Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP) Assay

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Background/Objectives. Per and polyfluoroalkyl substances (PFAS) are a family of hundreds of synthetic compounds used in a wide variety of industrial and commercial products. Each contains carbon (C) chains with fluorine (F) atoms attached to these chains. The C-F bond is the shortest and strongest bond in nature, and is responsible for most of the unique and useful characteristics of these compounds. PFAS include perfluorinated sulfonic acids (i.e., PFOS) and perfluorinated carboxylic acids (i.e., PFOA).

Current methodologies for the analysis of PFAS are designed to measure a discrete list of 14 to 30 compounds. There are many additional PFAS compounds that are not determined as discrete compounds by existing analytical methods, including Method 537. Hence, we may be underestimating the PFAS risk potential present in the environment. There is significant pressure from the public, environmental agencies, and others to apply methodologies that more closely measure the full extent of PFAS contamination. A new method, the Total Oxidizable Precursor (TOP) assay, can help measure the concentration of non-discrete and difficult to measure PFAS compounds that are not determined by conventional analytical methods. Assessment of TOP assay data may improve our understanding of potential PFAS environmental risk.

Approach/Activities. TestAmerica Sacramento implemented the TOP assay as a solution to this complex problem. The TOP assay rapidly converts polyfluorinated PFAA precursors into PFAAs including PFOA, using a hydroxyl radical-based chemical oxidation method. The TOP assay replicates what microorganisms in the environment would achieve after many years. The end result is to provide a range of PFAAs which are detectable by LC-MS-MS. The TOP assay quantifies the sum of PFAS that could be converted to PFAAs in the environment.

The TOP assay chemistry is fairly straightforward. The source of hydroxyl radicals used in the oxidation of PFAA precursors is a combination of potassium persulfate and sodium hydroxide. These oxidation reagents are added to the aqueous samples in 125 mL high density polyethylene (HDPE) containers. The assay containers are placed in a heated water bath for several hours. The oxidation is quenched and the post-treatment assay aliquots are ready for solid phase extraction and LC-MS-MS analysis per Method 537M. Quantitation of both a pre-treatment (Pre-TOP) sample aliquot and a post-treatment (Post-TOP) sample aliquot is required. The difference between the Pre-TOP concentrations and the Post-TOP concentrations is the concentration of the non-discrete oxidizable PFAA precursors.

Results/Lessons Learned. TOP assay data can help us understand the potential PFCA precursor content and it can provide valuable details regarding the carbon chain lengths of the PFCA precursors present at a site. There are also some limitations. Current analytical methods do not include all PFCAs; therefore, not all end products are determined and included in our PFCA precursor evaluation. In addition, PFCA concentrations are not molar corrected, so the TOP analytical results do not depict a mass balanced equation.