Optimization of Total Oxidizable Precursor Assay for Poly- and Per-Fluoroalkylated Substances (PFAS) Precursor Analysis

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Background/Objectives. Aqueous film-forming foams, AFFF are widely used to extinguish hydrocarbon-based fuel fires at Department of Defense (DoD) sites for fire-fighting training exercises and in the airports and oil refineries to stop the fire. These AFFF impacted sites are contaminated with many known and unknown per- and poly-fluorinated alkyl substances, PFASs along with other chlorinated solvents and hydrocarbons as co-contaminants. The PFAS composition in AFFF formulation is proprietary and many of the unknown polyfluorinated precursors present at the contaminated sites, can potentially convert to persistent perfluorinated alkyl acids, PFAAs by abiotic or biotic transformation. There are no analytical standards or methods available to quantify the concentrations of these unknown precursors. Total oxidizable precursor (TOP) assay developed by Houtz and Sedlak (2012), is an emerging technique, which has been applied to quantify the total concentrations of these unknown polyfluorinated precursors by comparing the concentrations of known PFAAs of different chain lengths measured before and after oxidation. TOP assay can used as the pre-screening tool for the PFAS contaminated site characterization and to estimate the level of PFAS contamination. We hypothesized that the level of co-contamination might affect the conversion of precursors to PFAAs, as there will be a competition for the persulfate between the PFAS precursors and the hydrocarbon co-contaminants and hence the concentration of persulfate needed for complete oxidation under these conditions needs to be optimized.

Approach/Activities. The method optimization in liquid and solid samples was performed using 8:2 fluorotelomer sulfonate in the presence of a range of initial persulfate concentrations and in the presence of varying concentrations of co-contaminants such as diesel fuel. The percent conversion of the precursors will be compared at varying concentrations of co-contaminants to result in maximum conversion to different chain length PFAAs. Sample analysis was performed in-house at Battelle following the performance-based methods, for analyzing the PFAS chemicals in liquids and solids, compliant with DoD's Quality Systems Manual 5.1 Table B-15 criteria.

Results/Lessons Learned. Given, there are more than 3000 PFAS related chemicals in the global market, the known quantifiable PFASs account for only very small fraction. Therefore, TOP assay provides the information on total oxidizable precursors present at the contaminated sites and can be used as the pre-screening tool for PFAS contaminated site assessments, ground water investigations and to estimate the level of PFAS contamination. The presentation discusses how the TOP assay results can be affected by the presence of different levels of co-contaminants and at varying concentrations of persulfate in the reaction.