

Closing the PFAS Mass Balance in Sediments and Tissues: The TOP Assay

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Background/Objectives. Per and polyfluoroalkyl substances (PFAS) are a family of hundreds of synthetic compounds. Each contains carbon (C) chains with attached fluorine (F) atoms. The C-F bond is the shortest and strongest bond in nature, and is responsible for most of the unique characteristics of these compounds.

Current methodologies for the analysis of PFAS are designed to measure a discrete list of ~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 procedure, 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. To date, the TOP assay has typically been applied to aqueous matrices. Additional challenges exist for more complex sediment and tissue matrices. Assessment of TOP assay data may improve our understanding of potential PFAS risk in sediment and tissue matrices.

Approach/Activities. TestAmerica Sacramento implemented the TOP assay on solid matrices 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 micro-organisms in the environment would achieve after many years. The end result is to provide a range of PFAAs which are detectable by LCMSMS. The TOP assay quantifies the sum of PFAS that could be converted to PFAAs in the environment.

The TOP assay chemistry is fairly straight forward. 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 sediment and tissue samples in 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 cleanup followed by LCMSMS analysis. 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 present.

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.