Perfluorinated Alkylated Substances (PFAS) in the European Nordic Environment

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Introduction

Perfluorinated alkylated substances (PFAS) have been industrially produced for several decades and are applied as stain and water repellents for surface treatment of textiles, carpets, leather and paper products. Perfluorooctane sulfonate (PFOS), a degradation product of several PFAS, has recently gained considerable attention because of its ubiquitous distribution in the environment[1-4] and its presence in human blood plasma[5,6]. Though most of the production volume of PFOS-based chemicals has been voluntarily phased out by the manufacturers, similar compounds with perfluorinated chains, including perfluorinated carboxylic acids, continue to be employed for comparable applications.

A first screening project on the distribution of PFAS in the environment of five Nordic countries was supported and financed by the Nordic Council of Ministers through the Chemicals Group and the Environmental Monitoring Group and national institutions. The aim of the study was to assess the levels and distribution of PFAS in the Nordic environment and to trace differences in contaminant concentrations and patterns between different countries and types of matrices.

Materials and Methods

Chemicals. Perfluorobutane sulfonate (PFBS, tetrabutylammonium salt; Fluka), perfluorohexane sulfonate (PFHxS, potassium salt; Interchim), perfluorooctane sulfonate (PFOS, potassium salt; Fluka), perfluorodecane sulfonate (PFDcS, ammonium salt; Sigma-Aldrich), perfluorohexanoic acid (PFHxA; ABCR), perfluoroheptanoic acid (PFHpA; Sigma-Aldrich), perfluorooctanoic acid (PFOA; Fluka), perfluorononanoic acid (PFNA; Sigma-Aldrich), perfluorodecanoic acid (PFDcA; Fluka) and perfluorooctane sulfonamide (PFOSA; ABCR) were used as reference standards for identification and quantification of the corresponding analytes. 7H-perfluoroheptanoic acid (7H-PFHpA; ABCR) was used as internal standard and 3,5-bis(trifluoromethyl)phenyl acetic acid (ABCR) as recovery standard for analysis of abiotic samples.

Samples. A sample set of totally 120 sediment, sewage sludge, water and biota samples was obtained from the participating Nordic countries, which were responsible for sample selection and collection. Samples were taken in industrialized or urbanized areas. Sample names consist of abbreviation codes for matrix and country and a number. Codes used in figures are: RW, rain

water; LW, lake water; SW, seawater; SE, sewage effluent; LF, landfill effluent; PI, pike; PE, perch; BU, burbot; TR, trout; CO, cod; AC, arctic char; FL, flounder; EP, eelpout; HE, herring; LD, long rough dab; DA, dab; SC, sculpin; GS, grey seal; MW, minke whale; PW, pilot whale; and for the countries: FIN, Finland; SWE, Sweden; NOR, Norway; DAN, Denmark; ICE, Iceland; FAR, Faeroe Islands.

Sample preparation and HPLC/MS analysis of abiotic samples. Sediment and sludge samples (approximately 5 g) were spiked with 5 ng internal standard and extracted using accelerated solvent extraction (ASE, Dionex). ASE was performed three times with methanol (17 min/cycle, 150 °C, 2000 psi). The combined extracts were concentrated to 200 µL. Subsequently, 10 ng recovery standard in 50 µl methanol and 250 µL 4 mM aqueous ammonium acetate was added. The samples were treated for 10 minutes in an ultrasonic bath and filtrated using a Microcon YM-3 centrifugal filter device (Millipore) before injection into the HPLC/MS system.

Water samples (500 mL) were acidified with 2.5 mL formic acid and filtered through a glass fibre filter. The filter containing the particles was spiked with 5 ng internal standard and extracted by ASE as described for sediment samples. To the water phase 80 mg ammonium acetate and 5 ng internal standard were added. The water samples were extracted on Oasis HLB Plus solid phase extraction (SPE) cartridges (0.25 g, Waters) at a speed of 2 drops/sec. The SPE cartridges were rinsed with 2 mL methanol/water (40:60) and eluted with 8 mL methanol. The methanol extract was concentrated to 200 µL, and recovery standard and aqueous buffer were added as described before.

