

Electrochemical Treatment of Perfluoroalkyl Acid (PFAA) Precursors and PFAAs in Groundwater Impacted with Aqueous Film Forming Foams

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Background/Objectives. While several oxidative technologies have been proposed for treatment of waters impacted by aqueous film forming foams (AFFFs), information is generally lacking regarding the transformation pathways associated with the wide range of chemical precursors to the perfluoroalkyl acids (PFAAs) typically present in such waters. This study examined the oxidative electrochemical treatment of poly- and perfluoroalkyl substances (PFASs), including precursors, in a series of bench-scale experiments for two natural groundwaters impacted by AFFF.

Approach. Electrochemical experiments were performed using boron-doped diamond anodes in both undivided and divided cell configurations. Two natural groundwaters were examined: a groundwater freshly spiked with an AFFF solution, and a groundwater collected from a former firefighting training area that represented an “aged” AFFF source. Groundwater was analyzed using LC-MS/MS to quantify the perfluoroalkyl acids (PFAAs), and using high resolution mass spectrometry (HRMS) to semi-quantitatively determine potential precursors. Defluorination was determined by fluoride analysis via ion chromatography. The total oxidizable precursor assay (TOP) also was performed on each groundwater to further assess precursor transformations.

Results. Results from the first groundwater studied (freshly spiked with AFFF) suggested a transformation pathway where sulfonamide-based PFASs oxidatively transformed to primarily perfluorinated sulfonamides and perfluorinated carboxylic acids (PFCAs), with subsequent defluorination of the PFCAs. Transient increases in the perfluorinated sulfonamides and PFCAs were observed. These results were consistent with those of the TOP assay performed on the untreated water, where substantial generation of PFCAs was observed. For the second groundwater studied (aged AFFF source), no transient increases in PFAAs were measured, despite the presence of similarly structured suspected PFAA precursors and substantial defluorination. Assessment of precursor compound transformation for the second groundwater by HRMS noted the formation of keto-perfluoroalkane sulfonates, which were not observed in the first groundwater studied. Together, these results confirm that oxidation and defluorination of suspected PFAA precursors in the second groundwater underwent transformation via a pathway different than that of the first groundwater.

For both waters, suspected precursors were the primary sources of the generated fluoride, not the PFAAs originally present. Thus, suspected PFAA precursors represented the bulk of the organofluorine content. For the second groundwater, no PFAA generation was observed following the TOP assay. This result suggests that the TOP assay may not be a good indicator of organofluorine content and suspected precursors originating from AFFF sources.