

# Insight to PFAS Precursors Contamination in Sediments via Total Oxidizable Precursor Assay

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## 1 Introduction

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic compounds that contain a perfluorinated methylene (-CF<sub>2</sub>-) or perfluorinated methyl group (-CF<sub>3</sub>) and are widely used in wide range of industries. (OECD 2021) Legacy PFASs such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were globally restricted and regulated since as early as 2009 due to the identification of PFASs as persistent organic pollutants (POPs). (Brennan et al. 2021) However, current PFAS target analysis have encountered various challenges, such as the lack of commercial standards leading to semi-quantification for many PFAS, including most per- and polyfluoroalkyl acid (PFAA) precursors, which are PFAS that are able to degrade to perfluoroalkyl acids of shorter chain length through biotic and abiotic natural processes. (Houtz and Sedlak 2012) Significance of the limitation increases with the increasing number of PFASs and the shift in production and application to novel PFASs and precursors with global legacy PFAS regulations. (Buck et al. 2011) To tack this challenge, total oxidizable precursor assay (TOPA) is a method developed by Houtz and Sedak in 2012 to quantify for unknown PFAA precursors which have no available commercial standard for their target analysis quantification. (Houtz and Sedlak 2012) In TOPA, PFAA precursors will be subjected to harsh oxidation condition through hydroxyl radical reaction at alkaline condition and high temperature, and are converted into quantifiable PFCAs of different chain lengths, depending on the identity of the precursor. Extractable organofluorine (EOF) analysis, on the other hand, is the method in quantifying fluorine contents in the sample extract through combustion. TOPA has been used in closing the fluorine mass balance in papers and textiles and aqueous film-forming foams. (Robel et al. 2017; Ruyle et al. 2021)

A previous study has identified paper product industries to be a source of PFAA precursors contamination to the environment. (Langberg et al. 2021) Therefore, river and lake sediments samples were collected near paper product factories across Sweden for screening study to 1) apply TOPA to reveal the amount of oxidizable precursor in the samples; to evaluate TOPA as a method to identify types of precursors based on the pattern in the samples; and to evaluate how TOPA close organofluorine mass balance in samples connected to paper product factories.

## 2 Materials and Methods

### 2.1 Sample collection and selection

A total of 66 sediment samples were collected in river and lake near 15 paper product factories across Sweden. Samples were stored in freezer and freeze-dried prior to extraction. Among them, 12 sediment samples from 9 different paper factories with detected EOF value greater than the limit of detection were selected for further analysis with TOPA.

### 2.2 Chemicals

All analytical standards of targeted perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sulfonates, FTSAAs, fluorotelomer carboxylates (FTCAs), fluorotelomer unsaturated carboxylates (FTUCAs), perfluoroalkyl sulfonamides (FASAs), perfluoroalkane sulfonamidoacetic acids (FOSAAs), polyfluoroalkyl phosphate esters (PAPs) and perfluorooctane sulfonamide phosphate diester (SAmPAPs) were purchased from Wellington Labs (Guelph, Canada). Methanol (MeOH) (LC-MS grade), 25% ammonia solution and formic acid (>98%) were purchased from Thermo Fisher Scientific (Loughborough, UK). Acetic acid and sodium hydroxide (NaOH) were purchased from Merck (Darmstadt, Germany). Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), sodium carbonate, sodium bicarbonate and ammonium acetate were purchased from Sigma-Aldrich (St Luis, MO, USA).

### 2.3 Sample extraction and clean-up

After homogenization, 0.5 g of freeze-dried sediment was alkaline digested and methanolic extracted. (Yeung et al. 2013) This was followed by ENVI-carb solid phase extraction (SPE) (Supelco, 100 mg, 1 mL) and Oasis WAX SPE (60 mg, 3 cc, 30 µm; Water Corporation, Milford, USA) clean-up. Procedure was modified based on previous study. (Fredriksson et al. 2022) Targeted analytes were eluted with 4 mL of 0.1% ammonia in MeOH. The eluates were concentrated to 500 µL under nitrogen, and split to fractions for target analysis, EOF analysis and TOPA.

