FLUORINE MASS BALANCE ANALYSIS - CHARACTERIZATION OF FLUORINE-CONTAINING COMPOUNDS IN WASTEWATER

Pontus Larsson, Anna Kärrman, Leo W.Y. Yeung
School of Science and Technology, Örebro University, 702 81 Örebro, Sweden
FLUOROS 2023

MAN TECHNOLOGY ENVIRONMENT RESEARCH CENTRE

BACKGROUND AND MOTIVATION

- A previous study demonstrated that only 2-8 % of "extractable organofluorine" (EOF) from municipal wastewater could be characterized as PFAS, while the remaining was unidentified (Yeung et al., 2016).
- Around 20 % of commercial pharmaceuticals contain fluorine and around 340 fluoro-pharmaceuticals have been developed since 1950s (Inoue et al., 2020). While not all are still approved and/or in use, >100 fluoro-pharmaceuticals are currently in use in Sweden. A recent publication by Spaan et al., (2023) revealed significant contribution of fluoro-pharmaceuticals and their transformation products (TPs) to the "EOF" mass balance in Swedish sludge.
- The inorganic anions hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-) used in, e.g., lithium-ion batteries, have previously been detected in the German environment (Neuvald et al., 2021), but were not reported within a fluorine mass balance context.

Research questions:

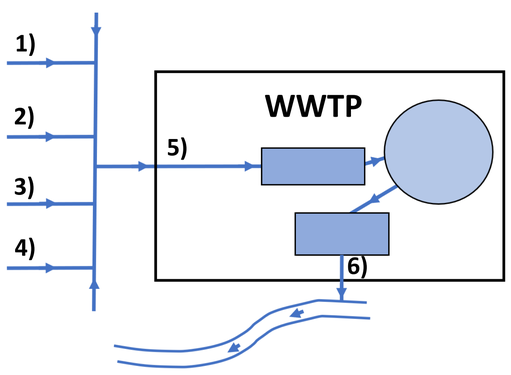
1) How much of the fluorine mass balance in municipal wastewater can be assigned to
   - **Conventional- and ultrashort PFAS?**
   - **Fluorinated pharmaceuticals and their TPs?**
   - **Selected fluorinated inorganic anions PF_6^- and BF_4^-?**
2) Do we risk overlooking potential "EOF" by using only weak-anion exchange solid phase extraction?

MATERIALS AND METHODS

Samples

Obtained from sewage system and wastewater treatment plant (WWTP) located in the city of Örebro, Sweden

- 24h composite from 4 points in the sewage system (1 to 4) - single extraction
- Influent (5), 24h composite (n=1) - triplicate extraction
- Effluent (6), 24h composite (n=1) - triplicate extraction



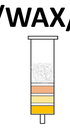
Extraction

Protocol 1

WAX SPE

Protocol 2

Multi-layered SPE (HLB/WAX/MCX)



Both protocols: Wash step verified to remove free fluoride from in-sample spike of 5 mg/L NaF

Instrumental analysis

Combustion IC for quantification of extracted and combustible fluorine ("EOF")

$C_{extractable\ and\ combustible\ fluorine}$

CIC

LC-HR-MS suspect screening for target discovery.
LC-TQ-MS and SFC-TQ-MS for target analysis and compound specific quantification over an expanded polarity range

