	100-900 (lw)	-	-	500-1000(lw) ¹⁹	600-1600(lw) ¹⁹	< LOQ - 2000(lw) ⁸	
seabirds (egg)	37 - 37.5	< LOQ - 0.5	39 - 40	24-285 ⁸	-	-	-	-	-	
				250 ²¹	-	47 ²¹	-	-	-	

dw = dry weight
lw = lipid weight

- ¹ Green et al. 2001 ⁵ Kleivane et al. 1994 ⁹ Haglund et al. 1997 ¹³ Schrock 2003 ¹⁷ AMAP 1998 ²¹ Mikkelsen et al. 2002
² Knutzen and Green 2001 ⁶ Henriksen et al. 1996 ¹⁰ Law et al. 1996 ¹⁴ Holte et al. 1994 ¹⁸ AMAP 2004 ²² Larsen and Dam 2003
³ Theobald et al. 1996 ⁷ Bernthoff et al. 1994 ¹¹ Sapota 2004 ¹⁵ Anonymous 2000 ¹⁹ Rimkus 2004 ²³ Temalford 2004.
⁴ Schulz-Bull et al. 1991 ⁸ Selström et al. 1998 ¹² Samsøe-Petersen 2003 ¹⁶ Berg et al. 2003 ²⁰ Kallenborn et al. 2001

5.5.10. Concentration comparison in fresh water fish

PCB and PFAS levels are found in a similar concentration range. However since PCB levels are reported on a lipid weight basis (lw), PCBs in freshwater fish might be even somewhat lower concentrated. Data from Faroe Islands Arctic char (Larsen and Dam 2003) indicate that PCB7 are in the same order of magnitude as reported for PFAS. Synthetic musks (HHCB and AHTN) and brominated flame retardants (PBDE 47) are found in considerably higher levels than reported for PFAS.

5.5.11. Concentration comparison in seabirds

PCB concentrations reported from glaucous gulls (Arctic) are in the same concentration range as found for PFAS in Fulmar eggs from the Faroe Islands (table 21). However PCB7 and HCB were also analysed in the Fulmar eggs used for the PFAS screening study (Mikkelsen et al. 2002). The PCB7 concentrations exceed the PFAS levels considerably whereas HCB was in the same concentration range as reported for PFAS (Table 20)

5.6. Toxicity and ecotoxicity

Today, very little is known about toxicity and ecotoxicity of PFAS related compounds. Some toxicity data exist for the already identified major environmental PFAS contaminants PFOS and PFOA (Butenhoff et al. 2004). Recently, evidence for neonatal toxicity on Sprague-Dawley rats was reported (Grasty et al. 2003, Thibodeaux et al. 2003). Even invertebrates show toxic effects when exposed to high levels of PFOS (Boudreau et al. 2003). PFOA has been identified as potent peroxisome proliferator in mice (Xie et al. 2003). Genotoxic effects in rates have been postulated for PFOA (Butenhoff et al. 2003). Strong influences on zooplankton populations upon PFOA exposure are reported recently (Sanderson et al. 2003). Hu et al. (2003) found for a comprehensive number of PFAS (incl. PFOS, PFBS, PFHxS) toxic properties leading to alterations in cell membranes. Boudreau et al (2001) reported low LC50 results for PFOA, PFOS and PFDA. There are no scientifically evaluated data reported or published neither on PHPA, PFHpS, PFDS nor on PFNA. A list of reported information on PFOS and PFOA is summarised in table 21.

Compared with the available toxicological and ecotoxicological data, all concentration values are well below the reported threshold levels (Table 20). The reported LC50 and NOEC values are all in the mg-range whereas the PFAS concentrations in the Nordic screening studies are found in the upper ng – lower µg range. However, no information about chronic exposure to low levels is available yet.

More detailed information about toxicology/Ecotoxicology of PFAS related compounds can be found in the references listed in table 21.

Table 21: Selected toxicological and ecotoxicological data for PFAS related compounds

Compound	Species/ test	Toxicity parameter	
PFOS	Shrimps (<i>Myxidopsis bahia</i>)	LC ₅₀ (Kemikalieinspektionen, 2004) 3.6 mg/L	NOEC (Kemikalieinspektionen, 2004) 0.25 mg/L
	Green algae (<i>Pseudokirchnerilla subcapitata</i>)	EC ₅₀ (Kemikalieinspektionen, 2004) 48.2 mg/L	NOEC (Kemikalieinspektionen, 2004) 5.3 mg/L
	African clawed frog (<i>Xenopus laevis</i>)		LOEC (Kemikalieinspektionen, 2004) 7.97 mg/L
	Honey bee (<i>Apis mellifera</i>)		NOEL (Kemikalieinspektionen, 2004) 1.93 mg/ind.
	Rat (<i>Rattus norvegicus</i>)		NOEL (Kemikalieinspektionen, 2004) 0.5 mg/kg
	Partridge (<i>Colinus virginianus</i>)	LC ₅₀ (Kemikalieinspektionen, 2004) 251 mg/kg	
	Microtox (Bacteria)	LD ₅₀ (Kemikalieinspektionen, 2004) 220 mg/kg food	
	Water Flea (<i>Daphnia magna</i>)	EC ₅₀ (3M, 2000) >280 mg/L	
	Rainbow trout (<i>Oncorhynchus mykiss</i>)	EC ₅₀ (3M, 2000) 79 mg/L	NOEC (Brook et al. 2004) 12 mg/L
	Sheepshead minnow (<i>Cyprinodon variegatus</i>)	LC ₅₀ (Brook et al. 2004) 7.8 mg/L	
PFOA	Bluegill sunfish (<i>Lepomis macrochirus</i>)	LC ₅₀ (Brook et al. 2004) >15 mg/L	
	Rat (<i>Rattus norvegicus</i>)		NOEC (Brook et al. 2004) <0.87 mg/L
	Rat (<i>Rattus norvegicus</i>)		NOAEL (US-EPA 2003) 10 mg/kg
	Fathead minnow (<i>Pimephales promelas</i>)	EPA-study (Hekster et al. 2002), LC ₅₀ 843 mg/L	
	Fathead minnow (<i>Pimephales promelas</i>)	EPA-study (Hekster et al. 2002), EC ₅₀ 720 mg/L	
	Fathead minnow (<i>Pimephales promelas</i>)		NOEC 360 mg/L
	Water Flea (<i>Daphnia magna</i>)		NOEC (Boudreau et al. 2001) 55.1 mg/L
PFDS	Fathead minnow (<i>Pimephales promelas</i>)	OECD study (Hekster et al. 2002), LC ₅₀ 4.8 mg/L	

5.7. Sources and environmental implications

The here presented Nordic screening exercise on the fate and occurrence of PFAS related residues in the environment confirmed that landfill deposition and sewage treatment are to be considered as important sources for the release of PFAS residues into the aqueous environment (seawater and freshwater). Landfills and waste deposition sites are obviously to be considered as major sources due to the comprehensive application profile of PFAS related products (household related products, textiles, flame retardants etc.). Thus, the Nordic screening on PFAS confirms the first suspicion the waste dumps might play a major role as primary sources for PFAS residues in the environments.

However, measurable amounts of PFAS were found also in precipitation samples from Sweden and Finland demonstrating, that selected PFAS chemicals are prone to atmospheric transport and sub-sequent wet deposition via rain. Thus, selected PFAS related contaminants should be evaluated with regard to long-range transport potential.

PFOS and PFOSA dominated the PFAS burden in top predating organisms and thus indicate strong bioaccumulation tendencies. These findings support earlier reports where PFOS and PFOSA were detected in high concentrations in top predating species even from Arctic regions. PFAS related compounds like PFOS and PFOSA must therefore be evaluated as persistent and bio-accumulative residues.

These basic properties characterising many PFAS related chemicals as persistent and bioaccumulative in conjunction with recent ecotoxicological studies supports the need to add PFAS into the UNEP category of PBT compounds: "Persistent, bioaccumulative and toxic".

5.8. Consequences and recommended actions

The here presented report contributes to the international scientific efforts to elucidate the hazardous potential of PFAS-related contaminants in the environment. The results presented illustrate the heterogeneity of this group of contaminants with regard to physico-chemical properties, accumulation potential and ecotoxicological potential.

PFAS related contamination was detected in all samples from all participating Nordic countries. These contaminants are present in all countries and, thus, an ubiquitous distribution must be assumed not only across the Nordic countries but globally.

Compounds with considerable bioaccumulation potential like PFOS and PFOSA are found in high concentrations in top predating marine mammals like harbour and grey seals as well as in pilot whales.

As earlier described, PFAS residues are practically not biodegradable and are, thus, expected to be present in the environment for many decades to come. It is therefore recommended to include these PFAS related chemicals major environmental hazards in the national and international monitoring programs for environmental contaminants.

