

PER- AND POLYFLUOROALKYL SUBSTANCES IN EFFLUENTS FROM HAZARDOUS WASTE TREATMENT FACILITIES

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Introduction

The phase-out of perfluorooctane sulfonic acid (PFOS) and related compounds have led to the need to dispose of products containing these substances thus creating hazardous waste. Waste products are generated by national efforts to reduce shelf-products such as fire-fighting foams. The origin of the waste can also be products that are legal to use, either PFOS-based products used under exception rules, or products containing substances that can potentially be transformed to persistent compounds such as PFOS and perfluorooctanoic acid (PFOA). The phase-out has led to an increasing use of other per- and polyfluoroalkyl substances (PFAS) as replacement for PFOS and related compounds. There is a risk that waste containing PFAS is not declared correctly and that the waste during and after treatment generate emissions containing PFOS, PFOA or other persistent perfluoroalkyl substances.

The aim of this study is to screen for per- and polyfluoroalkyl substances (PFAS) in effluents from hazardous waste treatment facilities. The concern is that PFAS are emitted into the environment after insufficient or incorrect treatment of hazardous waste.

Materials and methods

Water effluent (four replicates) and sludge (three replicates) were collected from each one of four selected treatment facilities in Norway in October 2013. Facility no. 1 treats waste from off-shore drilling activities and land-based industry. The facility also separates oil from waters and solids for further re-use. Facility no. 2 treats hazardous waste by thermal treatment and also recovers oil. Facility no. 3 treats water containing oil and chemicals by thermal treatment in which oil is separated for further re-uses. Facility no. 4 receives organic and oil waste, and also separates and re-use the oil fraction.

Five groups of PFAS were analyzed (total of 24 substances); perfluoroalkyl carboxylic acids (PFCAs) (n=11), perfluoroalkyl sulfonic acids (PFSA) (n=4), 6:2 fluorotelomer sulfonate, sulfonamides and sulfonamidoethanols (PFOSA/FOSA/E) (n=5), and fluorotelomer alcohols (FTOHs) (n=3). Native and labeled standards were from Wellington Laboratories (Guelph, Canada). Sludge was extracted using a modified version of the EPA draft procedure for analysis of perfluorinated carboxylic and sulfonic acids in sewage sludge and biosolids by HPLC/MS/MS¹, and water was extracted according to standard method ISO 25101².

Wet sludge samples (0.5g) were treated with alkali and extracted with methanol:acetonitrile (1:1). Clean-up was performed by using weak anion exchange, solid-phase extraction (Waters Oasis[®] WAX, Waters Corporation, Milford, USA). Water samples (200-1000 mL) were filtered through glass microfiber filters (GF/B, Whatman) before extraction using Oasis WAX. Neutral compounds were eluted with methanol and ionic compounds were eluted with NH₄OH/methanol.

FTOHs (only in sludge) were analyzed on an Agilent Technologies (Palo Alto, CA) 7890A GC system equipped with a 5975C mass selective detector (MSD) in positive chemical ionization (PCI) mode. The other compounds were analyzed on an Acquity UPLC Xevo TQ-S tandem mass spectrometer (Waters Corporation, Milford, USA) with an atmospheric electrospray interface operating in negative ion mode. Samples were quantified using isotope dilution and solvent calibration curves. Subsamples of sludge were dried in duplicates at 100°C for 48h to determine the dry content.

Results and discussion

The concentrations and patterns of PFAS varied among the studied treatment plants and between water and sludge samples. Replicates from the same facility were relatively consistent. Concentrations (mean of 3-4 replicates) of the different PFAS classes analyzed are presented in figure 1 and 2.

