Use of Isotope Dilution Methods and the Total Oxidizable Precursor Assay (TOP) to Evaluate Effectiveness of PFAS Remediation

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Background/Objectives. Remediation of sites contaminated by use of PFAS is a significant and ongoing challenge. While use of aqueous film forming foams (AFFF) for firefighting is responsible for most of these remediation issues, sites adjacent to PFAS manufacturing plants, chrome plating facilities, and others pose unique challenges. Accurate measurement of remediation targets is a critical component. Analysis of PFAS in water is relatively well characterized, with best practices around the use of isotope dilution and weak anion exchange (WAX) cleanup becoming standard in all but drinking water analysis. However, the analysis of contaminated soils and sediments present a bigger challenge with multiple variables including choice of solvent, pH and others influencing recovery and reproducibility. Also, with other contaminants including hydrocarbons being present at high levels in most remediation sites, interferences can result in false positives and false negatives. The use of isotope dilution, standardized comprehensive extractions and cleanup that goes beyond simple carbon treatment all contribute to increases in data certainty. While PFOS and PFOA are the focus of most attention due to their persistence, bioaccumulation and suspected effects on human and ecosystem health, they, along with other perfluorinated carboxylates and sulfonates, comprise a very small fraction of the mass balance of PFAS. Remediation targets that fail to account for the presence of PFAS precursors can result in ongoing liabilities due to the transformation of precursors into persistent perfluorinated acids. The use of comprehensive PFAS profiling techniques such as the total oxidizable precursor assay that converts unknown precursors into easily quantifiable perfluorinated acids produce a more comprehensive understanding in site characterization and remediation. The objectives of this study were to understand the role of TOP in estimating precursor amounts in soils/sediment from contaminated sites, and to explore the role of extraction pH on TOP results.

Approach/Activities. In this study, we use a DoD 5.1-compliant isotope dilution LC-MS/MS method coupled with acidic/basic extractions to characterize soils from contaminated sites. A previously validated TOP assay enhanced with isotopically labeled reaction monitoring/efficiency was used for the TOP analysis. Two different extraction techniques for the TOP assay, one using sequential basic extractions and one combining acid and basic methanol are tested in order to understand role of pH and solvent type on results obtained by TOP. Samples were spiked with isotopically labeled standard, extracted using the selected solvent system, and extracts were cleaned up using weak anion exchange. Samples were analyzed using UPLC-MS/MS. We also evaluated the role of WAX in removal of interferences from soil/sediment by comparing results from extracts with and without WAX cleanup.

Results/Lessons Learned. Preliminary results indicate that weak anion exchange cleanup can remove interferences present in extracts treated with carbon. Experiments are ongoing and results will be presented.