Biological and Chemical Transformation of a PFAS Precursor with Insights into PFAS Fate and Forensics

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Background/Objectives. Sites impacted by per- and polyfluoroalkyl substances (PFAS) from aqueous film forming foam (AFFF) contain co-contaminants that can stimulate biotransformation of polyfluoroalkyl substances. Here, we compare how microbial enrichments from AFFF-impacted soil amended with diethyl glycol monobutyl ether (DGBE; found in AFFF), aromatic hydrocarbons (present in co-released fuels), acetate and methane (substrates used or formed during bioremediation) impact the aerobic biotransformation of N-dimethyl ammonio propyl perfluorohexane sulfonamide (AmPr-FHxSA), a common AFFF ingredient. Our objective was to compare biotransformation rates and products using different microbial communities to provide insights into the fate of AmPr-FHxSA and similar PFAS precursors. Additionally, we examined chemical oxidation products of AmPr-FHxSA and its biotransformation product perfluorohexane sulfonamide (FHxSA). Understanding products that could be formed with different microbial communities can inform which PFAS to target for source attribution forensics analyses. When PFAS analytical methods are limited to a set of 30 to 40 compounds, many of which are perfluoroalkyl acids, some of the PFAS mass including unknown biotransformation products may be missed, thus underestimating PFAS contamination in a given sample.

Approach/Activities. We performed aerobic biotransformation batch tests in triplicate over 70 days, with an enrichment culture seeded from an AFFF-impacted site, and four different carbon sources to impact the microbial community. Carbon sources used were DGBE, aromatic hydrocarbons (mixture of benzene, toluene, ethylbenzene, and xylene), acetate, and methane. AmPr-FHxSA was added to each triplicate, and PFAS were monitored weekly or biweekly using liquid chromatography tandem mass spectrometry. Additionally, high resolution mass spectrometry (HRMS) was performed at the start and end of the experiment to capture non-targeted products. We also exposed AmPr-FHxSA and FHxSA to the total oxidizable precursor (TOP) assay, which is used to quantify the mass of unknown PFAS precursors in a mixed PFAS sample. For this reason, the TOP assay can be an extremely useful tool for PFAS forensics analyses to capture precursor mass and close mass balances. Finally, we tested mineralization of AmPr-FHxSA using sulfate radicals produced by heat-activated persulfate oxidation (HAPO).

Results/Lessons Learned. Methane and acetate oxidizing cultures resulted in the highest yields of identifiable, targeted products (38% and 30%, respectively), including FHxSA and perfluorohexane sulfonic acid (PFHxS). Using these data and HRMS results, we proposed and detailed a transformation pathway. AmPr-FHxSA was mineralized by HAPO and mostly transformed to perfluorohexanoic acid during the TOP assay, with a small percentage of yield going to PFHxS. Compounds similar to FHxSA may be key biotransformation products of a class of PFAS precursors but are currently not included in standard targeted PFAS analytical methods. In this poster, we will show these results and discuss the biotransformation pathways of these PFAS precursors in the context of fate, transport, and forensics analyses, including PFAS compounds indicative of biotransformation and site assessment considerations.