OCCURRENCE OF PERFLUORINATED ALKYLATED SUBSTANCES (PFAS) IN THE DANISH ENVIRONMENT

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Introduction

Perfluorinated alkylated substances (PFAS) occurs in the environment primarily as the stabile perfluorooctane sulfonate (PFOS) and the long chained perfluorocarboxylic acids (PFCAs) with carbon atoms between 7 and 14. Emission of PFAS occurs during production or use and disposal of consumer products containing PFAS. PFOS and PFCAs have been found to be widespread in different ecosystems all over the world (e.g. 1-3). These compounds are persistent and have therefore a tendency to bioaccumulate. PFAS are also widespread in the Nordic countries, as previously reported by Berger et al.[4,5]. This study included abiotic matrices (sewage sludge, sludge and water) and biota (freshwater and marine fish, and marine mammals) collected in 6 Nordic Nations including Denmark. This study provided the first indication of levels and distribution of PFAS in the Danish environment.

The aim of present study was to investigate point sources of PFAS in Denmark and their occurrence in marine and freshwater recipients. Samples have been collected during 2004 and 2005 at the stations included in the National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment.

Materials and Methods

Samples. Influent and effluent water and sewage sludge was collected from 7 municipal wastewater treatment plants. Effluent water was collected from 5 industrial wastewater plants and percolate was collected from two landfill sites. Water samples were filtered before extraction and the filters were extracted separately. Sediment samples were collected at 7 freshwater sampling stations and 6 marine stations. Biota samples for the marine environment included blue mussels (*Mytilus edulis*) and liver from plaice (*Pleuronectes platessa*), flounder (*Platichthys flesus)* and eel (*Anguilla anguilla*). Eel liver was also analysed for freshwater biota samples.

Extraction and analysis. The following compounds were analysed: perfluorooctane sulfonate (PFOS), perfluorooctane sufonamide (PFOSA), pefluorohexane sulfonate (PFHxS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA). ^{13}C perfluorodecanoic acid was used as recovery standard. Water samples were acidified and extracted with C18 solid phase cartridges (1 g). The analytes were eluted with 10 ml methanol; the extract was evaporated to dryness and reconstituted in the HPLC mobile phase. Sediment and sludge samples were extracted with methanol in ultrasonic bath. The methanol extract was mixed with 1 L water and then extracted with the same method as water samples. The extraction method for liver samples was based on ion pairing as described by Hansen[6]. All sample extracts were analysed by liquid chromatography-tandem mass spectrometry (LC-MS-MS) with electrospray ionization (ESI) operated in negative mode. The details for the LC-MS-MS method are given elsewhere[7]. The detection limits for the different compounds in the investigated matrices are summarized in Table 1.

Table 1. Detection limits of PFAS in the indicated matrices

	PFOS	PFOSA	PFHxS	PFOA	PFNA	PFDA	PFUnA
Wastewater (ng/L)	1.5	0.3	0.2	2.0	0.8	1.6	2.2
Sediment/sludge (µg/kg dry weight)	1.0	0.9	0.7	0.4	0.7	1.0	1.7
Biota(ng/g wet weight)	0.2	0.5	0.8	1.2	1.4	0.8	0.7

Results and Discussion

Point sources. The separate analysis of water and particulate phase from wastewater treatment plants indicated that PFAS are mainly found in the water phase. The results for municipal waste water treatments plants are given in Figure 1. PFAS have been found in both influent and effluent water. For some compounds, particularly PFOS and PFOA, the concentration in the effluent water was higher than in influent water. PFOA and PFOS are very stable degradation products of fluorotelomer alcohols and sulfonamidoethanols. These compounds are widely used in consumer products and have been found in sewage sludge[8]. Higher concentration of PFOS and PFOA in effluent water may be due to decomposition of precursor compounds present in the influent water, leading to the more stable PFOS and PFOA.

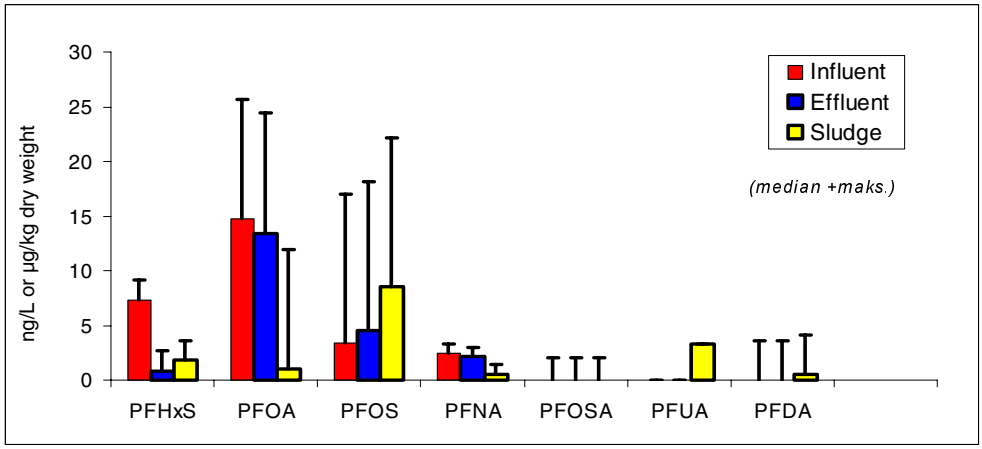

Figure1. Concentration of PFAS in influent and effluent water and sludge from 7 municipal wastewater treatment plants given as median values (coloured bars). The black bars indicate the maximum values.