6. Conclusions and suggestions

The here presented results from a first screening on perfluorinated alkylated substances (PFAS) is contributing to the international scientific efforts to evaluate and characterise the environmental behaviour of this very special group of environmental contaminants. A core group of 6 PFAS compounds (PFOS, PFOA, PFOSA, PFHxA, PFNA, PFHxS) was analysed in all 119 samples covering seawater, rain water, fresh water, sewage sludge, sewage effluent, landfill effluent, seabird eggs (Fulmar) and liver samples from 16 species of marine and freshwater fish as well as marine mammals. As a voluntary addition to the contracted work, PFHpA (perfluoroheptanoic acid), PFBS (perfluorobutane sulfonate) and PFDS (perfluorodecane sulfonate) were analysed.

PFAS residues were found in all environmental matrices analysed. Specific matrix-dependent distribution patterns were found. PFOS and PFOA were usually dominating in abiotic samples whereas PFOS and PFOSA were the predominant PFAS residues in biota. For abiotic samples, the highest PFAS levels were found in landfill effluent and sewage sludge whereas the top-predating grey seals were highest contaminated in the biota sample set.

The PFAS levels found were usually in the same order of magnitude or even higher than reported for conventional “legacy” persistent organic pollutants. In sewage samples, however, PCBs and synthetic musks were higher concentrated.

Until today, very little information is available on the ecotoxicological behaviour and effects of PFAS in biological systems. However, the concentrations found in landfill effluents and sewage are detected in concentration ranges where chronic exposure might cause adverse effects in ambient biosystems.

Based on the here presented results, PFAS compounds are identified as chemicals with considerable environmental distribution. Thus, the major contributors of this contaminant group should be implemented in on-going monitoring activities after analytical methods are adapted to this purpose. Due to their physico-chemical properties, most of the PFAS compounds are not accumulating in lipid-rich tissues. Thus, matrices bird eggs, like liver, bile and blood should be preferred for monitoring of PFAS. It is recommended to include freshwater fish located close to possible waste dumps since such locations may represent major sources for environmental distribution of PFAS. Long-range transport as a possible source should be included in future environmental monitoring planning. Thus, more in-depth sampling in coastal waters and remote atmosphere should give information on the long-range transport potential.

PFAS residues are virtually indestructible and, thus, will eventually reach concentrations in biota with effects on physiology and environmental health.

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Sample collection:

The following colleagues have been responsible for/ supported the study for the national sampling for the Nordic screening for PFAS related compounds in the environment. In addition numerous institutions/ organisation contributed with help, advise and personnel to the success of the here presented study:

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Denmark:

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Appendix 1: Sample characteristics

Biota

Sample ID	Country/ Location	Species	Sampling position	Sampling date	Sample type	Comments
	Denmark					
FLDAN01	Köbenhavn Amt	Flounder	55° 44,05' N – 12° 36,86' E		Liver	
FLDAN02	Köbenhavn Amt repl.	Flounder	55° 44,05' N – 12° 36,86' E		Liver	
FLDAN03	Köbenhavn Amt repl.	Flounder	55° 44,05' N – 12° 36,86' E		Liver	
FLDAN04	Köbenhavn Amt repl.	Flounder	55° 44,05' N – 12° 36,86' E		Liver	
EPDAN05	Roskilde fjord	Eelpout	55° 40,3' N – 12° 01,1' E		Liver	
HEDAN06	Roskilde fjord	Herring	55° 40,3' N – 12° 01,1' E		Liver	
HSDAN07	Limfjord1	Harbour seal	56° 40' N - 08° 20' E		Liver	
HSDAN08	Limfjord2	Harbour seal	56° 40' N - 08° 20' E		Liver	
HSDAN09	Hesselö	Harbour seal	56°.10' N - 11°.40' E		Liver	
HSDAN10	Samsö	Harbour seal	55°.50' N - 10°.30' E		Liver	
HSDAN11	Öresund	Harbour seal	55°.35' N - 12°.50' E		Liver	

	Finland					
PIFIN01	Helsinki City coast	Pike	60.11° N – 24.59° E		Liver	
Sample ID	Country/ Location	Species	Sampling position	Sampling date	Sample type	Comments
PIFIN02	Helsinki City coast	Pike	60.11° N – 24.59° E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
PIFIN03	Helsinki City coast	Pike	60.11° N – 24.59° E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
PIFIN04	Helsinki City coast	Pike	60.11° N – 24.59° E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
PIFIN05	Helsinki City coast	Pike	60°11'N - 24°59' E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
PIFIN06	Helsinki City coast	Pike	60°11'N - 24°59' E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
PIFIN07	Helsinki City coast	Pike	60°11'N - 24°59' E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
PIFIN08	Helsinki City coast	Pike	60°11'N - 24°59' E	2003	Liver	Vanhankaupungin lahti; Gammelstadsfjärden
	Faroe Islands					
SCFAR01	Kaldbak	Sculpin	62.03 N – 06.49° W	May 2002	Liver	
SCFAR02	Kaldbak	Sculpin	62.03 N – 06.49° W	May 2002	Liver	
DAFAR03	Kaldbak	Dab	62.03 N – 06.49° W	July 2002	Liver	
DAFAR04	Kirkjubö	Dab	61.57° N – 06.47° W	July 2002	Liver	
COFAR05	Torshavn	Cod	62.00° N – 06.46° W	June 2002	Liver	

ACFAR06a	á Mýranar, Bleiki I	Arctic char	62.10° N – 07.05° W	July 2002	Liver	Landlocked
ACFAR06b	á Mýranar , Bleiki I	Arctic char	62.10° N – 07.05° W	July 2002	Liver	Landlocked
ACFAR07	á Mýranar, Bleiki II	Arctic char	62.10° N – 07.05° W	July 2002	Liver	Landlocked
PWFAR09	Sandagerdi	Pilot whale	62.00° N – 06.46° W	September 2002	Liver	
Sample ID	Country/ Location	Species	Sampling position	Sampling date	Sample type	Comments
PWFAR10	Sandagerdi	Pilot whale	62.00° N – 06.46° W	September 2002	Liver	
PWFAR12	Sandagerdi	Pilot whale	62.00° N – 06.46° W	September 2002	Liver	
PWFAR13	Sandagerdi	Pilot whale	62.00° N – 06.46° W	September 2002	Liver	
FUFAR14	Vidareidi	Fulmar pool1	62.21° N – 06.30° W	21.05.2002	egg	Pooled samples
FUFAR15	Vidareidi	Fulmar pool2	62.21° N – 06.30° W	21.05.2002	egg	Pooled samples
	Iceland					
LDICE01a	Gufunes bay	Long rough dab	64.09° N, 21.48° W	17.10.2003	Liver	
LDICE01b	Gufunes bay	Long rough dab	64.09° N, 21.48° W	17.10.2003	Liver	
LDICE01c	Gufunes bay	Long rough dab	64.09° N, 21.48° W	17.10.2003	Liver	
LDICE02	Gufunes bay	Long rough dab	64.09° N, 21.48° W	18.10.2003	Liver	
SCICE03	Videyarbyggja	Sculpin	64.09° N, 21.51° W	09.09.2003	Liver	
DAICE04	Gufunes bay	Dab	64.09° N, 21.51° W	17.10.2003	Liver	

MWICE05	Atlantic ocean	Minke whale	66.10° N, 19.16° W	26.08.2003	Liver	
MWICE06	Atlantic ocean	Minke whale	66.12° N, 14.39° W	30.08.2003	Liver	
MWICE07	Atlantic ocean	Minke whale	63.50° N, 22° 49' W	27.08.2003	Liver	
MWICE08	Atlantic ocean	Minke whale	64.36° N, 22.51° W	30.08.2003	Liver	
MWICE09	Atlantic ocean	Minke whale	64.13° N, 22.39° W	15.09.2003	Liver	
Sample ID	Country/ Location	Species	Sampling position	Sampling date	Sample type	Comments
	Norway					
BUNOR01	Mjøsa: North of Gjøvik	Burbot	60.82° N – 10.67° E	Juni 2003	Liver	
TRNOR02	Mjøsa, central basin	Trout	60.72° N – 10.96° E	Juni-August 2003	Liver	Pooled samples
PINOR03	Mjøsa, North of Gjøvik	Pike	60.82° N – 10.67° E	Mai-June 2003	Liver	Pooled samples
PENOR04	Mjøsa, North of Gjøvik	Perch	60.82° N – 10.67° E	15.06.2003	Liver	
	Sweden					
PESWE01	Helgeån Gummastorpasjön	Perch	56.03° N – 14,15° E		Liver	
PESWE02	Helgeån Araslövssjön	Perch	56.03° N – 14,15° E		Liver	
PESWE03a	Helgeån Hammarsjön Ö repl.	Perch	56.03° N – 14,15° E		Liver	

