Screening of per- and polyfluoroalkyl substances (PFASs) and total organic fluorine in wastewater effluent from Nordic countries

Fangfang Chen[1], Ulrika Eriksson[1], Rudolf Aro[1], Leo Yeung[1], Thanh Wang[1], Roland Kallenborn[2], Anna Kärrman[1*]

[1] Man-Technology-Environment research centre (MTM), Örebro University, Örebro, Sweden

[2] Department for Chemistry, Biotechnology and Food Sciences (IKBM), Norwegian University of Life Sciences, Ås, Norway

INTRODUCTION

The discharge of per- and polyfluoroalkyl substances (PFASs) into the environment via wastewater is a pressing environmental issue. Apart from the frequently detected PFASs, such as PFOS and PFOA, more and more novel PFASs have been reported in the environment recently.

We used target screening to identify novel and legacy PFASs in the effluents from the Nordic wastewater treatment plants (WWTPs). The studied WWTPs varies in treatment processes, size, connection to industries, municipalities, hospitals and are therefore considered to represent a screening of Nordic conditions.

The aim of this project is to determine a suite of quantifiable PFASs and total organic fluorine (TOF) in wastewater effluents from the Nordic countries and self-governing areas, including Finland, Sweden, Norway, Denmark, Faroe Islands, Iceland and Greenland. The significance of the occurrence, levels and patterns of various PFASs in wastewater effluents are discussed.

MATERIALS & METHODS

Quantitative determination of target PFASs in effluent

The effluent samples were collected in September and October 2017. They were analyzed for a suite of PFASs (Table 1) and TOF, which include PFCAs, PFSAs, FTSAs, FOSAAs, FTCAs, FTSAs, FTUCAs, PFPAs, PFPiAs and diPAPs. 500 mL of effluent sample was splitted into two subsamples; one (spiked sample) was spiked with mass-labelled internal standards prior to extraction to determine the PFAS concentrations using LC-MS/MS. The other (non-spiked sample) without any mass-labelled standards, was used for TOF analysis using combustion ion chromatography (CIC). Both spike and non-spike samples were subject to the same extraction procedure. Mass-labelled internal standards were spiked to the non-spike sample for determining the PFAS concentrations in the extract using LC -MS/MS in order to calculate the proportion of identified and unidentified organofluorine in the sample.

Quantitative determination of TOF

The measured PFAS concentrations (ng/L) in the samples were converted into corresponding fluoride concentration (ng F/L) using the following equation. Levels of unidentified organofluorine were calculated by subtracting TOF from all identified PFAS.

$$C_F = n_F \times \frac{MW_F}{MW_{PFAS}} \times C_{PFAS}$$

C_F: corresponding fluoride concentration (ng F/mL); n_F: number of fluorine in PFAS; MW_F: molecular weight of fluorine; MW_{PFAS}: molecular weight of PFAS; C_{PFAS}: measured PFAS concentration using LC-MS/MS

RESULTS

Table 1. Target compounds analyzed in the study

Class	Abbreviation	Name
PFCA	PFBA	Perfluorobutanoic acid
	PFPeA	Perfluoropentanoic acid
	PFHxA	Perfluorohexanoic acid
	PFHpA	Perfluoroheptanoic acid
	PFOA	Perfluorooctanoic acid
	PFNA	Perfluorononanoic acid
	PFDA	Perfluorodecanoic acid
	PFUnDA	Perfluoroundecanoic acid
	PFDoDA	Perfluorododecanoic acid
	PFTrDA	Perfluorotridecanoic acid
	PFTDA	Perfluorotetradecanoic acid
PFSA	PFEtS	Pentafluoroethane sulfonic acid
	PFPrS	Perfluoro-1-propane sulfonic acid
	PFBS	Perfluorobutane sulfonic acid
	PFPeS	Perfluoropentane sulfonic acid
	PFHxS	Perflurohexane sulfonic acid
	PFHpS	Perfluoroheptane sulfonic acid
	PFOS	Perfluorooctane sulfonic acid
	PFNS	Perfluorononane sulfonic acid
	PFDS	Perfluorodecane sulfonic acid
	PFDoS	Perfluorododecane sulfonic acid
	6:2 Cl-PFESA	Potassium 9-cholorohexaadecafluoro-3-oxanonane-1-sulfonate
	8:2 Cl-PFESA	Potassium 11-choloroiocosafluoro-3-oxaundecane-1-sulfonate
	PFECHS	Potassium perfluoro-4-ethylcyclohexanesulfonate
FOSAA	FOSAA	Perfluoro-1-octanesulfonamidoacetic acid
	N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid
	N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid
FTCA	5:3 FTCA	5:3 Fluorotelomer carboxylic acid
	7:3 FTCA	7:3 Fluorotelomer carboxylic acid
FTSA	4:2 FTSA	4:2 Fluorotelomer sulfonic acid
	6:2 FTSA	6:2 Fluorotelomer sulfonic acid
	8:2 FTSA	8:2 Fluorotelomer sulfonic acid
FTUCA	6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylic acids
	8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylic acids
	10:2 FTUCA	10:2 Fluorotelomer unsaturated carboxylic acids
PFPA	PFHxPA	Perfluorohexyl phosphonic acid
	PFOPA	Perfluorooctyl phosphonic acid
	PFDPA	Perfluorodecyl phosphonic acid
PFPiA	6:6 PFPiA	Sodium bis(perfluorohexyl)phosphinate
	6:8 PFPiA	Sodium perfluorohexyl perfluorooctylphosphinate
	8:8 PFPiA	Sodium bis(perfluorooctyl)phosphinate
diPAP	6:2 diPAP	6:2 Fluorotelomer phosphate diester
	8:2 diPAP	8:2 Fluorotelomer phosphate diester
	6:2/10:2 diPAP	6:2/10:2 Fluorotelomer phosphate diester
	6:2/8:2 diPAP	6:2/8:2 Fluorotelomer phosphate diester
	8:2/10:2 diPAP	8:2/10:2 Fluorotelomer phosphate diester
	6:2/12:2 diPAP	6:2/12:2 Fluorotelomer phosphate diester