An HPLC system (1100 series, Agilent) in combination with a time-of-flight (TOF) mass spectrometer (LCT, Micromass) was used for quantification of all abiotic samples. Separation was performed on an ACE C_{18} column (150 x 2.1 mm, 3 µm particle size; ACT) employing a gradient of 200 µL/min 2 mM ammonium acetate in methanol and water. Electrospray ionisation in the negative ion mode (ESI-) was used applying the following parameters: Cone voltage -35 V; cone gas 10 L/h; desolvation gas 400 L/h. Mass spectra were recorded in full scan mode and for quantification extracted high resolution mass chromatograms were used.

Sample preparation and HPLC/MS analysis of biota samples. Biota samples were homogenized and ion-pair extracted using the method published by Hansen et al.[7]. All samples were homogenized with water, 1 mL homogenate was mixed with 2 mL 1 M sodium carbonate buffer and 1 mL 0.5 M tetrabutylammonium hydrogen sulfate (pH 10) and extracted twice with 5 mL *tert*.-butyl methyl ether. The combined extracts were evaporated to dryness and the residues dissolved in an exact volume of 500 µL methanol. The extract was filtered through a 0.46 µm PP-filter before HPLC/MS analysis.

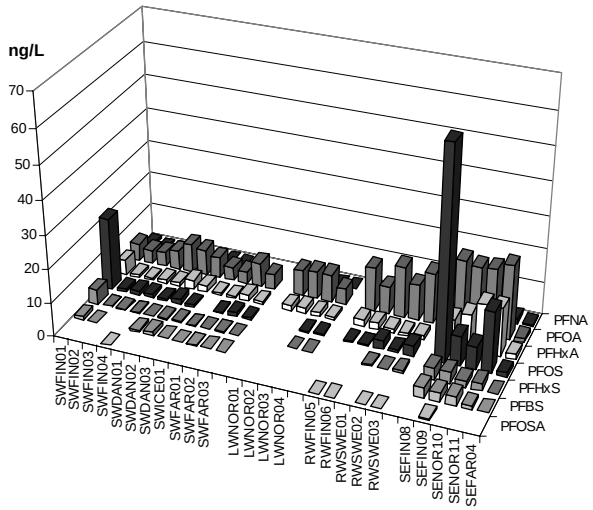
The HPLC system consisted of an Alliance 2690 pump (Waters) and a HyPurity C_{18} column (50 x 2.1 mm, 5 µm particle size; Thermo) with 10 mM ammonium acetate in methanol/water as eluent at a flow rate of 200 µL/min. A tandem quadrupole mass spectrometer (Quattro II, Micromass) in selected reaction monitoring mode applying ESI- was used for detection, as described by Giesy and Kannan[1]. Quantification was done using multilevel calibration curves of external standard mixtures and correcting for recovery of spiked and extracted samples of each matrix.

Results and Discussion

Sediment and sewage sludge samples. In general, sediment samples had lower PFAS content compared to sewage sludge samples. Sum PFAS concentrations in sediment ranged from below detection limit to 1150 pg/g ww for the highest contaminated Finnish sample. Indications for country specific application patterns were found. Sediment samples from Sweden, Iceland and Faeroe Islands hardly contained any detectable PFAS, whereas Finnish sediment was dominated by PFOS and Norwegian samples by PFOS and PFOA. High variability in sewage sludge was found. Sum PFAS values varied between 150 pg/g ww for the lowest contaminated Finnish sample and 3800 pg/g ww for the highest contaminated Swedish sample. In sewage sludge samples, PFOS and PFOA usually were the dominating PFAS. However, in two Finnish samples PFHxA dominated the contamination pattern.

Water samples. Five different types of water samples were analysed: Seawater, lake water, rain water, sewage effluent and landfill effluent. Compound specific results for all samples are given in Figure 1. Remarkable concentration differences were found for the different sample types. Highest levels were detected in landfill effluent samples (Figure 1, small figure; LFNOR06, sum PFAS 1540 ng/L). Sewage effluent was approximately one order of magnitude lower contaminated than landfill effluent (Figure 1, large figure). Lowest concentrations were found for seawater and lake water samples and rainwater levels ranged between lake water and sewage effluent.