PESWE03b	Helgeån Hammarsjön Ö repl.	Perch	56.03° N – 14,15° E		Liver	
PESWE04	Helgeån Hammarsjön N	Perch	62.08° N – 14.05° E		Liver	
COSWE05	Hoburgen	Cod	56.54° N - 18.10° E		Liver	
COSWE06	Hoburgen	Cod	56.54° N - 18.10° E		Liver	
COSWE07	Hoburgen	Cod	56.54° N - 18.10° E		Liver	
COSWE08	Hoburgen	Cod	56.54° N - 18.10° E		Liver	
COSWE09	Hoburgen	Cod	56.54° N - 18.10° E		Liver	
COSWE10	Hoburgen	Cod	56.54° N - 18.10° E		Liver	
Sample ID	Country/ Location	Species	Sampling position	Sampling date	Sample type	Comments
COSWE11	Hanöbukten	Cod	55.41° N -14.21° E		Liver	
COSWE12	Hanöbukten	Cod	55.41° N -14.21° E		Liver	
GSSWE13	Sörmland	Grey seal	58.50° N - 18.00° E		Liver	
GSSWE14	Uppland	Grey seal	60.30° N - 18.20° E		Liver	
GSSWE15	Gästrilkand	Grey seal	61.00° N - 17.50° E		Liver	

Seawater, freshwater, Sediment and sludge samples

Sample type	Sample ID	Sampling location	Sample amount analysed	Sampling date/ time	Additional information	Position: Lat. – Long.
Sea water	SWFIN01	Helsinki	497g	21.08.2003, 10.00 h	Brackish sea water, main city area	60.11° N' - 24.59° E
Sea water	SWFIN02	Helsinki	517g	21.08.2003, 13.00 h	Outside Helsinki	60.06° N - 24.45° E
Sea water	SWFIN03	Porvoo	490g	19.08.2003, 11.00 h	Brackish sea water	60.44° N - 25.33° E
Sea water	SWFIN04	Porvoo	503g	19.08.2003, 13.00 h	Brackish sea water	60.15° N - 25.32° E
Rain water	RWFIN05	Helsinki	492g	23.-27.08.2003	Urban + industrial influences	60.27° N - 24.87° E
Rain water	RWFIN06	Helsinki	490g	21.-22.08.2003	Urban + industrial influences	60.27° N - 24.87° E
Landfill effluent water (sub-samples)	LFFIN07a	Espoo	492g	02.09.2003	untreated effluent water	60.12° N - 24.32 ° E
Landfill effluent water (sub-samples)	LFFIN07b	Espoo	496g	02.09.2003	untreated effluent water	60.12° N - 24.32 ° E
Landfill effluent water (sub-samples)	LFFIN07c	Espoo	497g	02.09.2003	untreated effluent water	60.12° N - 24.32 ° E
Sewage effluent water	SEFIN08	Helsinki	504g	29.08.2003	Urban + industrial influences	60.27° N - 24.87° E
Sewage effluent water (sub-samples)	SEFIN09a	Porvoo	513g	29.08.2002	Urban + industrial influences	60.37° N - 25.61° E'
Sewage effluent water (sub-samples)	SEFIN09b	Porvoo	510g	29.08.2003	Urban + industrial influences	60.37° N - 25.61° E'
Sediment (sub-samples)	SDFIN10a	Helsinki	4.8g	21.08.2003	Site 1	60.06° N- 24.45° E

Sample type	Sample ID	Sampling location	Sample amount analysed	Sampling date/ time	Additional information	Position: Lat. – Long.
Sediment (sub-samples)	SDFIN10b	Helsinki	5.0g	21.08.2003	Site 1	60° 06' N- 24° 45' E
Sediment (sub-samples)	SDFIN10c	Helsinki	5.0g	21.08.2003	Site 1	60° 06' N- 24° 45' E
Sediment	SDFIN11	Porvoo	1.6g	19.08.2003, 11.00 h	Site 2	60.14° N - 25.33° E
Sediment	SDFIN12	Porvoo	2.1g	19.08.2003, 13.00 h	Site 1	60.15° N - 25.32° E
Sewage sludge	SSFIN13	Espoo	5.2g	01.09.2003	dewatered	60.11° N - 24.74° E
Sewage sludge (sub-samples)	SSFIN14a	Helsinki	5.3g	29.08.2003	dewatered	60.27° N - 24.87° E
Sewage sludge (sub-samples)	SSFIN14b	Helsinki	5.0g	29.08.2003	dewatered	60.27° N - 24.87° E
Sewage sludge (sub-samples)	SSFIN14c	Helsinki	5.0g	29.08.2003	dewatered	60.27° N - 24.87° E
Sewage sludge	SSFIN15	Porvoo	4.8g	28.08.2003	dewatered	60.37° 'N - 25.61° E
Sewage sludge	SSFIN16	Porvoo	4.3g	19.08.2003	dewatered	60.37° 'N - 25.61° E
Rainwater (sub-samples)	RWSWE01a	Råö	496g	02.10.2003- 11.11.2003		57.39° N - 11.91° E
Rainwater (sub-samples)	RWSWE01b	Råö	511g	02.10.2003- 11.11.2003		57.39° N - 11.91° E
Rainwater	RWSWE02	Råö	519g	11.11.2003- 03.12.2003		57.39° N - 11.91° E
Rainwater	RWSWE03	Råö	515g	03.12.2003- 15.12.2003		57.39° N - 11.91° E
Sediment	SDSWE04	Kristianstad, Arnslovssjön	5.2g	23.09.2003	Accumulation site	56,00° N – 14,15° E

Sample type	Sample ID	Sampling location	Sample amount analysed	Sampling date/ time	Additional information	Position: Lat. – Long.
Sediment	SDSWE05	Kristianstad, Hammarsjön II	4.0g	23.09.2003	Accumulation site	56.00° N – 14.15° E
Sediment	SDSWE06	Kristianstad, Hammarsjön I	4.5g	23.09.2003	Accumulation site	56.00° N – 14.15° E
Sewage sludge	SSSWE07	Kristianstad, Centrala ARV	4.5g	week 39, 2003	collected over the entire week	56.00° N – 14.15° E
Sewage sludge	SSSWE08	Köpinge ARV	3.0g	week 39, 2003	collected over the entire week	55.55° N – 14.15° E
Sewage sludge	SSSWE09	Tollarp ARV	3.7g	week 39, 2003	collected over the entire week	55.55° N – 14.00° E
Lake water	LWNOR01	Lillehammer	504g	01.07.2003	Lake Mjøsa	61.09° N – 10.45° E
Lake water	LWNOR02	Gjøvik	501g	01.07.2003	Lake Mjøsa	61.78° N – 10.71° E
Lake water	LWNOR03	Furnesfjorden	501g	01.07.2003	Lake Mjøsa	61.87° N – 10.93° E
Lake water	LWNOR04a	Hamar	515g	01.07.2003	Lake Mjøsa	60,78° N – 11.06° E
Lake water	LWNOR04b	Hamar	526g	01.07.2003	Lake Mjøsa	60,78° N – 11.06° E
Landfill effluent	LFNOR05a	Spillhaug	481g	29.09.2003, 06.45 h		59,92° N – 11,60° E
Landfill effluent	LFNOR05b	Spillhaug	479g	29.09.2003, 06.45 h		59,92° N – 11,60° E
Landfill effluent	LFNOR06	Støleheia	483g	26.09.2003	Effluent from komposting treatment	58.25° N - 07.90° E
Landfill effluent	LFNOR07	Gålås	528g	02/07/2003		60,85° N – 10,71° E
Landfill effluent	LFNOR08	Røyken	499g	27/08/2003	Coarse waste	59.70° N – 10.47° E
Landfill effluent	LFNOR09	Spillhaug	497g	18/09/2003	effluent from cleaning plant	59,92° N – 11,60° E
Sewage effluent	SENO10	Lillehammer	521g	01.07.2003	at lake Mjøsa	61.09°N – 10.45° E