#### 2.4 Total oxidizable precursor assay (TOPA)

TOPA procedure is modified based on the method developed by Houtz and Sedlak in 2012. (Houtz and Sedlak 2012) 100  $\mu\text{L}$  of the 500  $\mu\text{L}$  extract was dried to below 50  $\mu\text{L}$  under nitrogen, transferred to 50 mL PP tube, and amended with 45 mL of 120 mM  $\text{K}_2\text{S}_2\text{O}_8$  in MilliQ and 1.35 mL 10N NaOH solution. To monitor the oxidation efficiency of the experiment, 5 ng of mass labelled FOSA was spiked in each sample. Samples were placed at 85  $^\circ\text{C}$  water bath for 6 h. After the reaction, samples were cooled to room temperature and pH of each sample was modified to 2 with formic acid. Post reaction extraction followed similar procedure described in section 2.3, with 500 mg Oasis WAX SPE cartridges instead of 150 mg to reduce the elution of salt.

#### 2.5 Chemical analysis

Target analysis of targeted anionic and neutral PFASs were conducted on a Waters Acquity Ultra Performance Liquid Chromatograph (UPLC) with a C18 BEH column (2.1  $\times$  100 mm, 1.7  $\mu\text{m}$ ) coupled to a Waters XEVO TQ-S tandem mass spectrometer. Ultra-short chain PFCAs and PFASs (C1–C3) were analysed on supercritical fluid chromatography tandem mass spectrometry system. Electrospray ionization (ESI) was performed in negative mode with multiple reaction monitoring (MRM). Details of the instrumental analyses are provided elsewhere. (Fredriksson et al. 2022)

EOF analysis was performed on combustion ion chromatography (CIC) system (Analytik Jena, Germany and Metrohm, Switzerland). In brief, 100  $\mu\text{L}$  of the sample was combusted on a quartz glass boat under hydrolysis at 1050  $^\circ\text{C}$ . The separation of anions was performed with isocratic mode (20 mM sodium bicarbonate) on an ion-exchange column (Metrosep A Supp5, 4 mm  $\times$  150 mm). Details of the instrumental analysis are provided elsewhere. (Fredriksson et al. 2022) Quantification was done with 5-point external calibration curve (50–1000 ng mL).

#### 2.6 Quality control and quality assurance (QA/QC) measures

For target analysis, one procedural blank and one procedural recovery were included in every batch of samples. Instrumental blanks and quality control standards were injected for every 10 samples. The LOD was determined as the mean plus three times the standard deviation of signals in the procedural blank. If no contaminations, the lowest point in a 7-point calibration curve was used. PFASs were quantified based on isotope dilution method. If no mass labelled standard is available, compounds with similar structure and retention time was used. For TOP assay, a negative control spiked with 5 ng of 6:2 FTSA with no oxidation reagent were also included in the batch. For EOF analysis, sample boat was pre-cleaned by sonication in water and methanol. 8-point calibration curve were run before analysis. Combustion blanks were run after each sample to prevent carryover, and standard of 250 ppb PFOA were run every 10 samples to ensure instrument stability. LOD of EOF were derived from two times the average combustion blanks.

### 3 Results

#### 3.1 pre-and post-TOPA PFCA concentration

Pre-TOPA PFCA concentrations showed the PFCA concentration before TOPA, whereas post-TOPA PFCA concentrations showed the PFCA concentration after TOPA. Post-TOPA PFCA concentrations increased by 99%, between 25–690 ng/g<sub>dw</sub> in the samples. Br-PFCAs was detected in all the post-TOPA samples. The increase of PFCAs in most of the samples were mainly contributed by the increase on linear-PFOA(L-PFOA) and branched-PFOA(Br-PFOA), constituting more than 90% of the percentage yield. (Figure 1) In contrast, post-TOPA PFCAs concentration of paper factory G sample yielded PFCAs of chain length ranging from C3 to C12 of 3 – 180 ng/g<sub>dw</sub>. Linear/branched ratio of approximately 30% were found in all the samples, except for paper factory G. (Figure 1)

#### 3.2 Improvement of understanding on EOF after TOPA

EOF of the samples ranged from 600 to 1300 ng/g F, with the highest value found at paper factory G. Target analysis pre-TOPA have identified no more than 5% of the EOF in the samples. (Figure 2) Identified EOF increased by 0 – 58% depending on the sample, but in general more than 60% of EOF remain unexplained.