With few exceptions, PFOA represented the predominant PFAS in water samples, followed by PFHxA. Median levels for PFOA were 5.2 ng/L in seawater, 7.8 ng/L in lake water, 13.1 ng/L in rainwater, 20.5 ng/L in sewage effluent and 297 ng/L in landfill effluent. PFOS, the most prominent PFAS residue in solid abiotic samples, was not as dominant in the aqueous samples (median <1 ng/L for sea, lake and rainwater and 12.7 and 65.8 ng/L for sewage and landfill effluent, respectively). This is probably due to lower water solubility compared to the carboxylic acids. However, PFOS levels up to 60 ng/L have been reported for coastal seawater from Japan[8].



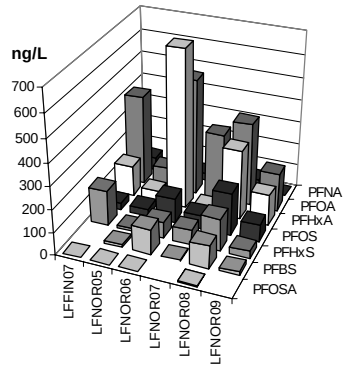


Figure 1
Compound specific levels of PFAS residues in water samples

Biota samples. PFAS concentrations found in biota were generally much higher than for abiotic samples. This is a strong indication for the bioconcentration potential of these compounds. Biota samples analyzed in this study are presented in three sub-groups: Freshwater fish, marine fish and marine mammals. The comprehensive selection of biota samples represented various biological and environmental endpoints.

Freshwater fish. In all but one freshwater fish samples, PFOS was the predominant PFAS constituent followed by PFOSA (Figure 2). Generally, the contamination levels in the Norwegian freshwater fish samples were considerably lower than found for Finnish pike and Swedish perch. Pike represented the freshwater top predator and showed the highest PFAS contamination in the analysed freshwater biota. The highest PFAS levels were found in a Finnish pike sample (PIFIN01, PFOS 551 ng/g ww, PFOSA 141 ng/g ww). Although the Swedish perch samples represent a lower trophic level than pike, the PFOS concentrations were not significantly lower. This might reflect a higher exposure to PFOS at the Swedish sampling sites. However, the PFOSA levels in perch were much lower than in pike, pointing towards food chain specific uptake or differences in transformation processes. In analogy with PCBs, PFOSA was expected to bioaccumulate in the food chain, since it is the only non-ionic and thus lipophilic PFAS analyte.

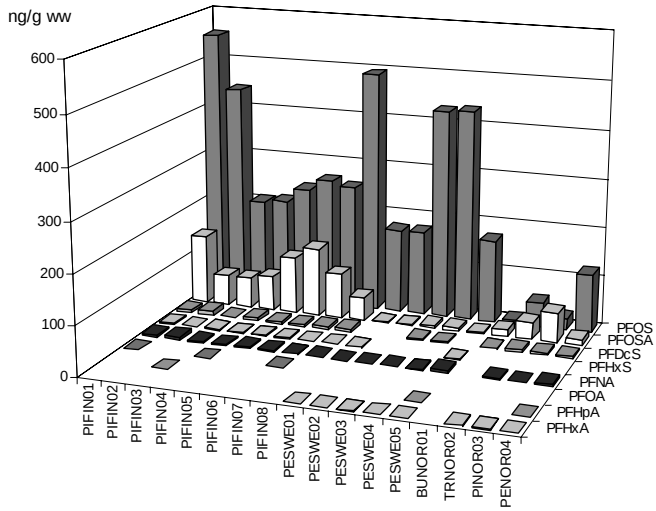


Figure 2
Compound specific levels of PFAS residues in freshwater fish samples

Marine fish. The PFAS distribution in marine fish species (Figure 3) was characterised by a surprisingly high variability reflecting differences in trophic levels, feeding habits, sampling regions as well as uptake and transformation mechanisms. Also for marine fish species, PFOS usually represented the predominant PFAS contaminant. However, in Faeroese sculpins PFOSA was higher concentrated than PFOS. In all Icelandic samples PFDcS was detected at surprisingly high levels (median 10 ng/g ww) and was usually more prominent than PFOSA. Furthermore, PFHxA was present in Icelandic marine fish samples at concentrations >1 ng/g ww. Besides, only Danish samples contained quantifiable amounts of the carboxylic acids PFHxA, PFHpA and PFOA. Marine fish samples from the Faeroe Islands were lowest contaminated. These are all indications for country specific application patterns and contamination levels. Nevertheless, marine fish species were approximately ten times lower contaminated compared to the previously described freshwater fish samples, indicating dilution effects with distance to primary sources. However, marine fish liver samples from the Western Scheldt estuary[9] (Belgium/Netherlands) and from Japan[8] were reported to contain PFOS levels up to 7.7 and 7.9 μg/g ww, respectively.