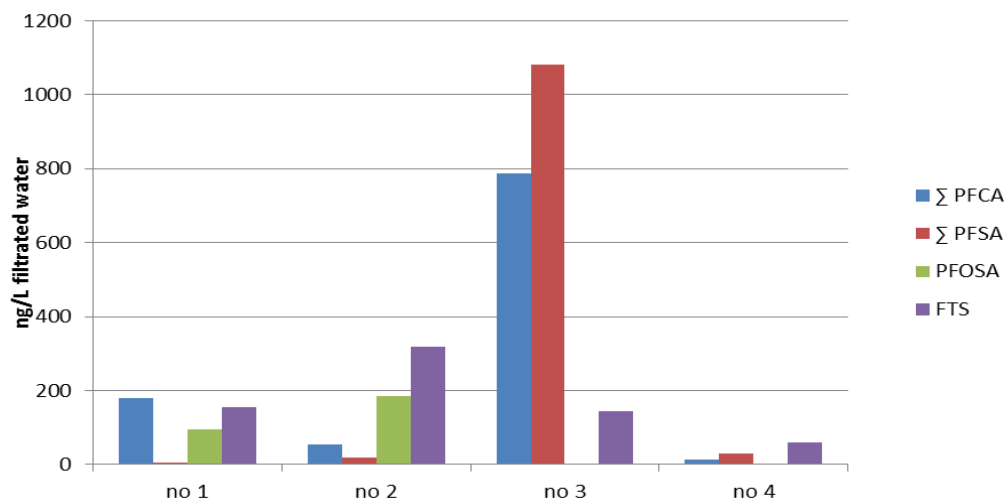


Figure 1. PFAS in water effluent from four hazardous waste treatment facilities (ng/L filtrated water, mean of 4 replicates)

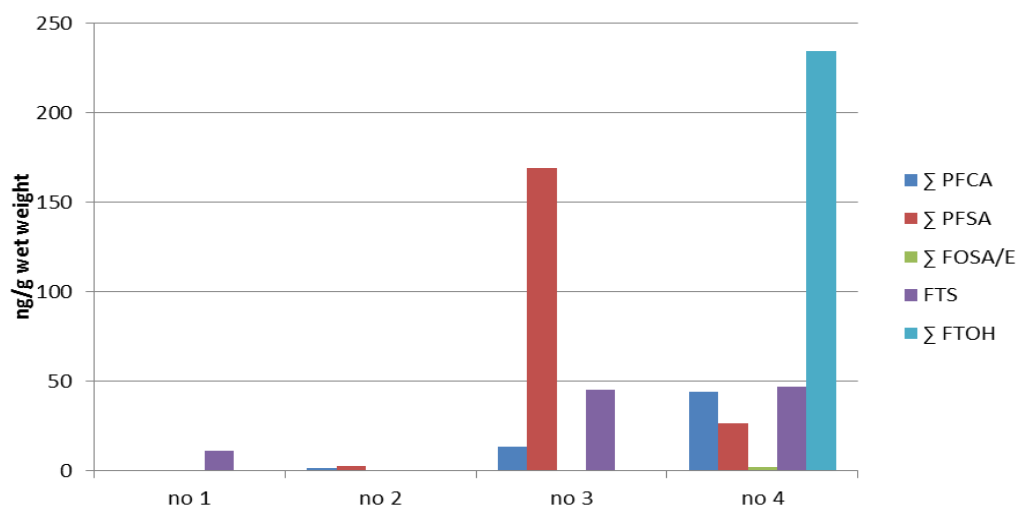


Figure 2. PFAS in sludge from four hazardous waste treatment facilities (ng/g wet weight, mean of 3 replicates)

The methods proved to work well for the sludge and water effluents but matrix effects were seen for some substances. Use of isotope labeled standards helped in some cases but some PFCAs could not be correctly quantified in some of the water samples and was therefore excluded. The method recovery of the individual substances (using internal standard quantification) was determined by addition of known concentrations of native compounds to a low contaminated sludge sample that were used as control and to ultra-pure water. Recovery was 75-109% for sludge with CV% (n=3-6) of 0.3-15%, except for PFOSA, 6:2 FTS and PFBA that could not be determined in the sludge due to high background signal in relation to added concentration. Recovery of ¹³C PFOSA, ¹³C 6:2 FTS and ¹³C PFBA was 35%, 238%, and 44% in the real sludge samples (n=12). Recovery was 54-105% for ultra-pure water with CV% of 1-26% except for FTOHs and FOSA/E that were not measured in any of the water samples.