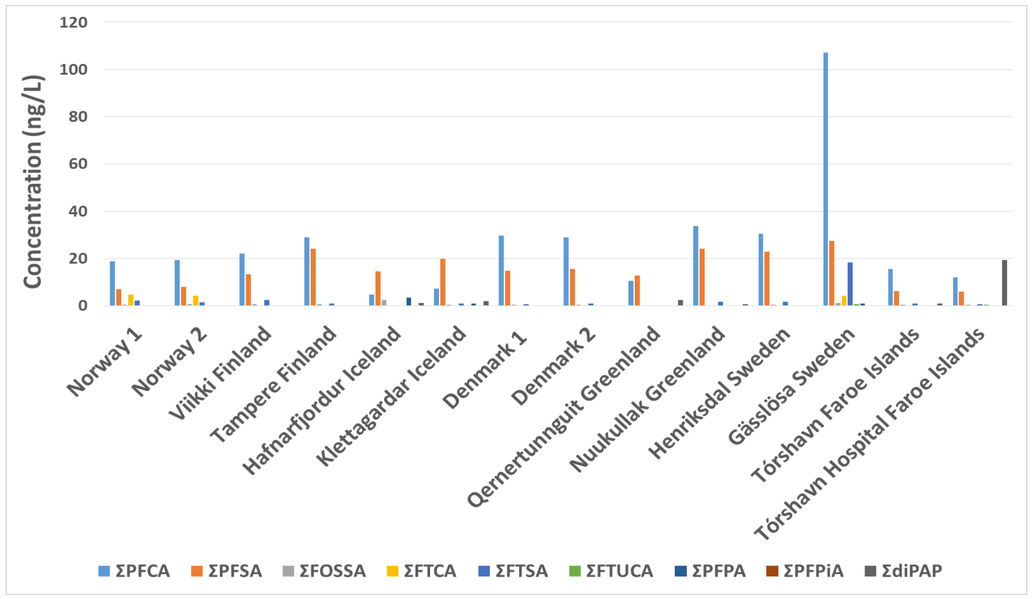

Figure 1. Concentrations (ng/L) of target PFASs in the wastewater effluent samples

