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Fate of PFAS precursors in Wetlands under Redox-Dynamic conditions

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The use of aqueous film-forming foams (AFFF) has significantly contributed to the release of per- and polyfluoroalkyl substances (PFASs) into the environment. Perfluoroalkyl acid (PFAA) precursors in AFFF undergo transformations into persistent perfluoroalkyl acids; however, the biogeochemical controls governing these transformations remain poorly understood. Wetlands, located at terrestrial–aquatic interfaces, regulate PFAS mobility and transformation, but the dynamics of precursors' fate in these systems are not well characterized. This contribution examines the fate of PFAA precursors in vegetated wetland mesocosms, focusing on: (i) the influence of hydrologically driven and rhizosphere redox gradients on precursor transformation; and (ii) the partitioning of precursors and terminal transformation products (TPs) among pore water, soil, and plant biomass as a function of molecular properties.

Four precursors were added to mesocosm soil: two anionic (5:3 FTCA and 6:2 FTS) and two zwitterionic compounds (6:2 FTAB and AmPr-FHxSA). Treatments included planted (Phragmites australis) or unplanted mesocosms maintained under continuously flooded (CF) or alternate wetting and drying (AWD) hydrology.

Precursor transformation was primarily driven by oxygen exposure, following the hierarchy: AWD unplanted > AWD planted > CF planted > CF unplanted. Time-resolved porewater analysis confirmed that 5:3 FTCA and 6:2 FTS concentrations decreased significantly following dry-down periods, identifying physical redox oscillations as more potent drivers of transformation than localized rhizosphere effects. Within oxic periods, 5:3 FTCA transformed more rapidly than 6:2 FTS. This pattern agrees with previous results from soil slurries, suggesting that rank-ordering of transformation rates persists across experimental scales. Conversely, the sulfonamide AmPr-FHxSA exhibited the lowest transformation efficiency, as strong soil sorption limited its bioavailability.

A complete mass balance reveals that total TP mass was highest in AWD systems, confirming that this hydrological regime accelerates the generation of mobile TPs. Analysis of bioaccumulation factors (BAF) showed highly selective plant uptake; while the sulfonate PFHxS showed limited translocation, carboxylic acids exhibited greater uptake, with BAFs showing a clear dependency on perfluorinated chain length. These findings demonstrate that in hydrologically dynamic wetlands, PFAS fate is governed by redox-driven transformation and chemical-specific partitioning, providing a mechanistic framework to predict attenuation of complex mixtures of PFAS at terrestrial-aquatic interfaces.