Aerobic Biotransformation and Biodefluorination of Fluorotelomer Carboxylic Acids (FTCAs) in Municipal Wastewater Treatment Sludge

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Background/Objectives. Fluorotelomer carboxylic acids (FTCAs, e.g., 6:2 FTCA and 5:3 FTCA) are essential precursors of perfluoroalkyl carboxylic acids (PFCAs). They are also reported as critical biotransformation intermediates of many other PFCAs precursors (e.g., fluorotelomer alcohols [FTOHs], fluorotelomer sulfonates [FTSs], and fluoroalkyl phosphates [PAPs]) leading to PFCA accumulation. FTCAs have been widely detected in landfill leachates, eliciting a higher bioaccumulating potential and toxicity than their corresponding PFCAs. The discharge of landfill leachates into municipal wastewater treatment plants (WWTPs) is one major path for FTCAs to enter aquatic environments. In this study, we conducted batch experiments to investigate the biotransformation and biodefluorination potentials of 6:2 FTCA and 5:3 FTCA by activated sludge from four municipal WWTPs in the New York Metropolitan Area. Microbial species that may contribute to the FTCA biotransformation were characterized by the combination of the next-generation sequencing and bioinformatics.

Approach/Activities. Sludge samples were centrifuged at 12,000 rpm and then washed three times with phosphate buffer saline (PBS). For each sludge, 1 g was inoculated into serum bottles (160 mL as the total volume) containing 50 mL of synthetic wastewater. 5:3 FTCA or 6:2 FTCA was spiked at an initial concentration of 80 μM. Microcosms were incubated at room temperature (24±3°C) while being shaken at 130 rpm. Killed controls were prepared with autoclaved sludge to distinguish the abiotic loss of FTCAs, while analytical controls were prepared with sterile Mili-Q water and FTCAs. Sampling was operated on 0, 1, 2, 3, 5, and 7 day. Quantificative analysis of FTCAs and their legacy metabolites was achieved by nano electrospray ionization high-resolution mass spectrometry (Nano-ESI-HRMS), operated by a high-resolution Q Exactive hybrid quadrupole−Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA). Fluoride concentration was determined using the Orion Star Meter equipped with fluoride electrodes (Thermo-Fisher Scientific). 16S rRNA amplicon sequencing was performed by the MiSeq Sequencing System (Illumina, San Diego, CA).

Results/Lessons Learned. After 7-day incubation, 40.0~62.4 μM of 6:2 FTCA was removed with significant defluorination (12 ~37 μM F-), and 25% to 37% of 6:2 FTCA removal was contributed by abiotic process (i.e., adsorption). An average of 0.5~1.7 fluorine was released per biotic removed 6:2 FTCA molecule. In contrast, 16.7~50.2 μM of 5:3 FTCA was removed with negligible abiotic removal (<1%) or fluoride release (< 4 μM). Legacy metabolites based on one-carbon removal pathway were identified and quantified. However, the molar discrepancy between removed FTCA and the sum of detected metabolites for 6:2 FTCA (20%-51%) and 5:3 FTCA (45%-87%) indicated the existence of metabolites that have not been characterized. These results also revealed 5:3 FTCA followed non-fluoride-releasing pathways that were unknown. 16S rRNA analysis implied that the genera of *Prosthecobacter*, *Sediminibacterium*, and *Dechloromonas* might contribute to the aerobic FTCA biotransformation. We are in the process of identifying the unknown biotransformation metabolites for both FTCAs using non-target and suspect screening workflow. Our research is of fundamental scientific value to advance our understanding of the fate, biotransformation mechanism, and environmental impact of FTCAs of distinctive structures.