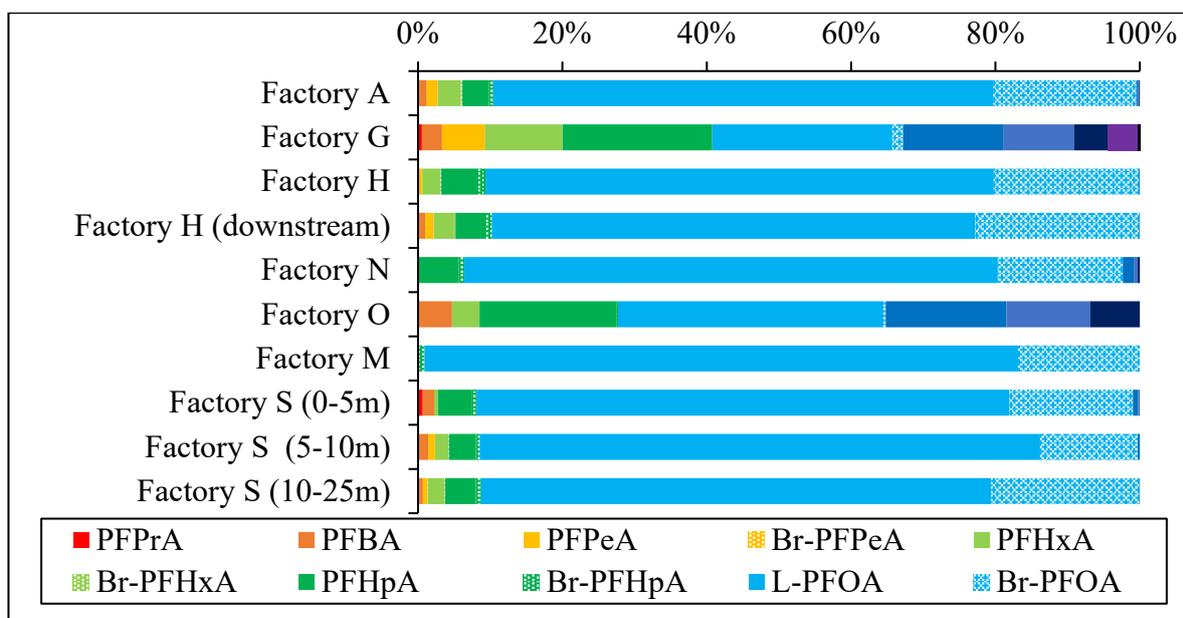


Figure 1: Profiles of C3 to C12 linear and branched PFCAs post-TOPA in 10 sediment samples from 7 different paper mills. Results of factory D and R were not shown due to no significant increase in PFCAs.

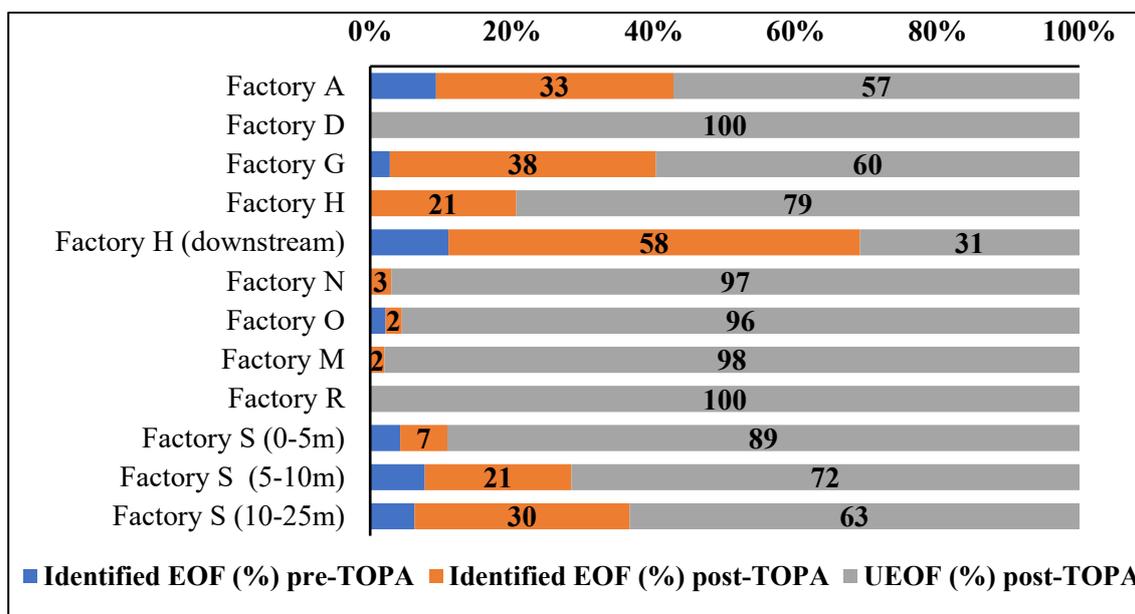


Figure 2: The portions of identified EOF pre- and post-TOPA assay in 12 sediments samples from 9 different paper mills.

