

Per- and polyfluoroalkyl substance homologue profiles, including ultrashort-chain compounds, and extractable organofluorine in wastewater treatment plant effluent and sludge from Nordic countries

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group anthropogenic compounds in widespread use due to their useful properties (e.g. lowering of surface tension) [1]. However, as they are very stable compounds, they are also persistent in the environment, which is further compounded as some PFASs have biomagnification potential [2]. Some PFASs have shown adverse effects on living organisms, such as developmental toxicity [3]. As perfluorooctanesulfonate (PFOS), was phased out by the main producers due to public health concerns, a variety of alternative PFASs have been introduced. Several thousands of PFASs are available on the global market [1], yet only a fraction of them are commonly monitored in environmental samples. Mass balance analysis, by combining both extractable organofluorine (EOF) and targeted analysis, can provide an insight to how much of the total target PFAS burden is quantified [4].

The present investigation was part of a multinational project, the Nordic Screening (<http://nordicscreening.org/>), aimed at screening for contaminants in the environment. Levels of more than 60 PFASs of different classes (e.g. perfluoroalkane sulfonic acids (PFSAs), perfluoroalkyl carboxylic acids (PFCAs), precursors of PFCAs and PFSAs, intermediates, perfluorinated phosphonic acids (PFPAAs) and perfluorinated phosphinic acids (PFPIAs)) were analyzed in wastewater treatment plant (WWTP) effluent and sludge (Figure 1); EOF was also measured in the sample for a mass balance analysis. The studied WWTPs from Denmark, the Faroe Islands, Finland, Norway, and Sweden varies in terms of size and treatment processes and are therefore consider as a screening of Nordic nations.

The aim of the current investigation was to give an overall picture of the PFAS contamination in participating countries. Therefore, the chosen samples would be representative of the prevailing conditions. As sewage is collected from a wider area to a single point, a wastewater treatment plant (WWTP), it presented an excellent opportunity to characterise a wider area with only a few samples. The sludge samples indicated which types of compounds, and to what extent, were captured; effluent samples showed the fraction of PFASs that were released back into the aquatic environment. The analysis of sludge is interesting as it is used in agriculture. In addition to the compound groups mentioned before, the amount of unidentified PFASs were elucidated from mass balance analysis. This allowed to screen for any possible regional differences in the PFAS homologue profiles and the fraction of still unidentified PFASs.

Materials and methods

The samples in this study were collected within the framework of the Nordic Screening project, the number of samples analysed per nation (effluent/sludge) was as follows: Finland (2/2), Sweden (2/4), Denmark (2/2), Norway (2/2), Faroe Island (2/2). The samples were collected in plastic bottles and stored at +4 °C. Each sample represents a different WWTP, thus allowing to cover a larger area with fewer samples and give a broader picture of the situation. Water samples were sonicated for 10 minutes, before taking an aliquot for analysis, to

counteract the adsorption of long-chained PFASs to the walls of the container. Sludge samples were freeze-dried before analysis, thus the results were reported on dry basis.

Sludge samples were first digested with sodium hydroxide, followed by an ion-pair extraction, adapted from [5]; whereas water samples were first filtered with 0.7 μm glass microfiber filters and then extracted with solid-phase extraction (SPE) using Oasis Weak Anion Exchange (WAX) sorbent [6]. Samples were extracted in duplicate; one was spiked with internal standards before the extraction – the sample used for target analysis; the other duplicate sample was extracted without spiking any internal standard. The non-spiked duplicate was split after extraction; one fraction analysed on UPLC for mass balance and one fraction used for EOF analysis. Each sample extract was further divided into two subfractions; 100 μL of extract was diluted up to 250 μL with appropriate amounts of Milli-Q water and methanol to achieve organic solvent contents of 40 % and 80 %. Most of the analytes were quantifiable from the extract with a 40% organic solvent content, the second extract of 80% organic solvent was used for polyfluorinated phosphate esters (PAPs) and ultrashort chained PFASs. The PAPs would strongly adsorb to the surface of vials if the water content in the extract is high.

