

What Total Oxidizable Precursor Assay Can and Cannot Tell Us about Precursors of Perfluoroalkyl Acids

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What are precursors of perfluoroalkyl acids?

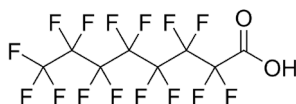
Per- and polyfluoroalkyl substances (PFAS) have been manufactured and used for the past sixty years as surfactants, processing aids, oil and water-repellent coatings and firefighting foams. Perfluoroalkyl acids (PFAAs), which belong to a subgroup of PFAS and have a fully-fluorinated carbon backbone, are persistent, recalcitrant and have been widely detected in the environment and human sera. Federal and state health advisory levels have been established for some PFAAs (ITRC 2018).

PFAA precursors are those fluorochemicals that can be biotically and abiotically transformed into PFAAs.

Although no US regulatory criteria have been established for PFAA precursors, concerns regarding their migration and transformation into PFAAs are growing. PFAA precursors can include compounds that originated in the original PFAS formulations or are polyfluorinated intermediate transformation products. The number of PFAA precursors quantifiable with commercially available analytical methods (using LC-MS/MS) is very limited. The USEPA Method 537.1 for PFAS analysis in drinking water only includes two PFAA precursors: N-methylperfluoro-1-octanesulfonamidoacetic acid and N-ethylperfluoro-1-octanesulfonamidoacetic acid. The lack of quantification is due in large part to the absence of available analytical standards for these precursor compounds. This limitation for quantifying PFAA precursors using current standard methods restricts our understanding of occurrence and extent of PFAA precursors and their potential to be transformed into PFAAs.

Example of PFAAs

Perfluorooctanoic acid (PFOA)
 $C_8HF_{15}O_2$

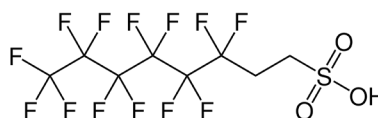


Perfluorooctanesulfonic acid (PFOS)
 $C_8HF_{17}O_3S$



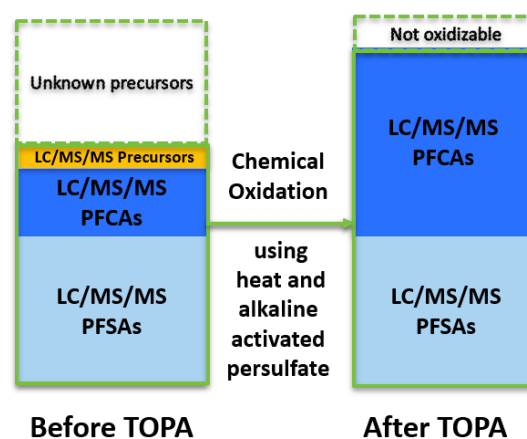
Example of PFAA Precursors

6:2 Fluorotelomer Sulfonate (6:2 FtS)
 $C_8H_5F_{13}O_3S$



What is Total Oxidizable Precursors Assay (TOPA)?

Houtz and Sedlak (2012) developed an assay to assess the presence of PFAA precursors in a sample. This assay includes steps to oxidize PFAA precursors using heat and alkaline activated persulfate. During the oxidation process, this assay generates an excess of hydroxyl radical to fully convert PFAA precursors to perfluoroalkyl carboxylates (PFCAs, e.g., PFOA). PFCAs under such oxidation conditions are the end products and cannot be further oxidized. The converted PFCAs after TOPA can then be quantified using LC-MS/MS.



When PFAA precursors are present in a sample, the precursor concentrations are estimated by looking into the difference in the sum of PFCA concentrations ($\Delta\Sigma\text{PFCAs}$) in molar basis before and after TOPA.

Do commercial laboratories offer TOPA?

TOPA is offered by commercial laboratories in the US and Canada. However, **there is no USEPA validated standard method for performing TOPA**. The TOPA data may not be comparable from one laboratory to the next due to non-standardized numbers of PFCAs included in the LC/MS/MS analysis and data quality requirements.

For instance, USEPA Method 537 and 537.1 do not include perfluorobutanoic acid (PFBA). When TOPA is run, the reported post-TOPA results using USEPA Method 537 or 537.1 may miss the mass from some precursor conversion into PFBA. However, commercial laboratories may offer PFBA analysis using their established PFAA analytical method.

Because TOPA requires analyzing the sample twice (i.e., before and after oxidation procedures), it is an expensive assay. The data objectives and limitations should be understood before conducting TOPA. The commercial laboratory will report both pre-TOPA and post-TOPA data.

Where has TOPA been used for PFAS investigation?