#### 4 Discussion

The various oxidation pattern and the increase in identified EOF post-TOPA have shown the strength of TOPA analysis in providing insight to PFAS pollution in the samples for rapid screening and potential further analysis. The increase in identified EOF for sediments from half of the samples have illustrated the underestimation of PFAS and PFAA precursors contamination in the environment, if only a few regulatory PFAS target analysis was carried out. The percentage increase can also provide an insight to the potential composition of contaminants in the sample. For example, the 37% increase of identified EOF in paper factory G have hinted potential composition of more oxidizable precursors, such as FTSA, FTCAs, PAs, FASAs, and FOSAAs, or fluoropolymers that contains cleavable sidechain. (Houtz and Sedlak 2012; Martin et al. 2019; Fredriksson et al. 2022) On the other hand, the very limited increase in EOF post-TOPA could suggest the sources of contamination from unoxidizable novel compounds such as perfluoroalkyl ether carboxylic acids, or precursors that does not convert to monitored PFCAs during TOPA, such as polyfluoroalkyl ether carboxylic acids(Zhang et al. 2019), or monomer of polymers. At samples of various depth from factory S, the identified EOF post-TOPA increased with depth at Factory S, which potentially indicates the increase usage of unoxidizable fluorinated chemicals in recent years due to the shift to replacement alternatives.

Post-TOPA molar conversion yield also indicates whether the oxidizable precursors in the samples are perfluoroalkane sulfonyl-based or fluorotelomer-based precursor. The production of 90% of branched and linear PFOA in the samples suggests the vast contribution of perfluoroalkane sulfonyl-based precursors, such as SAMPAPs, FOSAAs and FASAs which are produced through electrochemical fluorination (ECF). ECF are also known to produce 20 – 30% branched isomers. (Buck et al. 2011) Oppositely, the limited contribution of Br-PFOA and the production of PFCAs in a range of chain-lengths suggested the contribution of fluorotelomer precursors such as FTSAs, FTCAs and PAPs. (Houtz and Sedlak 2012) The detection of PFCAs up to C12 also suggest the presence of C>12 precursors. Indeed, the target analysis of the samples have revealed the presence of FOSAAs and diSAM PAP in most of the samples, while mono- and di-PAPs for various chain lengths contribute more to the detected PFAS in paper factory G. (Kärman et al. 2022) This evidence can potentially provide information required for identification of potential sources in environmental pollution.

However, the current TOPA method suffers from several limitations. The obtained results are also likely to be an underestimation to the overall PFAS contamination, due to loss of potential precursors through extractions and clean-up, such as cationic and zwitterionic precursors. Previous experiments in our laboratory have shown potential loss of precursors through washing steps in the SPE clean-up, producing varying TOPA result. Oxidation of precursors can also lead to non-PFCAs end-products. (Zhang et al. 2019) Therefore, TOPA in combination to EOF analysis and suspect and non-target screening will provide a more comprehensive PFAS assessment in the samples. Despite the limitations, TOPA remains a powerful method in obtaining deeper insight to PFAS contamination in many circumstances, especially for laboratories with limited resources for instruments and commercial standards.

## 5 Conclusions

To conclude, in this study TOPA was applied to river and lake sediment collected from paper factories. Identified EOF after reaction increased up to 37%, leading to 58% to 78% of EOF remain unknown. Oxidation pattern can be used to reveal the difference in PFAS contamination in the locations, such as chain-length and production type of precursors. Although limitations such as incomplete oxidation and are only selective for oxidizable and extractable precursors, TOPA remained to be a powerful method in preliminary semi-quantification of total PFAS in the environment. Further method development will be required, and results from TOPA can be further analyzed through suspect and non-target screening for more comprehensive results.

## 6 Acknowledgments

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