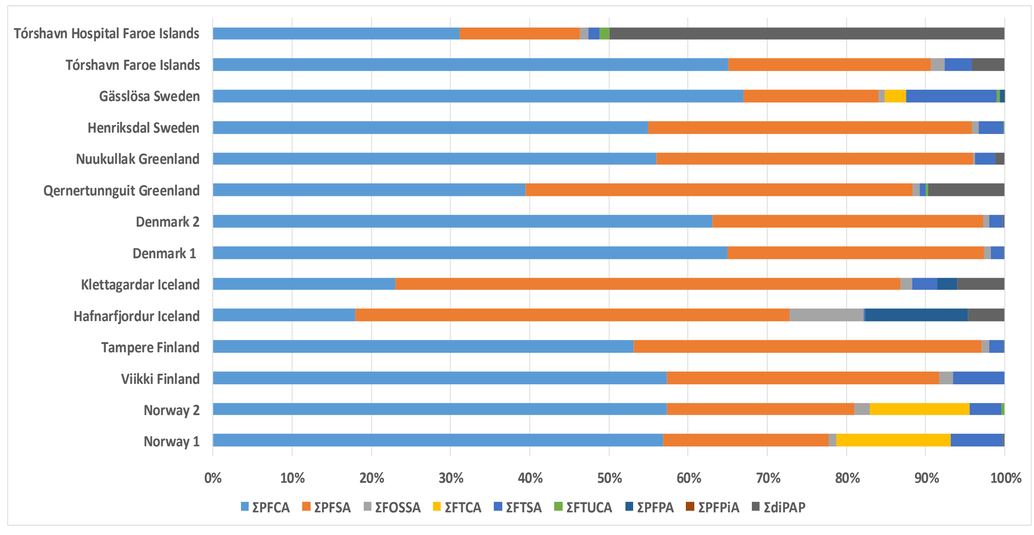

Figure 2. Composition (%) of identified organofluorine in the wastewater effluent samples

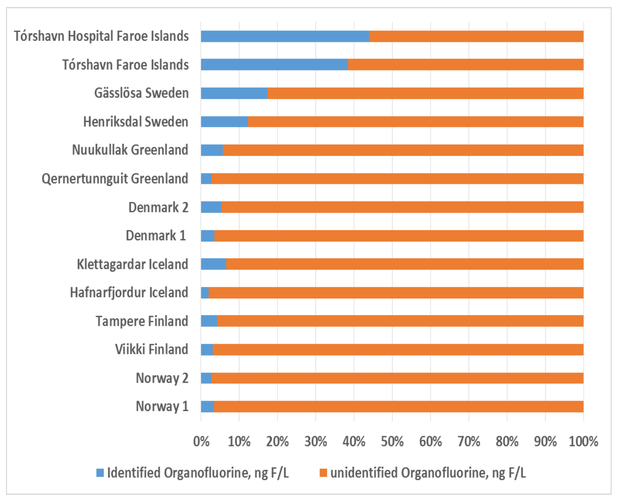

Figure 3. Composition (%) of identified and unidenfitied organofluorine in the wastewater effluent samples

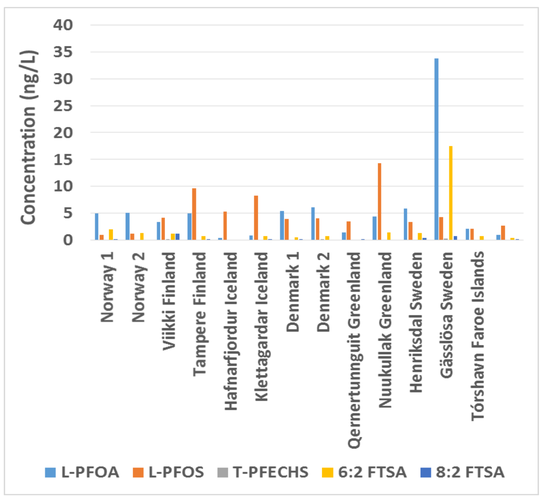

Figure 4. Concentrations (ng/L) of selected legacy PFASs and newly identified PFASs in the wastewater effluent samples

CONCLUSIONS

- PFCAs, PFSAs, FOSAAs, FTSAs, FTCAs, FTUCAs, PFPAs and diPAPs were detected in the effluents, but not PFPiAs.
- Approximately 56% (median) of the total PFASs were contributed by PFCAs, followd by 34% (median) of PFSAs, 3% (median) of FTCAs and 1% (median) of FOSAAs.
- Short-chain (C4-C7) PFCAs accounted for 73% of the total PFCAs; PFBA, PFPeA and PFHxA were the major components. PFOA was the major component of the long-chain (C8-C18) PFCAs.
- The identified PFAS only accounted for approximately 2 – 44% of the TOF. The major proportion (56-98%) of TOF remained unidentified.
- PFECHS was detected in the effluents, with detection frequency of 36%.

REFERENCES

1. Yeung, L.W.Y., Mabury, S.A., 2016. Are humans exposed to increasing amounts of unidentified organofluorine? Environ. Chem. 13, 102. doi:10.1071/EN15041

2. Yeung, L.W.Y., Miyake, Y., Taniyasu, S., Wang, Y., Yu, H., So, M.K., Jiang, G., Wu, Y., Li, J., Giesy, J.P., Yamashita, N., Lam, P.K.S., 2008. Perfluorinated compounds and total and extractable organic fluorine in human blood samples from China. Environ. Sci. Technol. 42, 8140–8145.

ACKNOWLEDGEMENTS

The project was funded by the Nordic Chemical Group under the Nordic Council of Ministers. Financial support was also provided by the Knowledge Foundation through the EnForce project. We thank all country participants for sampling.