Sample type	Sample ID	Sampling location	Sample amount analysed	Sampling date/ time	Additional information	Position: Lat. – Long.
Sewage effluent	SENOR11a	Gjøvik	482g	01.07.2003	purified outlet	60,78° N – 10.71° E
Sewage effluent	SENOR11b	Gjøvik	503g	01.07.2003	purified outlet	60.78° N – 10.71° E
Sediment	SDNOR12	Furnes	5.5g	02.09.2003	Lake Mjøsa	60.86° N – 10.92° E
Sediment	SDNOR13	Hamar	5.5g	01.09.2003	Lake Mjøsa	60.78° N – 11.06° E
Sediment	SDNOR14	Gålås	3.5g	02.07.2003	Lake Mjøsa	60.85° N – 10.71° E
Sewage sludge	SSNOR15	Gjøvik	4.9g	week 36, 2003	collected over the entire week	60.78° N – 10.71° E
Sewage sludge	SSNOR16	Lillehammer	5.1g	week 36, 2003	collected over the entire week	61.09° N – 10.45° E
Sea water	SWDAN01	Limfjorden (Ringkøpingamt)	512g	12.11.2003		56° 34,89' N – 08° 29,21' E
Sea water (sub-samples)	SWDAN02a	Odensefjord	503g	24.10.2003	S1: Seden strand	55° 26,34' N - 10° 25,6' E
Sea water (sub-samples)	SWDAN02b	Odensefjord	497g	24.10.2003		55° 26,34' N - 10° 25,6' E
Seawater	SWDAN03	Roskilde	494g	30.10.2003	Station 60	55° 42,78' N - 12° 04,0' E
Sewage	SSDAN04	Bjergmarken, Roskilde	4.9g	09.12.2003		55 °41,56' N – 11° 51,03' E
Sewage	SSDAN05	Stige, Fyns amt	5,2g	24.10.2003		55° 26,4' N - 10° 25,4' E
Sewage	SSDAN05	Stige, Fyns amt	5.2g	24.10.2003		
Sewage	SSDAN06	Lynetten,	4,8 g	28.10.2003		55° 41,0° N - 12° 38,0'

		(Copenhagen)				E
Sea water (sub-samples)	SWICE01a	Gufunes bay	501g	17.10.2003		64.08° N - 21.49° W
Sea water (sub-samples)	SWICE01b	Gufunes bay	524g	17.10.2003		64.08° N - 21.49° W
Sample type	Sample ID	Sampling location	Sample amount analysed	Sampling date/ time	Additional information	Position: Lat. – Long.
Sea water (sub-samples)	SWICE01c	Gufunes bay	484g	17.10.2003		64.08° N - 21.49° W
Sea water (sub-samples)	SWICE01d	Gufunes bay	517g	17.10.2003		64.08° N - 21.49° W
Sediment (sub-samples)	SDICE02a	Gufunes bay	5.3g	17.10.2004		64.08° N - 21.49° W
Sediment (sub-samples)	SDICE02b	Gufunes bay	5.1g	17.10.2005		64.08° N - 21.49° W
Sediment (sub-samples)	SDICE02c	Gufunes bay	5.4g	17.10.2006		64.08° N - 21.49° W
Sediment (sub-samples)	SDICE02d	Gufunes bay	5.0g	17.10.2007		64.08° N - 21.49° W
Sediment (sub-samples)	SDICE02e	Gufunes bay	4.9g	17.10.2008		64.08° N - 21.49° W
Sewage (sub-samples)	SSICE03a	Klettagardar	4.5g	16.09.2003, 10.00 h		64.09° N - 21.51° W
Sewage (sub-samples)	SSICE03b	Klettagardar	5.6g	16.09.2003, 10.00 h		64.09° N - 21.51° W
Sewage (sub-samples)	SSICE04a	Ananaust	5.1g	16.09.2003, 10.15 h		64.09° N - 21.56° W
Sewage (sub-samples)	SSICE04b	Ananaust	4.8g	16.09.2003, 10.15 h		64.09° N - 21.56° W
Sea water	SWFAR01	Torshavn, Utfyri skipasmiduna	531g	21.08.2003		62.00° N – 06.46° W
Sea water	SWFAR02	Torshavn, Utfyri skipasmiduna	362g	21.08.2003		62.00° N – 06.46° W
Sea water	SWFAR03	Torshavn, Utfyri skipasmiduna	520g	21.08.2003		62.00° N – 06.46° W
Sewage effluent	SEFAR04	Yviri vid Strond	512g	15.10.2003, 11.00h		62.00° N – 06.46° W

Sediment	SDFAR05	Landingarplassi i Vagsbotni	5.0g	21.08.2003		62.00° N – 06.46° W
Sediment	SDFAR06	Torshavn, Utfyri skipasmiduna	5.2g	21.08.2003		62.00° N – 06.46° W
Sample type	Sample ID	Sampling location	Sample amount analysed	Sampling date/ time	Additional information	Position: Lat. – Long.
Sediment	SDFAR07	Fjordakanningar	4.8g	02.09.2003		62.00° N – 06.46° W
Sewage	SSFAR08	Torshavn, Sersjandvikin	5.1g	19.08.2003		62.00° N – 06.46° W

Appendix 2: Sampling manual

Nordic cooperation on screening of perfluorinated substances

Sampling and sample handling manual

Prepared by

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1. Introduction and objectives of the study

These guidelines concern the sampling, sample handling and shipping of water, sediment, sludge, fish liver and seal liver for trace analysis of organic contaminants. They are suitable for perfluoroalkylated substances (PFAS) such as perfluoroalkylated acids, perfluoroalkylated sulfonates and their derivatives. The institutes performing the chemical trace analysis do not take any responsibility for representativeness of samples or contamination problems during sampling, sample storage and shipping to the respective laboratories. These guidelines should be followed as precisely as possible and any deviations from the guidelines must be reported in the sampling protocols.

The purpose of this study is a first quantitative screening of perfluorooctyl sulfonate (PFOS), perfluorohexyl sulfonate (PFHS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorooctyl sulfonamide (PFOSA) (Figure 1) contaminants in water (freshwater, seawater, effluents and rainwater), sediment, sludge, fish liver and seal liver from the Nordic countries (i.e. Denmark, Sweden, Finland, Norway, Iceland and Faeroe Islands). This will allow to assess the existing level of contamination (spatial distribution monitoring) possibly indicating regional differences. The spatial distribution monitoring programme will enable to determine the representativeness of the monitoring sites with regard to spatial variability in contaminant concentrations and will give information about the ubiquity of PFAS distribution in the Nordic countries.

2. Perfluoroalkylated substances (PFAS)

Perfluoroalkylated substances (PFAS) have been manufactured for more than 50 years. They are used for a large number of industrial applications such as protection of carpets, textiles, leather products as well as in the production of fire-fighting foams, herbicides and insecticides, lubricants, paints, adhesives and acid etching solutions (Kannan et al., 2001; Laikhtman and Rohrer, 1998; RIKZ 2002). About 3250 tons of PFOS-based chemicals were produced by the 3M company (USA) in 2000. Though the manufacturer voluntarily has phased out most of this production volume, similar compounds with long perfluorinated chains, continue to be produced for comparable applications. Compared to hydrocarbons, perfluorinated compounds display exceptional physical properties:

- I) They are immiscible with most other liquids.
- II) Fluoro-organics are non-flammable and non-corrosive.
- III) Perfluorinated compounds have a very high insulation resistance.

The exceptional properties making man-made PFAS so attractive for industrial applications also impose a risk for the environment and ecological systems. The strength of the carbon-fluorine bond makes these compounds very persistent towards degradation. Recent publications indicated that PFAS and especially PFOS are widely distributed over the northern hemisphere, including remote areas such as the Arctic (Giesy and Kannan, 2001; Hansen et al., 2002; Kannan et al., 2001).

3. General sampling strategy

Sampling should be performed in accordance with general sampling strategies for chemical trace analysis. In case of questions about the practicability of procedures or

usability of special material and equipment NILU must be contacted (Roland Kallenborn, phone: +47 77 75 03 86, e-mail: roland.kallenborn@nilu.no; Urs Berger, phone: +47 77 75 03 85, e-mail: urs.berger@nilu.no). The sampling strategy should take into account the specific objectives of the monitoring programme, including the quantitative objectives. Natural variability within the samples should be reduced by an appropriate sampling design. The sampling strategy is an intrinsic component of the data, and may limit their use and interpretation.

3.1 Sampling site selection / representative sampling

Nothing is known about the homogeneity of the distribution of PFAS in the Nordic environment, since no comprehensive screening has been performed in these countries yet. Therefore, it is difficult to give recommendations about the choice of representative sampling sites. Only a relatively high number of samples taken from as many different places as possible can overcome this challenge and will add to our knowledge about distribution patterns of PFAS in the environment. The detailed sampling site selection lies within the responsibility of the sampling institutes. Sampling sites must be indicated on the sampling protocols as accurate as possible (preferably with latitude/longitude data).

3.2 Homogeneity of samples

Primary sample amounts should be as large as feasible and homogenised on site to yield sub-samples of at least the required volume for analysis (see Chapter 5). Larger sample amounts are preferred (and mandatory for some samples of each matrix) to perform laboratory replicate studies. These as well as field replicate studies (see Chapter 7.2) are an integrated part of the quality assurance programme of the planned study.