A brief summary of the PFAS concentrations in water and sludge from the different waste treatment facilities (no 1 – no 4) are given below. Concentrations are given as mean value of replicate samples (n=4 for water, n=3 for sludge).

- no 1 Water indicated a relatively high contamination of PFPeA (42 ng/L), PFHxA (118 ng/L), and 6:2 FTS (154 ng/L) while PFOS was below detection limit (<0.25 ng/L). Sludge contained low levels of all studied substances with 6:2 FTS at the highest concentration (11 ng/g wet weight).
- no 2 Water contained elevated levels of 6:2 FTS (320 ng/L) and PFOSA (186 ng/L). PFCAs were low but unknown substances disturbed the analysis of the shorter PFCAs which were not quantified. Sludge only contained traces of PFAS with PFOS at highest concentration (2.4 ng/g wet weight).
- no 3 The water samples showed a broad and elevated contamination of PFCAs and PFSA's despite the fact that some of the short chain PFCAs were omitted from the quantification due to interferences. PFPeA, PFHxA, PFHpA, and PFOA were detected in the range 92-259 ng/L. Elevated levels were measured for PFBuS (108 ng/L), PFHxS (636 ng/L), PFOS (337 ng/L) and 6:2 FTS (144 ng/L). The sludge also contained PFBuS (1.3 ng/g), PFHxS (27 ng/g), 6:2 FTS (45 ng/g) and PFOS (141 ng/g) but only low levels of PFCAs (<LOD-9.2 ng/g).
- no 4 Water samples contained low levels of PFCAs and the levels of PFOS and 6:2 FTS were in the lower range (24 and 59 ng/L, respectively). In contrary, sludge samples indicated emissions of PFPeA (33 ng/g), PFOS (18 ng/g) and 6:2 FTS (47 ng/g). FTOHs were also detected in the sludge samples; 111 ng/g 6:2 FTOH, 89 ng/g 8:2 FTOH, 34 ng/g 10:2 FTOH.

The results show that there is an uncontrolled emission of a range of PFAS from hazardous waste treatment facilities in Norway. All the studied PFAS were detected in at least one sample. Treatment facilities and landfills have in previous studies been identified as sources of PFAS in the environment³. The hazardous waste treatment plants included in this study can be suspected to receive PFAS-containing waste, for example firefighting foam, as they process waste from oil drilling.

Norwegian Environmental Protection Agency has set a reference value for PFOS in soil at 0.1 mg/kg dry weight⁴. This value is exceeded for PFOS in sludge from facility no 3. The highest PFOS value (170 ng/g wet weight) corresponds to a dry weight of 0.664 mg/kg. This is consistent with a study on sewage sludge from the United States (308-618 ng/g)⁵, but higher than sewage sludge in Denmark with PFOS ranging from 4.8 to 74.1 ug/kg dry weight⁶, and Sweden (1.6 to 37.1 ug/kg dry weight)⁷. PFOS was also found at highest concentration in water from facility no 3 (531 ng/L). PFOS was however not the PFAS found at highest concentration, the highest concentration in water was for PFHxs from facility no 3 (512-730 ng/L). Reference values for other PFAS than PFOS and PFOA are missing.

The presence of FTOHs, FTS, PFHxS and PFBuS is indicative of the turnover from PFOS-based usage to shorter chain analogues and telomer-based substances. High levels of PFCAs with chain lengths shorter than

eight can also be indicative of use of precursor compounds, for example telomers, that degrade to persistent PFCA_s^{8,9}. FTOHs detected in sludge from facility no 4 correspond with the concentrations of FTOH measured in sludge added to soil near Decatur, Alabama, USA, where 8:2 FTOH ranged from 5 to 73 ng / g dry weight and 10: 2 FTOH ranged from < 5.6 to 166 ng/g¹⁰. High levels of 6:2 FTS has previously been indicative of firefighting foam pollution^{11,12}.

Acknowledgements

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