Majority of the analytes were quantified by ultra performance liquid chromatography electrospray ionization tandem mass spectrometry (UPLC-ESI-MS/MS) in negative mode. The chromatographic system consisted of a Waters Acquity UPLC with a BEH column (2.1 \times 100 mm, 1.7 μm) coupled to a Waters XEVO TQ-S tandem mass spectrometer. The mobile phases were MeOH and 30:70 MeOH:water mixture, both with 2 mmol/L ammonium acetate and 5 mmol/L 1-methylpiperidine as additives. Ultrashort-chain compounds (C2-C3) were separated by a supercritical fluid chromatographic system (Waters Ultra Performance Convergence Chromatograph) coupled to the Waters XEVO TQ-SMS/MS detector [7]. The EOF content of the sample was determined using a combustion ion chromatography system (CIC) from Metrohm AG.

Results and discussion:

At least two samples of both matrices were taken from each country; 39 and 32 out of 63 target analytes showed quantifiable levels in effluent and sludge, respectively. The total concentrations of PFASs ($\Sigma 63\text{PFAS}$) were between 34 ng/L and 109 ng/L in effluent and between 36 ng/g and 143 ng/g (d.w. – dry weight) in sludge samples (Figure 1), the reported values are the mean values for corresponding nations.

Swedish effluent samples had the greatest $\Sigma 63\text{PFAS}$ (mean: 109 ng/L), which was approximately twice as high as the $\Sigma 63\text{PFAS}$ in samples from other nations (34 ng/L to 46 ng/L). In effluent samples the largest contributors to the $\Sigma 63\text{PFAS}$ were PFCAs and PFSAs, averaging around 50 % and 20 % of the $\Sigma 63\text{PFAS}$ accordingly. The samples from Faroe Island stood out as having a concentration of PAPs, 30 % of $\Sigma 63\text{PFAS}$. Perfluoroethane sulfonic acid (PFEtS) and perfluoropropane sulfonic acid (PFPrS), the ultrashort-chain PFSAs, were present in effluent samples from Finland, Sweden and Faroe Islands; they accounted for up to 5 % of the $\Sigma 63\text{PFAS}$. The ultrashort-chain PFCA (perfluoropropanoic acid) was found in all effluent samples, making up between 4 % and 9 % of $\Sigma 63\text{PFAS}$. Altogether, the C2 and C3 compounds accounted between 4 % and 9 % of the $\Sigma 63\text{PFAS}$. The fluorotelomer carboxylic acids (FTCAs) and fluorotelomer sulfonic acids (FTSAs) had a significant contribution as well, their sum accounted for over 10 % of the $\Sigma 63\text{PFAS}$ in Swedish and Norwegian effluent samples.