4. Sampling equipment / risk of contamination

All equipment, materials and containers that come in contact with the samples must be rinsed with high-purity water and methanol before use. Fluoropolymeric materials pose a significant risk of contamination with PFAS, especially for PFOA. Equipment made of or containing fluoropolymers such as PTFE ('Teflon') or Viton rubber (sealing rings etc.) must not be in direct contact with the samples and should completely be avoided when handling, storing or shipping samples. The target analytes are surface-active compounds. Furthermore, they display very poor solubility both in water and organic solvents. Currently there is no consensus among experts as to whether PFAS adsorb irreversibly to glass surfaces or not. Glass containers should therefore be avoided and replaced by polyethylene (not PTFE!). NILU must be contacted in case of questions about the usability of certain materials in contact with samples (Roland Kallenborn, phone: +4777750386, e-mail: roland.kallenborn@nilu.no; Urs Berger, phone: +4 77750385, e-mail: urs.berger@nilu.no). Samples should be collected in the same containers in which they are cooled/frozen, stored and shipped to the analysing laboratories to avoid losses due to adsorption and change of vessels.

5. Field sampling / required sample amounts

5.1 Water

General water sampling strategies for chemical trace analysis should be followed. Sample amounts of 500 – 1000 ml are required to guarantee good detection limits. The sampling depth in lakes and the sea is crucial. Due to their surface-active

properties, PFAS might form a layer on water surfaces or preferably bind to particles. Therefore, it is important to state if samples were collected on the water surface, several meters from surface and bottom or close to the bottom. Water samples should be kept cool (but not frozen) and in darkness in order to avoid degradation of analytes.

5.2 Sediment

General sediment sampling strategies for chemical trace analysis should be followed. PFAS are expected to be distributed unevenly in sediments. Therefore, as much sediment as feasible should be collected over a large area and thoroughly blended before an aliquot is taken. A homogenous aliquot of approx. 100 g should be sent cooled to the analysing laboratory.

5.3 Sludge

PFAS are expected to be distributed unevenly in sludge. Therefore, as much sludge as feasible should be collected and thoroughly mixed before an aliquot is taken. A homogenous aliquot of approx. 100 g should be sent cooled to the analysing laboratory.

5.4 Fish and seal liver

Fish and seals should be dissected immediately after collection and liver samples should be removed and frozen. The fish liver samples should be pooled samples prepared from at least 10 individuals of similar size (weight and length). The weight of the total pooled sample should in any case exceed 5 g. Fish caught during the non-breeding season is preferred over fish from the breeding period. The seal liver samples should preferably be prepared as pooled samples from several individuals if this is feasible, since seals have shown a large variability in PFAS concentrations. A minimum of 5 g seal liver sample is requested for analysis. All biological samples must be frozen immediately after catch and preparation.

6. Storage and shipping of samples

The target analytes are generally very stable towards degradation. Therefore, the time between sampling and analysis is not expected to be crucial in this study. However, little is known about enzymatic degradation, therefore all samples should be kept cold and especially biological samples should be frozen (-18 °C) immediately after collection.

All samples must be collected, stored and shipped in clean, fluoropolymer-free containers, preferably polyethylene vessels should be used (see Chapter 4). Containers should not be changed from the moment of sampling or preparation to the arrival at the analytical laboratories.

6.1 Water, sediment and sludge samples

Water, sediment and sludge samples must be cooled (< 4 °C) after collection. Water samples should not be frozen. All samples should be stored and shipped at low temperatures and in darkness. They must be clearly and unmistakably marked with a sample name and sent together with their sampling protocols by an express delivery service (TNT, DHL, EMS or similar) to the following address:

Norwegian Institute for Air Research (NILU) , Instituttveien 18 ,NO-2027 Kjeller
Norway

To assure that samples reach the destination within short time (usually within the same day), they should be sent early in the morning and not on a Friday (preferably Monday to Wednesday). When sending the samples a notice including the airway bill number (AWB) of the package must be sent to NILU to the following fax number: ++47 6389 8050 addressed to Arve Bjerke and Ellen Katrin Enge. The delivery should be marked with “samples NMR-PFAS study” to avoid unnecessary delay during the registration procedure at the analysing institute.

6.2 Fish and seal liver samples

Biological samples (fish and seal liver) must be kept frozen during storage (< -18 °C). During transportation, an insulated box should be used to ensure that the temperature does not exceed thawing temperature (< 0 °C). All samples must be clearly and unmistakably marked with a sample name and sent together with their sampling protocols by an express delivery service (TNT, DHL, EMS or similar) to the following address:

Ulf Järnberg : Institute of Applied Environmental Research (ITM) , Stockholm University SE-106 91 Stockholm , Sweden

To assure that samples reach the destination within short time (usually within the same day), they should be sent early in the morning and not on a Friday (preferably Monday to Wednesday). When sending the samples a notice including the airway bill number (AWB) of the package must be sent to ITM to the following fax number: ++46 8 674 7637 addressed to Ulf Järnberg. The delivery should be marked with “samples NMR-PFAS study” to avoid unnecessary delay during the registration procedure at the analysing institute.

7. Sampling quality assurance

Quality assurance is a management scheme required to ensure the consistent delivery of quality controlled data. To minimise the risk of contamination or the loss of analytes (and so to avoid the generation of false data) all procedures including sampling, storage and shipping must be evaluated and controlled. This is partly done by analysing field blanks and replicates. Furthermore, sample replicates allow to assess the precision of the complete analytical method. Field blank and replicate samples will be analysed and reported in addition to the 100 samples without additional costs. The steering group of the Nordic Chemicals Group decides where blank and duplicate samples will be taken and is responsible for the distribution of these tasks (see also 7.1 and 7.2).

7.1 Field blanks

Field blanks must be taken parallel to the samples for all matrices at five different sampling sites. For water, sediment and sludge the blank surrogate matrix must be treated in exactly the same way as the real samples from the moment of sampling in the field. As surrogate matrix for water analysis high-purity water should be used, for sediment analysis high-purity silica should be employed. A slurry mixture of high-purity water and silica with similar water content as the sludge samples (i.e. only silica if desiccated sludge is sampled) should be used as blank surrogate matrix for sludge analysis. For fish and seal liver the blank surrogate matrix must be treated in exactly the same way as the real samples from the moment of dissection of the animal and isolation of the liver. Triolin (= 1,2,3-tri-(cis-9-octadecenoyl) glycerol) should be used as liver surrogate matrix for field blank experiments.

7.2 Field replicates

Additionally to the blank and real samples, duplicate samples must be taken for all matrices at a minimum of three different sampling sites (preferably three different countries). These samples will be used to assess the repeatability and representativeness of the sampling procedures. The duplicates must in each case be two independent samples simultaneously taken from the same site and not two aliquots from the same primary sample homogenate. It has to be indicated on the sampling protocols which samples belong together as field duplicates.

8. References

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Annex 1: Sampling protocol for sea-/river-/lake-water samples

Sample name:	Sample material:
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<i>Sampling</i>		Comments
Date and time:		
Site (description, preferably with latitude/longitude data):		
Approx. sampling depth (distance from surface):		
Approx. distance from bottom/shore:		
Sample volume:		
Water temperature:		
Transport temperature after sampling:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by NILU

Annex 2: Sampling protocol for effluent water samples

Sample name:	Sample material:
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<i>Sampling</i>		Comments
Date and time:		
Site (description, preferably with latitude/longitude data):		
Origin of effluent water (industry, households, hospital etc.):		
Effluent treatment before sampling (biological, filtration etc.):		
Sample volume:		
Water temperature:		
Transport temperature after sampling:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by NILU

Annex 3: Sampling protocol for rainwater samples

Sample name:	Sample material:
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<i>Sampling</i>		Comments
Date (period of rainwater collection):		
Site (description, preferably with latitude/longitude data):		
Rainwater collection device:		
Sample volume:		
Transport temperature after sampling:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by NILU

Annex 4: Sampling protocol for sediment samples

Sample name:	Sample material:
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<i>Sampling</i>		Comments
Date and time:		
Site (description, water depth, latitude/longitude):		
Water current conditions at sampling site:		
Sample layer depth (digging depth):		
Total primary sample amount:		
Homogenous aliquot amount:		
Transport temperature after sampling:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by NILU

Annex 5: Sampling protocol for sludge samples

Sample name:	Sample material:
--------------	------------------

<i>Sampling</i>		Comments
Date and time:		
Site (description, preferably with latitude/longitude data):		
Total primary sample amount:		
Homogenous aliquot amount:		
Transport temperature after sampling:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by NILU