LC-QToF-MS

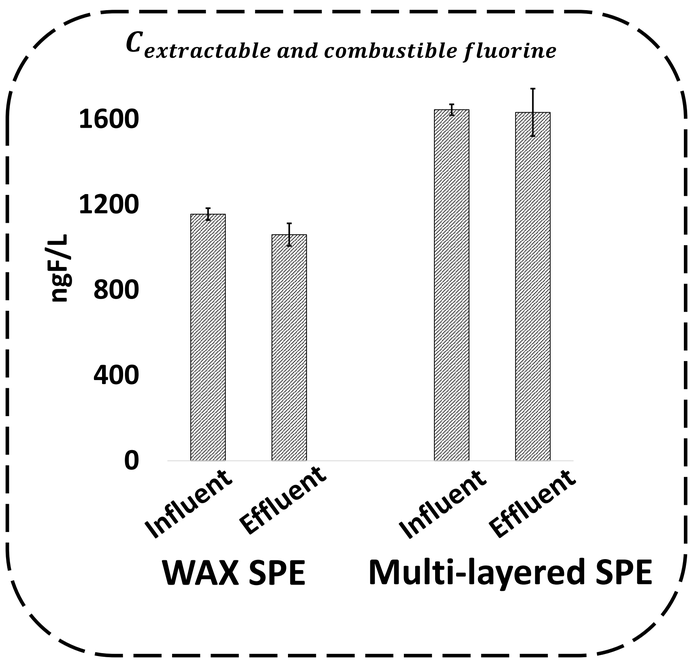
LC-TQ-MS

SFC-TQ-MS

$$C_F = \frac{n_F MW_F}{MW_{analyte}} * C_{analyte}$$

Fluorine mass balance analysis

RESULTS AND DISCUSSION



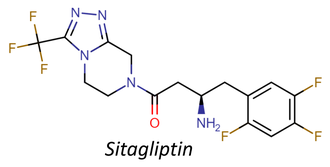
Concentration in effluent and influent of "EOF" in ng/L F. Error bar display 2x SD (n=3).

Conventional- and ultrashort PFAS

- Conventional PFAS (n=19) were minor contributors (~1%) to "EOF" in both influent and effluent.
- Within the subgroup of ultrashort PFAS, trifluoroacetic acid contributed with most of the "EOF".

Fluorinated pharmaceuticals and their TPs

- 15 fluoro-pharmaceuticals and metabolites have so far been confirmed with reference standards, contributing 8-12% in influent and 9-12% in effluent.
- While most pharmaceuticals were extracted in both extraction methods, the concentration and/or "EOF" contribution of some compounds varied significantly between WAX- and multi-layered SPE. Sitagliptin alone contributed 4-6% of the "EOF" for multi-layered SPE but only 0.2% for WAX-SPE. This indicate potential "EOF" may be missed using only WAX-SPE.

