

Introduction

Per- and polyfluoroalkyl substances (PFAS) are persistent, bioaccumulating and toxic anthropogenic chemicals. Ubiquitously present in our environment and used in an array of different applications. Discharge patterns from PFAS containing waste piles are influenced by several factors, e.g., which type of waste, age and storage conditions. Therefore, the emissions could fluctuate over time. PFAS monitoring programmes focus on a limited number of compounds, even though over 4700 PFAS have a CAS number. Combustion ion chromatography (CIC) is a technique that measures the extractable organofluorine (EOF) content, accounting for organic bound fluorine in samples, after combustion in 1000-1050 °C. Total oxidizable precursor assay (TOP assay) oxidises precursors into measurable short chained (PFCA C3-6, PFSA C4-5) and long chained (PFCA ≥ C7, PFSA ≥ C6) PFAS. After TOP assay target analysis is conducted to understand which chemistry the precursors are based upon.

Sampling and aim

During February, April and May 2021, three water samples were taken within a hazardous waste management facility.

- What are the PFAS and EOF concentrations from the hazardous waste management facility?
- How much EOF does PFCA explain pre-TOP assay?
- Can TOP assay improve the contribution with explained EOF?

Materials and methods

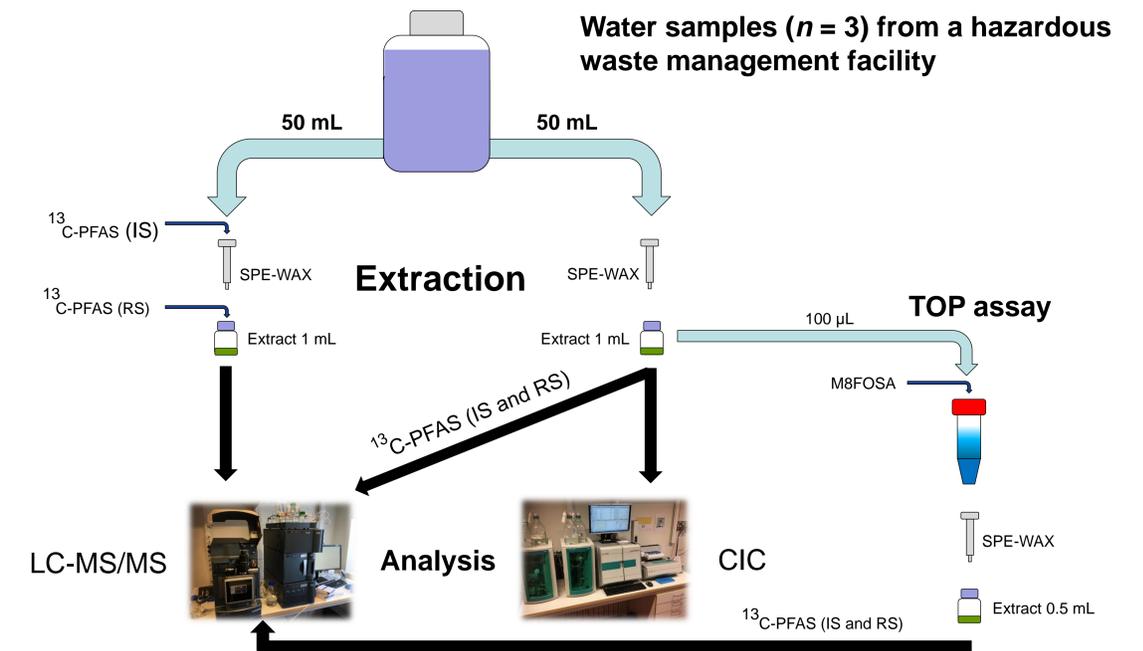


Figure 1: Schematic image of the workflow from sample preparation, applied TOP assay with mass-labelled FOSA as an oxidising standard and instrumental analysis.

Results

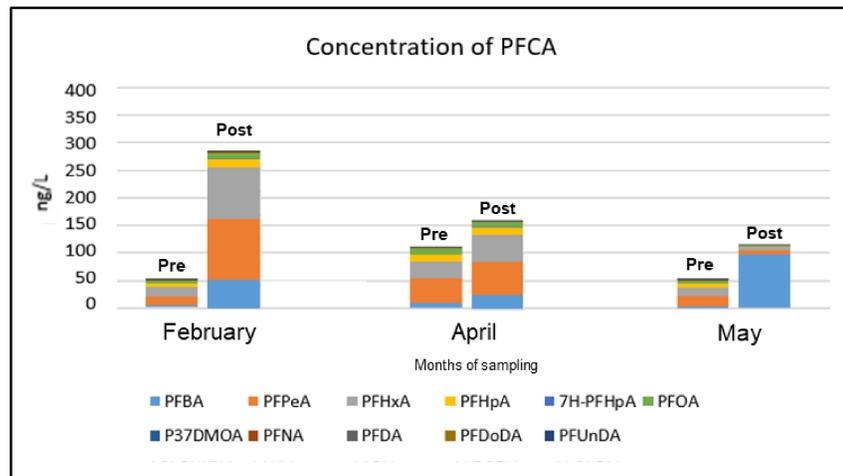


Figure 2: Histograms of PFCA (n = 11) concentrations (ng/L) in water samples from a hazardous waste management facility before and after TOP assay.

Table 1: List of selected PFCA with changes in molar concentration higher than 20 percent after TOP assay.

Compound	February	April	May
PFBA	27 %	<20 %	44 %
PFPeA	44 %	<20 %	<20 %
PFHxA	30 %	<20 %	<20 %

For each consecutive sampling time, the EOF concentrations were 15, 79 and 38 ng/mL F. Converting the PFCA pre-TOP assay into fluorine, results in 33, 72 and 33 pg/mL F. Post-TOP assay the fluorine content rose to 219, 103 and 73 pg/mL F. Therefore, TOP assay yielded an increase of 1.3, 0.4 and 0.1 percent of the explained EOF, leaving >98 percent of unexplained.

Discussion

Results of targeted analysis of PFCA were similar for February and May. The EOF results show a larger variety with results from May twice as high as from February. Indicating that there is a discharge of other fluorinated compounds within the hazardous waste management facility. In April both PFCA and EOF concentrations are clearly higher, then the other two sampling dates. Post TOP assay the total PFCA increased in consecutive order of 570, 40 and 120 percent. All three samples show a presence of oxidisable precursors, where February results giving the highest increase. At the hazardous waste management facility, the waste is stored openly without protection from rainfall and wind, which are factors that will increase discharge of PFAS. The extremely high EOF are not coming from oxidisable precursors but of other PFAS.

Conclusion

Main findings:

- TOP assay does not contribute with enough information to the unexplained EOF in water samples taken from a hazardous waste management facility
- Samples had low presence of precursors and extremely high concentrations of organofluorine
- Workflow could be used for other environmental matrices and should be tested in future work