The contribution of short chain PFCAs and unknown PFASs to total organic fluorine in environmental samples

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Over 3000 of per- and polyfluoroalkyl substances (PFASs) are being produced and used in consumer and industrial products. Due to analytical limitations, only a small fraction of PFASs are currently identified and monitored and the remain majority is “unknown”. In the present study, to reveal the contribution of this unknown PFASs, the total oxidizable precursor (TOP) assay has been applied to precipitation samples collected from twenty-eight cities and leachate samples collected from seven municipal solid wastes (MSW) disposal facilities in Tianjin. The occurrence of unknown precursors of perfluoroalkyl acids (PFAA-precursors) as revealed by TOP was for the first time uncovered in precipitation, contributing 6%-56% of the total molar concentrations of PFASs with maximum estimated fluxes of C6 and C8 PFAA-precursors at 3.1×10^3 and 4.3×10^3 ng/m^2/d, respectively. The relative contribution of ultrashort-chain perfluoroalkyl carboxylic acids (PFCAs), i.e., trifluoroacetic acid (TFA, C2) and perfluoropropionic acid (PFPrA, C3), ranged from 22% to 91% of ∑PFASs. Unknown C4-C12 PFAA-precursors were found contributing 10.1%-97.3% in leachate samples by molar concentrations accounting for additional mass loads of 15.1%-43.1%. Using an optimized treatment method, TFA and PFPrA were for the first time determined before and after TOP assay in leachate samples at dominant levels of 1.90×10^4-8.07×10^4 ng/L with estimated mass loads of 7.54×10^{-2}-2.63 kg/y/site. The unknown precursors were found contributing 12.1%-93.0% to ultrashort-chain PFCAs in leachate samples with estimated mass loads of 0.101-2.96 kg/y/site. After treatment, unknown precursors remained contributing 0.35%-68.3% to C2-C12 PFAAs in leachate. These results bear critical concerns on underestimation of PFAS mass load from precipitation and leachate to surface environment and groundwater ascribed to monitoring data solely on known PFASs. The present study renders a more accurate estimation of mass load of PFASs from precipitation and MSW facilities by evaluating ultrashort-chain PFCAs and unknown PFAA-precursors.