The results for industrial wastewater plants and landfill sites are summarized in Figure 2. High concentration of PFOS (1.12 µg/L) was found in one industrial wastewater plant. PFAS concentrations from the two landfill sites were very low.

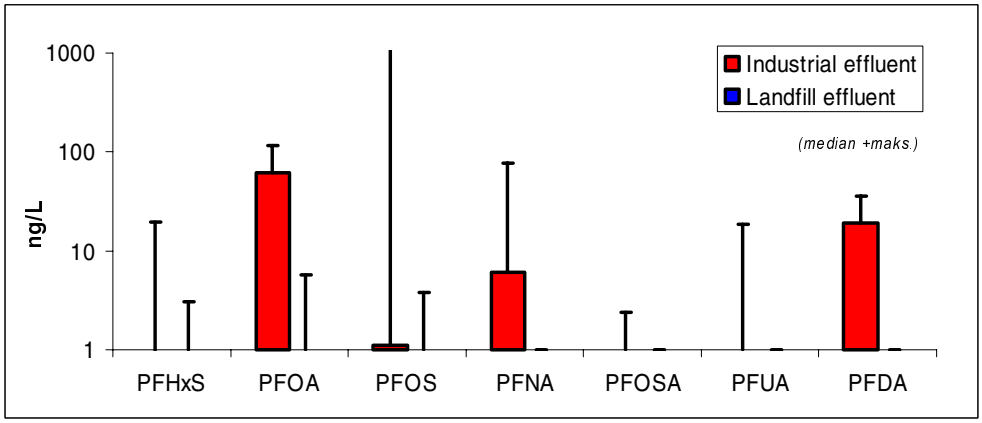

Figure 2. Concentration of PFAS in industrial (4 plants) and landfill (2 sites) effluent given as median values (coloured bars). The black bars indicate the maximum values.

The results for municipal and industrial wastewater treatment plants indicate that in some particular cases industrial effluent water may be an important source of PFAS in the aquatic environment. Otherwise wastewater treatment plants will contribute only to a low and diffuse contamination of the aquatic environment.

Freshwater and marine environments. Sediment samples collected at freshwater and marine monitoring stations did not contain PFAS at concentrations above the detection limit (Table1). Blue mussels did not contain detectable concentrations of PFAS. The concentrations of PFAS found in fish liver from both freshwater and marine stations are summarized in Figure 3. PFOS is the predominant PFAS constituent followed by PFOA.

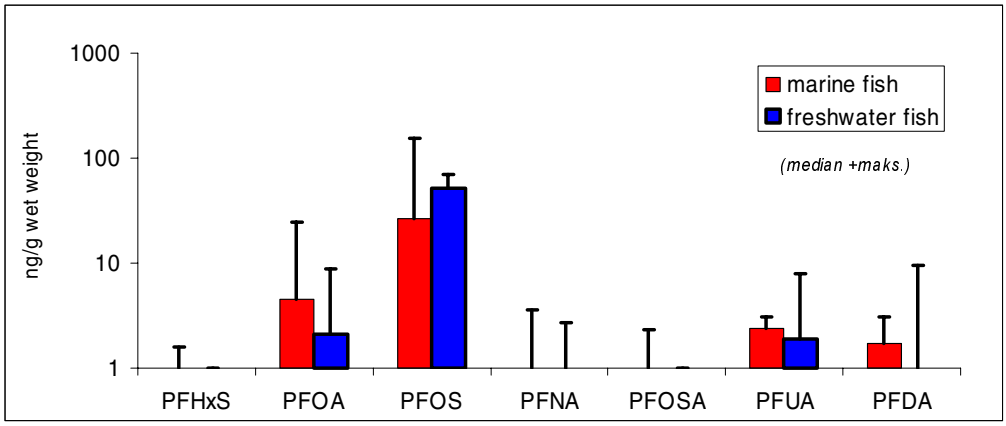

Figure 3. PFAS concentrations in freshwater and marine fish given as median values (coloured bars). The black bars indicate the maximum values.

The concentrations of PFAS in freshwater fish are comparable to those found by other authors in fish from freshwater recipients[9]. The highest concentration of PFOS was found in plaice from the Skagerak (156 ng/g w.w.). PFAS concentrations in marine fish are comparable to those measured in areas not directly contaminated by point sources such as industrial production of perfluorinated compounds.

The results of the present investigation indicate that there is a diffuse contamination from PFAS in the Danish environment. The absence of predominant primary sources results in low contamination of the water environment. However, the concentrations found in marine fish species are high enough to lead to much higher concentrations in marine mammals, as already found in Danish grey seals[4,5].

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