**Analysis of ultrashort-chain and volatile PFAS in water. A perspective on sample preparation and analysis by 19F NMR.**

Routine targeted LC-MS analytical methods are unable to identify a significant fraction of total fluorine in environmental water samples. As much as 97% of the total fluorine in some samples remains unknown as evidenced by the unaccounted fluorine during mass balance.

We posited that by analytically capturing ultrashort-chain (USC) and volatile PFAS, either introduced to wastewater in their native form or created via degradation from larger PFAS precursors, we can narrow the gap in the fluorine mass balance.

Analyses by 19F NMR, ion chromatography (IC), targeted LC-MS, and supercritical chromatography were employed to quantify the loss of USC and volatile PFAS (trifluoroacetic acid, fluoroacetic acid, difluoroacetic acid, perfluorobutanoic acid and 6:2-FTOH). The PFAS analytes were spiked into water samples and concentration by (i) lyophilization, and (ii) solid phase extraction coupled with solvent removal under nitrogen. Results show that full solvent or water removal during nitrogen drying and lyophilization, respectively, greatly diminishes the recovery of USC and volatile PFAS. Similarly, we demonstrate that the temperature control of lyophilization is beneficial for more complete PFAS recovery.

The results from this research may be used to inform best practices for the analysis of USC and volatile PFAS and more effectively interrogate the unaccounted fluorine in environmental water samples.