

# Shifting of Target and Non-Target Per- and Polyfluorinated Alkyl Substances (PFAS) over Municipal Wastewater Treatment

Chen Wu, Qi Wang, Hao Chen, and **Mengyan Li** (mengyan.li@njit.edu) (New Jersey Institute of Technology, Newark, NJ, USA)

**Background/Objectives.** Per- and polyfluoroalkyl substances (PFAS) have recently drawn great attention due to their wide occurrence and bioaccumulation capability, including more than 5,000 structures. Following the USEPA, over 20 states have set up ultra-strict regulation or advisory levels (from 10 to 70 parts per trillion, ppt) to manage the aqueous concentration of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), the two most essential perfluoroalkyl acids (PFAAs). Wastewater treatment plants (WWTPs) are hot spots where different sources of PFAS commingle. Previous studies have been centered on the investigation of target PFAS, primarily PFAAs, at WWTPs. In this study, we applied a rapid, sensitive, and robust PFAS analysis system via nano electrospray ionization high-resolution mass spectrometry (Nano-ESI-HRMS), allowing the synchronous absolute quantification of 22 PFAS compounds (including 17 PFAAs and 5 precursors) and profiling of non-target PFAS features that have been scarcely reported before.

**Approach/Activities.** Water samples were collected from three domestic WWTPs (Plant R, P, and L) in northern New Jersey between July and August 2020. At each WWTP, wastewater samples were collected in sequence from the primary influent tank (after coarse filtration), the aeration tank (with activated sludge), the secondary clarifier tank, and the final effluent (after disinfection), designated as INF, ARE, CLA, and EFF, respectively. A series of analytical calibration solutions (containing 17 PFAA, 5 precursor analytes) at the level from 39 parts per trillion to 10,000 parts per trillion, spiked with four isotope-labeled internal standards, were examined and compared by LC/MS/MS (minor modified EPA537.1) and Nano-ESI HRMS system. For Nano-ESI HRMS analysis, a high-resolution Q Exactive hybrid quadrupole–Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA) was equipped with nano-ESI. The emitter tip was pulled using a laser puller (Model P-2000, Sutter Internet, Novato, CA) with a 2  $\mu\text{L}/\text{min}$  sample injection flow rate and -3.0 kV potential. Suspect PFAS mass features were screened when their relative abundances exhibited an increasing or increasing-then-decreasing trend. Collision-induced dissociation was employed to identify fragmentation patterns and moieties and make predictions on the formula and structure of the suspect mass features, which were further validated using commercially available structural analogs and by matching mass spectra with those in our local database based on a mass error threshold of 5 ppm. A 2-level classification scheme was implemented to combine the absolute quantification of target PFAS and semi-quantification of suspect PFAS detected in wastewater samples.

**Results/Lessons Learned.** First, significant elevation of PFPeA, PFHxA, and PFHpA concentrations was evident across three WWTPs in the effluents compared to the influents, when individual target PFAS concentration data were pooled among three WWTPs to statistically discern the contribution of major wastewater treatment processes using the two-way Mann-Whitney U-test. Second, the generation of several PFCAs was observed at aeration tanks, including PFPeA, PFHxA, PFHpA, and PFOA. Third, clarifier tanks were another hot spot where PFAS biotransformation might occur, presumably through anaerobic processes, as evident by the generation of PFHxA and PFPeA. On the other hand, the decrease of PFBA, PFPeA, and PFHxA at Plant R might be resulted from either the adsorption to the biosolids and/or biotransformation. Forth, using suspect screening, we identified 16 possible PFAS features in WWTP matrices. Notably, two representative ultrashort-chain PFAAs,

trifluoroacetate (TFA) and TFMS, were found in all WWTP samples, with 9.4- and 3.0-fold increments from the influent to the effluent at Plant R, as well as 7.9- and 2.6-fold increments at Plant P. Further, hydrido-perfluoropentanoic acid (H-PFPeA), 3:8 FTAm, PFASAC (n=1), and N-dihydroxybutyl (diHOB) dimethyl ammoniopropylperfluoroalkanesulfonamide (N-diHOBAmP-FASA, n=2) were detected in multiple samples. In addition, several highly defluorinated FTCAs (e.g., 3:3 FTCA and 2:9 FTCA) and associated features with unsaturation (e.g., 3:3 FTUCA) and hydrogen substitution (e.g., H-4:9 FTCA) tended to emerge in the aeration tanks or clarifiers and decline over the subsequent treatment(s). Observation of these PFAS features corroborated their essential roles in the biotransformation of unknown long-chain precursors in the wastewater. Some of these PFAS features can also be precursors for short and ultrashort-chain PFAAs, underscoring future investigations on their fate and transport in aquatic environments.