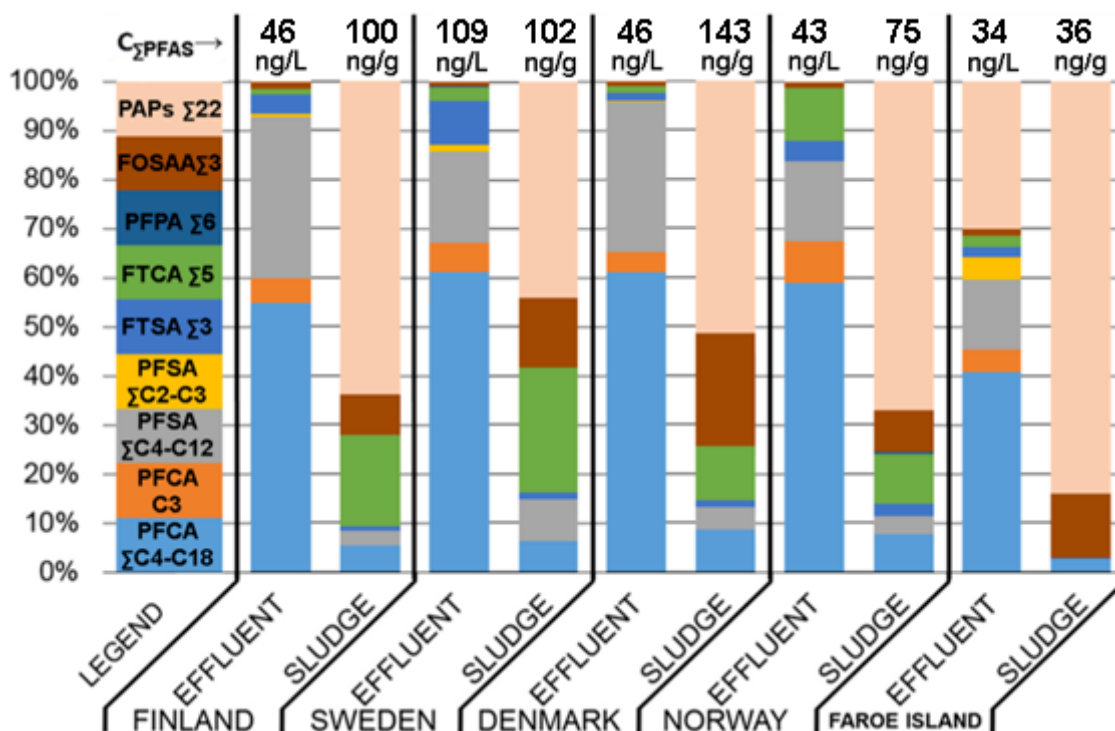


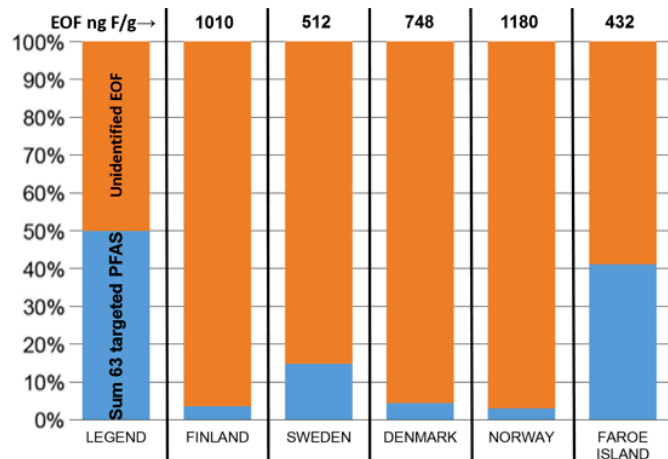
Figure 1. PFAS homologue profiles in effluent and sludge (dry weight) in Nordic countries.

The highest Σ_{63} PFAS in sludge was observed in the samples from Denmark (mean: 143 ng/g, d.w.). While the Σ_{63} PFAS were quite similar in Finland and Sweden, 100 ng/g (d.w.) and 102 ng/g (d.w.) respectively; Faroe Island and Norwegian samples had much lower Σ_{63} PFAS at 36 ng/g (d.w.) and 75 ng/g (d.w.), accordingly. The main contributors to the Σ_{63} PFAS in sludge were PAPs, found at all locations, making up 44 % to 84 % of Σ_{63} PFAS. The perfluorooctanesulfonamidoacetic acids (FOSAAs) were also found at all locations, with a mean contribution of 13 %. In Sweden, FTCAs were a significant contributor to Σ_{63} PFAS in sludge, accounting for 26 % of the total. However, no FTCAs were found in any of the samples from Faroe Island. The ultrashort-chain compounds were not present at quantifiable levels in the sludge samples; this can be attributed to their far higher polarity and thus a tendency to stay in the water phase; the latter was supported by their presence in effluent samples that was discussed earlier.

The mass balance analysis was performed for the effluent samples; the results are shown in Figure 2. The total EOF concentrations varied between 432 ng F/g and 1180 ng F/g. No observable correlation between the amount of identified and unidentified EOF. While the amount of identified EOF was highest in the samples from Faroe Island, it had the lowest total EOF, thus leading to a comparatively low percentage of unidentified EOF. The amount of identified EOF in Norwegian samples was one of the lowest, yet the total EOF was the largest.

As discussed in the introduction, there is a large number of fluorinated chemicals commercially available and only a small fraction is monitored. This is compounded by the results from this study, the 63 targeted

compounds only accounted for approximately 40 % of the total extractable organofluorine. However, in most cases between 85 % and 95 % of the EOF remained unexplained.



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Figure 2. Levels of identified and unidentified PFAS in effluent samples from Nordic countries.

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