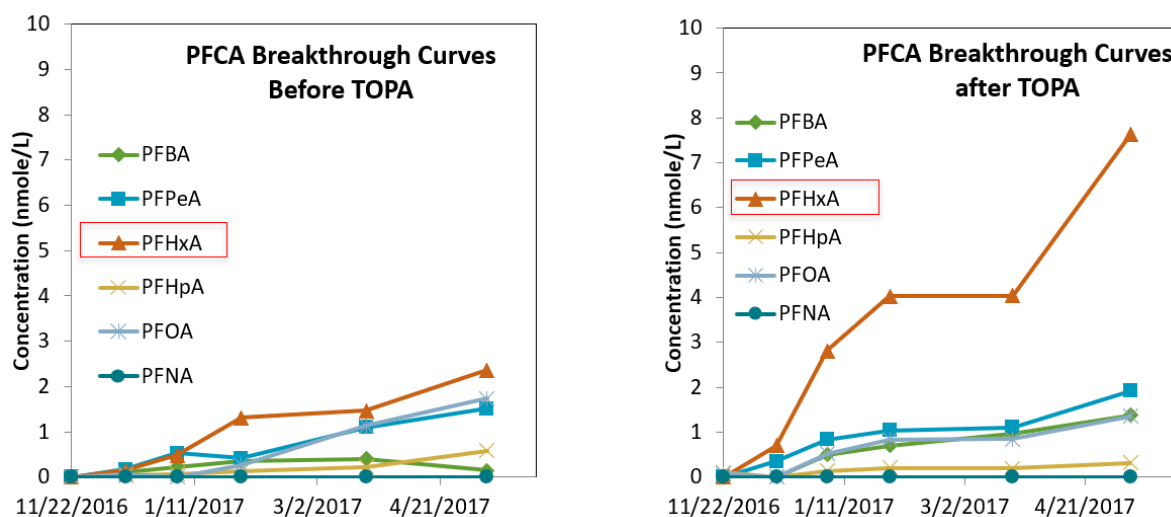
Although site-specific, the common objectives of collecting TOPA data are to:

- Verify the presence and storage of PFAA precursors in the PFAS impacted areas
- Understand the presence and transformation of PFAA precursors in the influent and effluent of water, groundwater and wastewater treatment systems
- Understand the fate and transport of PFAAs and their precursors
- Estimate future risk from transformation of PFAA precursors

TOPA has been used to verify PFAA precursors in wastewater treatment and water reuse systems (Houtz et al., 2016, Glover et al., 2018, Houtz et al, 2018). These studies verified the presence of PFAA precursors, particularly short chain PFAA precursors in the effluent, suggesting short chain PFAA precursors can be predominant in the influent and subsequently

escape from the treatment processes without treatment. PFAA precursors can account for ~30-60% of total PFAS mass on a molar basis in the effluent. TOPA has been used to estimate storage and migration of PFAA precursors during subsurface investigations (Weber et al., 2017, Casson and Chiang, 2018). Martin et al. (2019) tested groundwater samples containing zwitterionic, cationic and anionic PFAA precursors; all three types of PFAA precursors can be completely or incompletely oxidized using TOPA. This paper also pointed out the uncertainties of TOPA data quality.

To verify PFAS treatment effectiveness, TOPA has been performed to verify the presence and breakthroughs of precursors in the effluent of a GAC lead vessel (Chiang et al., 2018).



Data Source: AFCEC BAA Project 765 (PI: Dr. Jack Huang, U of Georgia, Co-PIs: Dr. Dora Chiang, AECOM (currently with CDM Smith) and Dr. Jennifer Field, Oregon State U.)

TOPA was also performed to verify the generation of intermediates during the process of electrochemical degradation of PFAS. Although intermediates were identified using LC- high resolution mass spectrometry (HRMS, e.g. quadrupole time-of flight; Q-TOF), they were not converted into PFCAs after TOPA (Schaefer et al., 2018).

It has also been used to investigate the mass balance of PFAS in materials amended with aqueous film-forming foam (AFFF) mixtures after aerobic and anaerobic biotransformation (Harding-Marianovic et al., 2015 and Yi et al., 2018).

What can TOPA tell us about PFAA precursors?

- Whether a significant molar mass of precursors is present
- The presence of precursors that may transform into PFAAs, although complete transformation may not occur under natural conditions
- Some chain length & branched and linear isomer information
- Total PFAS loading to a treatment system when designing and evaluating remedial systems
- Precursor transformation during and after a water treatment system comprising multiple physical, chemical or biological treatment processes

What can't TOPA tell us about PFAA precursors?

- TOPA does not quantify nor identify the structures of individual PFAA precursors nor can it be relied upon to quantify all of the fluorinated mass in a sample
- TOPA does not account for PFAA precursors that are resistant to oxidation method used in TOPA
- TOPA does not account for precursors that are oxidized to unmonitored PFAAs
- The oxidation process converts the PFAA precursors into PFCAs only. This assay does not replicate some biotransformation processes that occur in the environment. For instance, perfluorooctane sulfonamide (PFOSA or FOSA) is a frequently detected PFOS precursor at AFFF sites and, based on previous biotransformation studies (Mejia-Avenidaño et al., 2016), it should be transformed into PFSAs. TOPA will most likely transform FOSA into PFCAs and not PFSAs
- TOPA process is an aggressive oxidation under laboratory-controlled conditions. The results are not indicative of the PFAS mass that is susceptible to oxidation in the natural environment and, as such, the TOPA results represent a 'worst-case' or potential scenario.
- TOPA provides limited value for forensics

What other considerations are important?

- As the oxidation procedures are not chemical selective, the presence of competing organic molecules within a sample may interfere with the complete oxidation of PFAA precursors. PFAA precursors may be partially oxidized when matrix interference is significant
- Low and variable recoveries may lead to false negatives, especially in samples that are not heavily impacted with PFAS
- PFAS cross contamination may be present in the chemical reagents used for TOPA

Technology trends for PFAA precursors analysis

Although not yet commercially available, other lines of evidence, such as liquid chromatography high resolution quadrupole time of flight mass spectrometry (LC-QToF) have been established and used by academia to semi-quantitatively identify precursors (McDonough et al, 2018). Using TOPA in conjunction with non-target LC- QToF can greatly improve the understanding of PFAA precursors. There are also other methods, such as particle-induced gamma ray emission, extractable organic fluorine (EOF) and Adsorbable organic fluorine (AOF) assays that can be used to estimate total fluorine mass. Quantitative analysis of individual precursors will become more consistent and potentially commercially available in near future as more standards for precursors become available.

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