

Fate, Transport, and Transformation of Poly- and Per-fluorinated Substances (PFAS) in Wastewater Treatment Plants

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Background/Objectives. Poly- and perfluoroalkyl substances (PFAS), also known as “forever chemicals”, are a complex group of over 4800 manufactured chemicals that are ingredients in various everyday products. The wide-spread use of PFAS in different applications ranging from non-stick surfaces to aqueous film forming foams (AFFFs) for firefighting and their persistence in the environment have resulted in PFAS detections in the influent, effluent, and sludge and biosolids of many wastewater treatment plants (WWTPs). PFAS that can degrade to generate perfluoroalkyl acids (PFAAs), known as stable end-metabolites, are referred to as precursors. Precursors in WWTP sewage can be converted into PFAAs or other intermediates through wastewater treatment processes such as biological treatments. As a result of such processes, the concentrations/masses of PFAAs and/or intermediates can increase from influent to effluent. Understanding the prevalence of these precursor compounds provides a basis for understanding PFAS fate in WWTPs. However, the analytical standards are limited to <100 PFAS compounds limiting the quantification of most of the PFAS compounds including precursors. Therefore, closing the PFAS/organofluorine mass balance in such systems remains a challenge. The main objective of this study is to assess spatial and temporal variability of PFAS in WWTPs and evaluate potential transformation and/or biotransformation of PFAS in these systems.

Approach/Activities. As part of an Environmental Protection Agency (EPA) study, we evaluated the spatial and temporal variability of PFAS in six different WWTPs. PFAS analysis included but was not limited to EPA-1633 draft method, total organic fluorine (TOF) and total oxidizable precursors (TOP) assay. More specifically, the main activities of this study were to 1) collect biweekly samples of up to 16 locations in WWTPs to understand the spatial variability of PFAS in these systems, 2) perform intensive sampling including daily sampling and 8-hour sampling periods to better assess the temporal variability, 3) conduct a comprehensive data interpretation and analysis to evaluate the potential precursor degradation occurring in different treatment processes including any biological or oxidation processes, 4) integrate the flowrates and solids loading rates into PFAS analysis to assess the mass transport of PFAS in these systems, 5) perform additional PFAS analysis including TOF and TOP assay to assess the organofluorine mass balances, and 6) make recommendations for possible PFAS removal from different streams especially recycling flows in WWTPs.

Results/Lessons Learned. Initial data indicated that for most of the WWTPs studied here, the measured PFAS mass increased in effluent compared to influent which was attributed to potential PFAA/intermediate (e.g., 5:3 fluorotelomer acid) generation from precursors through different treatment processes including biological nutrient removal systems or wet oxidation processes. Although the study is still going on, our initial hypothesis for candidate precursors is polyfluoroalkyl phosphate monoesters (PAPs) and polyfluoroalkyl phosphate diesters (diPAPs) which have been documented in WWTP samples at much higher concentrations than commonly measured PFAS and they have been shown to biodegrade to PFAAs. We will test this hypothesis by measuring these compounds in WWTP samples. Additional results showed that the high concentration of oxidizable organic matter in these samples resulted in incomplete oxidation of PFAA precursors in TOP assay leading to underestimation of precursor mass in WWTPs when compared to total organofluorine data. In addition, for some WWTPs, high non-PFAS organic fluorine sources resulted in high total adsorbable organic fluorine (typically performed on liquids) leading to a challenge in assessing PFAS associated organic fluorine while

extractable organofluorine (typically performed on solids) provided more promising results given the selectivity of the extraction method for PFAS compared to other organofluorine compounds such as pharmaceuticals.