Annex 6: Sampling protocol for fish liver samples

Sample name:	Sample material:
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<i>Sampling</i>		Comments
Date:		
Site (description, preferably with latitude/longitude data):		
Number and size of individuals used for the pooled fish liver sample:		
Age and sex of the individuals (if possible):		
Physiological condition of individuals when caught:		
Storage temp. after sampling:		
Date and site of dissection:		
Total liver sample amount:		
Special observations (e.g. thawing and re-freezing for dissection):		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by ITM

Annex 7: Sampling protocol for seal liver samples

Sample name:	Sample material:
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<i>Sampling</i>		Comments
Date:		
Site (description, preferably with latitude/longitude data):		
Number of individuals used for the pooled liver sample:		
Age and sex of the individuals (if possible):		
Cause of death:		
Storage temp. after sampling:		
Date and site of dissection:		
Exact tissue location of prepared sample, in case only a part of tissue was prepared:		
Total liver sample amount:		
Special observations / deviations from sampling procedure:		

<i>Storage</i>		Comments
Storage time:		
Storage temperature:		
Special observations:		

<i>Shipping</i>		Comments
Date sample sent:		
Shipping temperature:		
Date sample received*:		
Condition upon receipt*:		
Special observations*:		

* To be filled in by ITM

Nordic cooperation on screening of perfluorinated substances

Supplementary information:

Sampling and sample handling manual from 04.07.2003

Sludge samples:

Recent literature suggested that PFOS and PFOA could be anaerobically biodegraded in activated sludge (Schröder, 2003). This problem might occur in wet sludge samples kept at ambient or higher temperatures. To avoid the possibility of degradation of analytes the following recommendations should be followed when sampling, storing and shipping sludge samples: • Drained sludge samples (dry samples) are preferred over wet samples. Analysing only dry sludge would also guarantee the comparability between sludge samples from different countries. • Samples should be frozen immediately after sampling and kept frozen during storage and shipping. • If dry or drained sludge is not available, wet sludge samples with high water content can be deactivated by adding 0.5 % (weight) of formic acid (HCOOH). This treatment must be clearly indicated on the sampling protocol. These samples should be cooled but not frozen (compare also water samples).

Reference: *Schröder H.F. (2003) J. Chrom. A (2003), 1020: 131-151*

Appendix 3: Concentration list

Sample no	Type	Sediment-sludge						SUM
		PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFNA	
SDFIN10a	Sediment (sub-samples)	<LOQ	45	892	138	<LOQ	72	1147
SDFIN10b	Sediment (sub-samples)	<LOQ	47	861	159	<LOQ	64	1131
SDFIN10c	Sediment (sub-samples)	<LOQ	44	1014	135	<LOQ	46	1238
SDFIN11	Sediment	<LOQ	26	222	<LOQ	<LOQ	<LOQ	247
SDFIN12	Sediment	<LOQ	41	290	46	<LOQ	<LOQ	377
SSFIN13	Sewage sludge	<LOQ	91	158	1152	754	171	2326
SSFIN14a	Sewage sludge (sub-samples)	<LOQ	46	846	792	546	<LOQ	2230
SSFIN14b	Sewage sludge (sub-samples)	<LOQ	38	663	932	580	<LOQ	2213
SSFIN14c	Sewage sludge (sub-samples)	<LOQ	51	925	838	707	<LOQ	2521
SSFIN15	Sewage sludge	<LOQ	<LOQ	327	<LOQ	602	119	1048
SSFIN16	Sewage sludge	<LOQ	<LOQ	55	<LOD	<LOQ	95	150
SSSWE07	Sewage sludge	<LOQ	17	167	<LOQ	<LOQ	<LOQ	184
SSSWE08	Sewage sludge	<LOQ	<LOQ	274	<LOQ	250	<LOQ	524
SSSWE09	Sewage sludge	94	46	2644	<LOQ	779	229	3793
SDSWE04	Sediment	<LOQ	<LOQ	69	<LOQ	<LOQ	<LOQ	69
SDSWE05	Sediment	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
SDSWE06	Sediment	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Sample no.	Type	PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFNA	SUM
SDNOR12	Sediment	<LOQ			143		32	175
SDNOR13	Sediment	<LOQ	8	394	80	278	88	848
SDNOR14	Sediment	<LOQ	30	217	102	312	<LOQ	661
SSNOR15	Sewage sludge	<LOQ	25	1023	126	377	103	1654
SSNOR16	Sewage sludge	<LOQ	18	449	<LOQ	391	190	1048
SSDAN04	Sewage	<LOQ	14	1041	<LOQ	392	87	1533
SSDAN05	Sewage	20	13	316	<LOQ	306	<LOQ	655
SSDAN06	Sewage	<LOQ	9	416	<LOQ	675	232	1333
SSICE02a	Sediment (sub-sample)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
SSICE02b	Sediment (sub-sample)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
SSICE02c	Sediment (sub-sample)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
SSICE02d	Sediment (sub-sample)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
SSICE03a	Sewage (sub-samples)	<LOQ	19	160	<LOQ	<LOQ	<LOQ	179
SSICE03b	Sewage (sub-samples)	<LOQ	15	220	<LOQ	<LOQ	<LOQ	234
SSICE04a	Sewage (sub-samples)	<LOQ	15	69	<LOQ	298	<LOQ	381
SSICE04b	Sewage (sub-samples)	<LOQ	12	79	<LOQ	251	<LOQ	342
SDFAR05	Sediment	<LOQ	<LOQ	111	<LOQ	<LOQ	<LOQ	111
SDFAR06	Sediment	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
SDFAR07	Sediment	<LOQ	<LOQ	54	93	<LOQ	31	178
SSFAR08	Sewage	<LOQ	15	241	346	1075	<LOQ	1677

Aqueous samples

[ng/L]

Sample no.	Type	PFOSA	PFBS	PFHxS	PFOS	PFHxA	PFOA	PFNA	SUM
SWFIN01	Sea water	<LOQ	0.93	4.39	21.7	4.35	5.19	0.84	37
SWFIN02	Sea water	<LOQ	0.12	0.24	0.86	0.77	3.97	0.18	6
SWFIN03	Sea water	<LOQ	<LOQ	0.32	1.10	0.61	4.24	0.25	6
SWFIN04	Sea water	0.07	<LOQ	0.25	1.11	0.94	5.60	0.24	8
RWFIN05	Rain water	0.07	<LOQ	<LOQ	0.32	1.90	13.1	0.74	16
RWFIN06	Rain water	0.10	<LOQ	<LOQ	0.24	1.97	8.23	0.69	11
LFFIN07a	Landfill effluent water (sub-samples)	0.71	<LOQ	158	33.5	139	399	55.0	785
LFFIN07b	Landfill effluent water (sub-samples)	0.64	68.0	112	30.2	165	300	61.3	737
LFFIN07c	Landfill effluent water (sub-samples)	0.51	61.3	159	34.7	152	306	51.3	764
SEFIN08	Sewage effluent water	<LOQ	3.01	3.71	62.6	8.08	20.9	7.09	105
SEFIN09a	Sewage effluent water (sub-samples)	0.48	2.61	3.40	8.83	10.4	19.9	2.42	48
SEFIN09b	Sewage effluent water (sub-samples)	0.46	3.09	4.66	10.0	13.5	22.8	2.51	57
RWSWE01a	Rainwater (sub-samples)	<LOQ	<LOQ	0.39	2.54	1.10	15.3	1.34	21
RWSWE01b	Rainwater (sub-samples)	<LOQ	<LOQ	0.36	2.39	1.18	16.8	1.26	22
RWSWE02	Rainwater	0.07	<LOQ	0.15	0.83	0.81	10.7	0.63	13
RWSWE03	Rainwater	0.14	<LOQ	0.59	2.97	1.14	15.1	1.41	21

