What Total Oxidizable Precursor Assay Can and Can't Tell Us about PFAS Precursors

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Background/Objectives. Per- and polyfluoroalkyl substances (PFAS) have been manufactured and used for the past 60 years as surfactants, processing aids, oil and water repellent coatings, and in firefighting foams. Perfluoroalkyl acids (PFAAs, which include perfluorooctanoic acid, PFOA, and perfluorooctane sulfonic acid, PFOS) are persistent, recalcitrant and have been widely detected in the environment and human sera. Precursors can biotically and abiotically transform into PFAAs. Although no U.S. regulatory criteria have been established for PFAA precursors, concerns regarding their migration and transformation into PFAAs is growing. PFAA precursors include PFAS that originated in the original aqueous film-forming foam (AFFF) formulations or are polyfluorinated intermediate transformation products. The number of precursors measurable with commercially available analytical methods (typically LC-MS/MS) is currently limited. The total oxidizable precursor assay (TOPA) is the only newly available commercial method that is based on the oxidation of polyfluorinated precursors to PFCAs. The abundance of precursors is estimated based on the net increase in individual PFCA concentrations after oxidation. At this point, there is no US EPA standard analytical method established for the TOPA. Many questions have been raised about including TOPA as a tool to investigate the extent of precursor contamination in the environment. However, the assay has value for understanding remedial targets and remedial technology effectiveness. TOPA is currently the only commercially available tool to estimate the abundance of precursors. The objectives of this paper are to provide evidence on the advantages and limitations of this assay based on case studies and to reveal the misconceptions of using this assay for understanding PFAS mass balances.

Approach/Activities. The data generated from TOPA, include analysis of samples from: a) PFAS-impacted sites with AFFF sources, b) PFAS destruction processes, and c) PFAS removal during GAC treatment operations. The abundance of precursors is estimated based on TOPA. We also compared TOPA data to liquid chromatography high resolution quadrupole time of flight mass spectrometry (LC-QToF) to identify the intermediate products during PFAS destruction processes. The findings shed light on how to use TOPA data to estimate the presence of precursors with understanding of its limitations, and whether TOPA is needed for your PFAS site management.

Results/Lessons Learned. This evaluation reveals TOPA is useful as a tool for understanding remedial technology effectiveness and the presence of precursors at a PFAS site. However, TOPA does not quantify nor identify the structures of individual PFAA precursors nor can it be relied upon to close PFAS mass balance in a sample. The oxidation process converts the PFAA precursors into PFCAs only; these detected PFCAs may not be the transformation products under natural conditions (some precursors biologically transform into perfluoroalkyl sulfonates [PFSAs]). Practitioners should also pay attention to the challenges of getting consistent TOPA data when the background oxidant demand is too high, resulting in incomplete oxidation of a sample. When TOPA data are in question or when significant levels of precursors are found via TOPA, the recommendation is to verify with other lines of evidence, such as LC-QToF. Additionally, as more standards of precursors become available, quantitative analysis of individual precursors will become more consistent and potentially commercially available.