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Identification of PFAS Hotspots in German Rivers: Target Analysis vs. the Direct Total Oxidizable Precursor Assay

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Abstract

The group of per- and polyfluoroalkyl substances (PFAS) comprises several thousand substances. The ever growing number is a major challenge for their chemical analysis. One analytical approach to overcome the complexity of PFAS are sum parameters, such as the total oxidizable precursor (TOP) assay. In this study, we conducted a spatial monitoring study with more than 210 suspended particulate matter (SPM) and sediment samples from rivers and lakes from Germany and the Netherlands to analyse spatial differences and identify contamination hotspots. All samples were analyzed by target analysis and a modified TOP assay (‘direct’ TOP (dTOP) assay, in which a small amount of sample is completely digested, converting previously unmeasurable precursors to measurable perfluorinated compounds.

The analysis revealed substantial differences between the different water bodies in both, the level and type of contamination. The ∑PFAS concentrations ranged from <0.5 to 53.1 µg/kg dry weight (dw) in the target analysis and from <1.0 to 336.8 µg/kg in the dTOP assay. The levels of perfluoroalkyl acids (PFAA) were substantially higher in the dTOP assay compared to the target analysis demonstrating the significant presence of unidentifed precursors in the samples.

As a simplistic approach to identify hotspots of PFAS contamination the 90th percentiles (P90) for target analysis ($P90_{Target}$: 7.11 µg/kg dw) and dTOP assay ($P90_{dTOP}$: 67.6 µg/kg dw), respectively, were used as thresholds. Both methods identified 17 hotspots, but only five of the sampling sites were consistently identified as hotspots by both methods. Thus, the majority of hotspots identified with the dTOP assay was overlooked by the classical target analysis.

The results of this study demonstrate the ubiquitous burden of PFAS in German rivers especially by unknown precursors. Only some of the hotspots identified in this study were (publicly) known before. At many of the hotspots and other sampling sites, however, the source of the PFAS contamination remains unknown and must be elucidated in the future to prevent further discharge into the environment.