Sample no.	Type	PFOSA	PFBS	PFHxS	PFOS	PFHxA	PFOA	PFNA	SUM
LWNOR01	Lake water	<LOQ	<LOQ	<LOQ	<LOQ	1.47	7.77	0.24	9
LWNOR02	Lake water	<LOQ	<LOQ	<LOQ	<LOQ	1.68	8.23	0.23	10
LWNOR03	Lake water	<LOQ	<LOQ	0.10	0.43	1.27	8.21	0.12	10
LWNOR04a	Lake water	<LOQ	<LOQ	0.11	0.48	0.76	4.82	0.30	6
LWNOR04b	Lake water	<LOQ	<LOQ	0.08	0.40	0.91	5.01	0.30	7
LFNOR05a	Landfill effluent	0.06	12.7	11.6	33.0	47.9	91.3	4.16	201
LFNOR05b	Landfill effluent	0.09	12.2	13.1	33.0	43.7	93.5	3.50	199
LFNOR06	Landfill effluent	3.28	112	70.9	108	697	516	30.9	1537
LFNOR07	Landfill effluent	<LOQ	5.64	62.6	56.4	26.4	293	61.5	505
LFNOR08	Landfill effluent	3.04	98.9	143	187	311	367	51.9	1162
LFNOR09	Landfill effluent	<LOQ	15.5	30.1	75.1	137	168	4.70	430
SENR010	Sewage effluent	<LOQ	2.60	1.80	6.89	14.5	20.2	3.55	49
SENR011a	Sewage effluent	<LOQ	1.00	2.30	18.3	14.4	22.2	1.25	59
SENR011b	Sewage effluent	<LOQ	1.32	2.27	16.7	13.9	22.5	1.34	58
SWDAN01	Sea water	<LOQ	0.71	0.17	0.55	1.12	8.48	0.19	11
SWDAN02a	Sea water (sub-samples)	<LOQ	1.09	0.30	1.50	2.63	7.67	0.42	13
SWDAN02b	Sea water (sub-samples)	<LOQ	1.08	0.33	1.57	2.95	7.82	0.39	14
SWDAN03	Sea water	<LOQ	0.30	0.53	0.72	1.95	6.20	0.28	10
SWICE01a	Sea water (sub-samples)	<LOQ	0.05	0.08	<LOQ	0.65	4.02	0.31	5
SWICE01b	Sea water (sub-samples)	<LOQ	0.08	<LOQ	<LOQ	0.63	3.53	0.21	4
SWICE01c	Sea water (sub-samples)	<LOQ	0.06	0.08	<LOQ	0.65	3.78	0.20	5

SWICE01d	Sea water (sub-samples)	<LOQ	0.06	<LOQ	<LOQ	0.73	3.83	0.21	5
Sample no.	Type	PFOSA	PFBS	PFHxS	PFOS	PFHxA	PFOA	PFNA	SUM
SWFAR01	Sea water	<LOQ	0.06	0.08	0.31	0.59	3.62	<LOQ	5
SWFAR02	Sea water	<LOQ	0.11	0.24	1.18	1.85	7.24	<LOQ	11
SWFAR03	Sea water	<LOQ	0.05	0.08	0.52	0.81	4.67	<LOQ	6
SEFAR04	Sewage effluent	<LOQ	0.20	0.26	1.22	1.61	1.26	0.44	5

Biota [ng/g ww]

Sample	Type	PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFHpA	PFNA	PFDS	SUM
PIFIN01	Pike	141	3.4	551	<LOD	0.89	<LOD	4.3	5.7	707
PIFIN02	Pike	62	2.1	440	<LOD	<LOD	<LOD	6.1	9.0	519
PIFIN03	Pike	61	2.3	204	<LOD	<LOD	0.41	2.2	2.4	273
PIFIN04	Pike	70	1.3	211	<LOD	<LOD	<LOD	2.1	5.8	291
PIFIN05	Pike	115	1.8	240	<LOD	<LOD	<LOD	3.0	4.1	364
PIFIN06	Pike	139	1.4	263	<LOD	<LOD	<LOD	2.0	4.3	410
PIFIN07	Pike	92	1.4	253	<LOD	1.42	<LOD	1.5	5.1	354
PIFIN08	Pike	48	1.3	492	<LOD	<LOD	<LOD	1.9	6.2	549
PESWE01	Perch	0.60	1.4	172	1.08	<LOD	<LOD	0.23	<LOD	175
PESWE02	Perch	1.02	<LOD	172	0.90	<LOD	<LOD	0.63	<LOD	174

PESWE03a	Perch	5.5	<LOD	427	0.66	<LOD	<LOD	1.5	3.6	438
PESWE03b	Perch	6.1	<LOD	432	0.62	<LOD	<LOD	1.3	3.2	443
Sample	Type	PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFHpA	PFNA	PFDS	SUM
PESWE04	Perch	2.17	0.79	169	0.66		0.30	6.3	<LOD	179
COSWE05	Cod	0.85	<LOD	9.1	<LOD	<LOD	<LOD	0.53	<LOD	10
COSWE06	Cod	0.41	<LOD	8.1	<LOD	<LOD	<LOD	0.55	<LOD	9
COSWE07	Cod	0.75	<LOD	8.7	<LOD	<LOD	<LOD	0.47	<LOD	10
COSWE08	Cod	1.16	<LOD	20	<LOD	<LOD	<LOD	0.86	1.26	23
COSWE09	Cod	0.41	<LOD	6.4	<LOD	<LOD	<LOD	0.94	<LOD	8
COSWE10	Cod	0.48	<LOD	6.4	<LOD	<LOD	<LOD	0.55	<LOD	7
COSWE11	Cod	6.1	<LOD	23	<LOD	<LOD	<LOD	9.0	<LOD	38
COSWE12	Cod	3.9	<LOD	62	<LOD	<LOD	<LOD	18	<LOD	83
GSSWE13	Grey seal	15	2.0	537	0.62	0.6	<LOD	29	11	594
GSSWE14	Grey seal	7.5	0.67	422	0.48	1.4	<LOD	36	13	481
GSSWE15	Grey seal	17	1.1	331	0.62	1.8	<LOD	35	9	395
BUNOR01	Burbot	14	<LOD	8.1	<LOQ	<LOD	<LOD	<LOD	1.9	24
TRNOR02	Trout	35	<LOD	51	0.86	<LOD	<LOD	2.7	5.6	95
PINOR03	Pike	60	<LOD	24	1.1	<LOD	<LOD	1.1	4.2	90
PENOR04	Perch	11	<LOD	120	1.49	<LOD	0.57	4.5	4.0	141
FLDAN01	Flounder	3.3	<LOD	20	0.74	<LOD	<LOD	0.78	<LOD	25
FLDAN02	Flounder	3.8	<LOD	19	<LOD	<LOD	<LOD	1.3	<LOD	25
FLDAN03	Flounder	14.6	<LOD	21	<LOD	<LOD	<LOD	0.95	<LOD	36
FLDAN04	Flounder	4.7	<LOD	18	<LOD	<LOD	<LOD	0.92	<LOD	24
EPDAN05	Eelpout	7.5	<LOD	60	0.90	1.02	<LOD	2.1	2.6	74