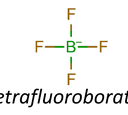


Sitagliptin

Fluorinated inorganic anions

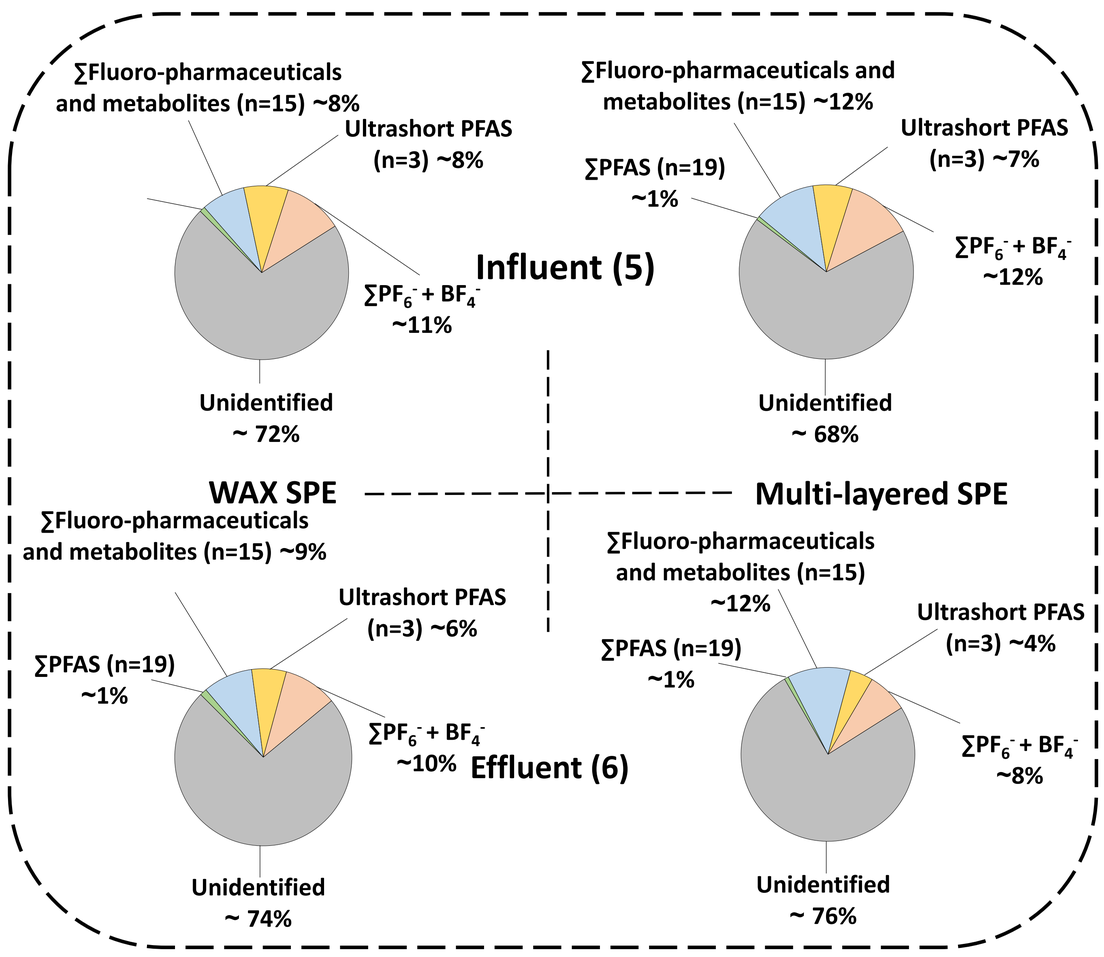
- The fluorinated inorganic anions PF_6^- and BF_4^- together contributed 8-12% to the "EOF", further suggesting that the term "extractable organofluorine" may not accurately represent the fluorine signal from the protocol used.
- Approximately 20x higher concentration of BF_4^- found in the incoming influent line 4 compared to the combined WWTP influent (no. 5) suggests a specific source

Hexafluorophosphate



Tetrafluoroborate

Fluorine mass balance analysis



KEY FINDINGS AND FUTURE WORK

- Using a WAX-only SPE, the concentration of "EOF" may be underestimated.
- Conventional PFAS only accounted for 1% of the fluorine mass balance of municipal wastewater.
- Preliminary results indicate fluorinated pharmaceuticals contribute at least 8-12% to the fluorine mass balance, but more work is needed to identify additional unconfirmed pharmaceuticals and transformation products, to further close the fluorine mass balance.
- The inorganics hexafluorophosphate and tetrafluoroborate were significant drivers of the fluorine mass balance, accounting for 8-12%.

References

Yeung et al., 2016. A pilot study on unidentified poly- and perfluoroalkyl substances (PFASs) in sewage in Sweden . Report from Swedish EPA.
Inoue M., Sumii Y., Shibata N. 2020. Contribution of organofluorine compounds to pharmaceuticals. ACS Omega. 2020;5:10633–10640
Neuwald I, et al. 2021. Filling the knowledge gap: A suspect screening study for 1310 potentially persistent and mobile chemicals with SFC- and HILIC-HRMS in two German river systems. Water Res. 2021 Oct 1;204:117645.
Spaan K.M, and Seilitz F., et al. 2023. Pharmaceuticals Account for a Significant Proportion of the Extractable Organic Fluorine in Municipal Wastewater Treatment Plant Sludge Environ. Sci. Technol. Lett. 2023, 10, 4, 328–336

Acknowledgements

Fredric Seilitz, Anna Rotander, Kevin Hernandez, Karin Saverman, Stefan Hagman

This research was supported by Formas

Contact

Pontus.Larsson@oru.se