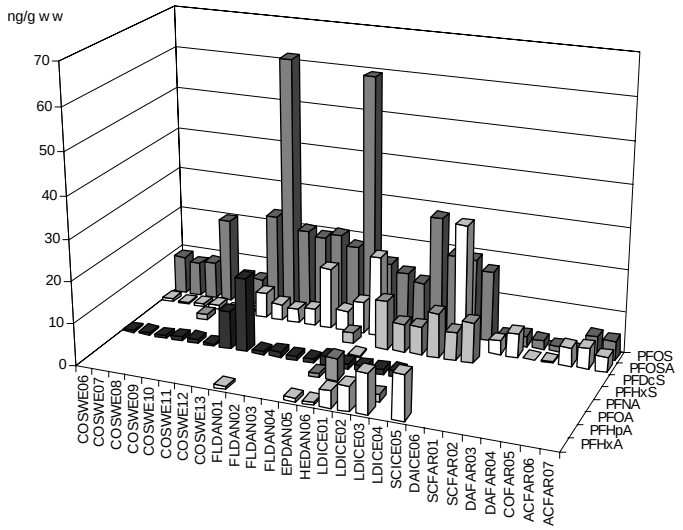


Figure 3
Compound specific levels of PFAS residues in marine fish samples

Marine mammals. The 17 marine mammal samples analyzed in this study represented top predators of the marine environment. They were considerably higher contaminated than marine and freshwater fish, which indicates bioaccumulation of PFAS in the aquatic environment. Results are shown in Figure 4. Greyseals from Denmark and Sweden were highest contaminated and characterized by dominant PFOS concentrations (up to 1 µg/g ww). A PFOS concentration gradient was observed from the northernmost site in the Baltic Sea to the more densely populated area between Sweden and Denmark. Icelandic minke whales contained relatively low PFAS levels compared to pilot whales from the Faeroe Islands, indicating correlations with the position in the food chain and feeding habits. Usually PFOS was the dominating PFAS residue also in marine mammals. However in the Faeroese pilot whales PFOSA was equally contributing to the PFAS burden, in two cases even exceeding the PFOS levels. In most marine mammal samples PFNA and PFDcS were found in considerable amounts, indicating the bioaccumulation potential for larger and hence less water soluble PFAS. The concentrations found corresponded well with values reported in literature for seal liver from the Baltic Sea and Bothnian Bay[2].

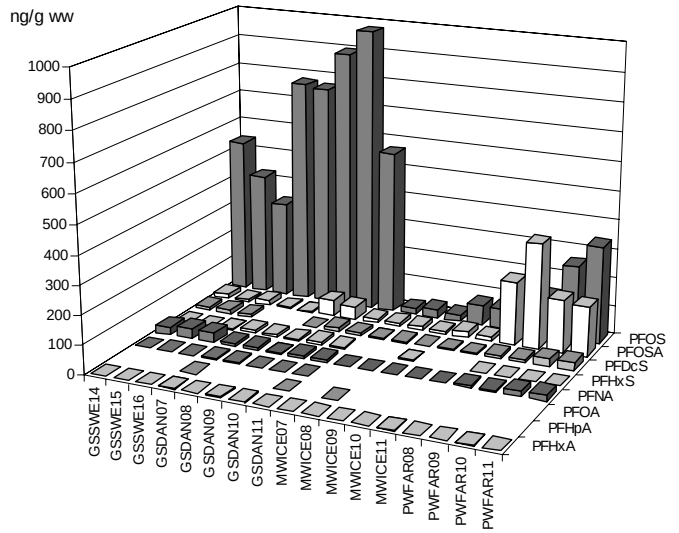


Figure 4
Compound specific levels of PFAS residues in marine mammals

Acknowledgment
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