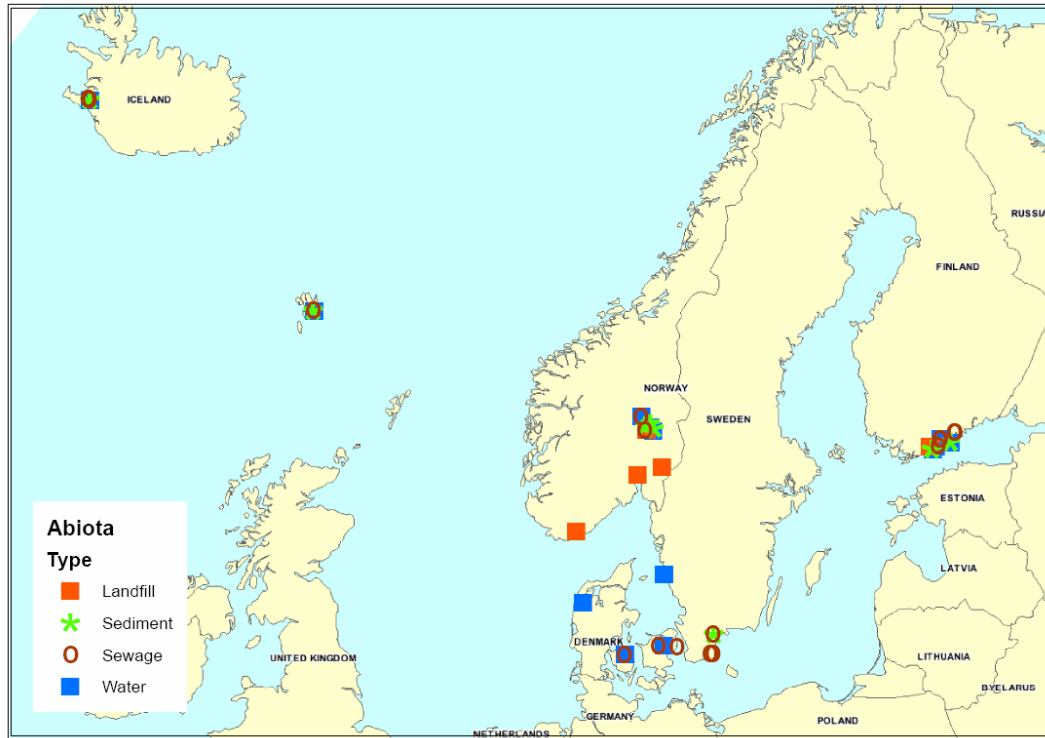
HEDAN06	Herring	19.2	0.42	15	0.66	5.4	<LOD	1.2	<LOD	42
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Sample	Type	PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFHpA	PFNA	PFDS	SUM
HSDAN07	Harbour seal	4.1	10	772	1.4	5.0	0.4	11.5	<LOD	805
HSDAN08	Harbour seal	0.93	8.0	762	1.0	5.6	<LOD	11.1	<LOD	789
HSDAN09	Harbour seal	55	5.3	892	3.5	0.3	<LOD	2.5	2.4	961
HSDAN10	Harbour seal	46	10	977	3.2	1.3	<LOD	9.0	13	1060
HSDAN11	Harbour seal	11	5.0	565	1.2	1.1	0.5	8.1	10	602
LDICE01a	Long rough dab	<LOD	<LOD	13	4.2	<LOD	<LOD	1.26	11.6	31
LDICE01b	Long rough dab	<LOD	<LOD	12	5.9	<LOD	0.56	1.26	6.8	26
LDICE01c	Long rough dab	<LOD	<LOD	28	9.6	<LOD	1.8	1.44	6.8	48
LDICE02	Long rough dab	<LOD	<LOD	19	<LOD	<LOD	<LOD	<LOD	10.7	30
SCICE03	Sculpin	30	<LOD	19	11	<LOD	<LOD	<LOD	6.8	67
DAICE04	Dab	<LOD	<LOD	17	<LOD	<LOD	<LOD	<LOD	9.7	27
MWICE05	Minke whale	13	<LOD	19	0.94	<LOD	<LOD	1.1	3	37
MWICE06	Minke whale	12	<LOD	28	0.90	<LOD	0.23	1.6	4	47
MWICE07	Minke whale	7.2	1.1	21	0.94	<LOD	<LOD	1.1	4	35
MWICE08	Minke whale	19	<LOD	71	0.68	<LOD	<LOD	2.3	5	98
MWICE09	Minke whale	14	<LOD	67	0.99	<LOD	<LOD	2.4	5	89
SCFAR01	Sculpin	3.4	<LOD	2.0	<LOD	<LOD	<LOD	<LOD	<LOD	5
SCFAR02	Sculpin	5.8	<LOD	2.5	<LOD	<LOD	<LOD	<LOD	<LOD	8
DAFAR03	Dab	0.21	<LOD	2.1	<LOD	<LOD	<LOD	<LOD	<LOD	2

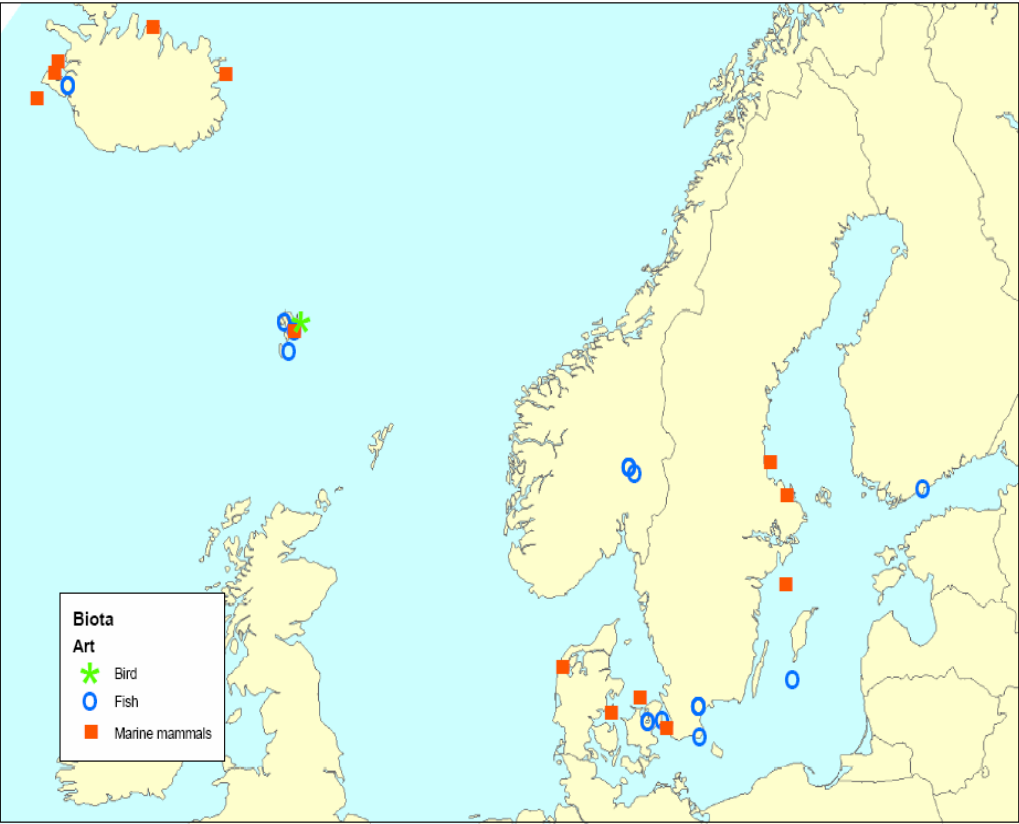
DAFAR04	Dab	0.36	<LOD	1.3	<LOD	<LOD	<LOD	<LOD	<LOD	2
COFAR05	Cod	4.5	<LOD	0.85	<LOD	<LOD	<LOD	<LOD	<LOD	5
ACFAR06a	Arctic char	4.2	<LOD	4.8	<LOD	<LOD	<LOD	<LOD	<LOD	9
Sample	Type	PFOSA	PFHxS	PFOS	PFHxA	PFOA	PFHpA	PFNA	PFDS	SUM
ACFAR06b	Arctic char	5.7	<LOD	5.3	<LOD	<LOD	<LOD	<LOD	<LOD	11
ACFAR07	Arctic char	3.6	<LOD	4.7	<LOD	<LOD	<LOD	<LOD	<LOD	8
PWFAR08	Pilot whale	218	0.66	88	0.53	0.45	<LOQ	5.5	11	324
PWFAR09	Pilot whale	364	0.39	136	1.00	0.35	<LOQ	5.4	12	519
PWFAR10	Pilot whale	184	0.52	256	0.89	1.7	<LOQ	17	27	486
PWFAR11	Pilot whale	172	1.0	336	0.84	1.3	<LOQ	20	30	560
FUFAR12	Fulmar pool1	<LOD	<LOD	31	<LOD	<LOD	0.4	1	<LOD	33
FUFAR13	Fulmar pool2	0.46	<LOD	37.5	<LOD	<LOD	0.45	1.3	<LOD	40

Appendix 4: Sampling locations

Sample locations: Abiota



Sample locations: Biota



Appendix 5: Abbreviations list

Abbreviation	Explanation
AHTN	Polycyclic musk, Tonalide
ASE	Accelerated Solvent extraction
ECF	Electrochemical fluorination
EPA	U.S. Environmental Protection Agency
DEFRA	UK Department for Environment; Food and Rural Affairs
EC ₅₀	Concentration of an agonist, which produces 50% of the maximum possible response for that agonist in a test population.
ESI	Electrospray ionisation
FTOH	Fluoro-telomer alcohols
HCB	Hexachlorobenzene
HCH	hexachlorocyclohexane
HHCB	Polycyclic musk, Galaxolide
HPLC	High performance liquid chromatography
ITM	Institute of Applied Environmental Research (Stockholm University, Sweden)
ISTD	Internal standard
K _{ow}	Octanol-water partitioning coefficient
LC ₅₀	Lethal concentration for 50 % of the test population
LOD	Limit of detection
LOEC	Lowest observed effect concentration
LOQ	Limit of quantification
LLOQ	Lowest limit of quantification
NDFDA	nonadecafluoro- <i>n</i> -decanoic acid
NILU	Norwegian Institute for Air Research
NIVA	Norwegian Institute for Water Research
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
NOEL	No observed effect limit
NTEM	Nordic Terrestrial Monitoring Group
PFAS	Perfluorinated alkylated substances
PBDE	Polybrominated diphenyl ethers
PCDD/F	Chlorinated- <i>p</i> -dibenzodioxins and furans
peq	person equivalent (contribution to sewage)

Abbreviation	Explanation
PET	Polyethylene
PP	Polypropylene
RSTD	Recovery standard (volume standard)
SFT	Statens forurensningstilsynet (Norwegian State Pollution Control Authorities)
SRM	Selected reaction monitoring
STP	Sewage treatment plant
TOF	Time-of-flight mass spectrometry
UNEP	United Nations Environmental Programme