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Closing PFAS analytical gaps: Inter-method evaluation of total organofluorine techniques for AFFF-impacted water

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ABSTRACT

Multiple poly- and perfluoroalkyl substances (PFASs) are present in aqueous film-forming foams (AFFF) used for firefighting activities. Currently, no single analytical technique provides a complete accounting of total PFASs or total organofluorine content in AFFF-contaminated samples. To provide insight into the performance of existing methods, we compared ten previously described PFAS measurement techniques. In AFFF-amended tap water, US EPA Methods 533 and 1633, adsorbable organic fluorine with particle induced gamma emission spectroscopy (AOF-PIGE) and fluorine-19 nuclear magnetic resonance (^{19}F NMR) provided similar estimates of total fluorine. The total oxidizable precursor (TOP) assay, suspect screening, and adsorbable organic fluorine with combustion ion chromatography (AOF-CIC) yielded estimates of total organic fluorine that were about two to three times higher than the other techniques. Proximate to AFFF sources, suspect screening and modified EPA Method 1633 yielded higher results, while the TOP assay results were between the other two sets of analyses. Further from sources, suspect screening, modified EPA Method 1633, and the TOP assay yielded similar results that were 4-fold higher than results from targeted quantification methods, such as EPA Method 1633. These results are consistent with expectations about PFAS behavior and inform the selection of analytical techniques used for PFAS contamination characterization efforts.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) include over 8000 compounds utilized for various industrial and commercial applications (Evich et al., 2022; Buck et al., 2011). The use of PFAS-containing aqueous film-forming foams (AFFF) for firefighting at military bases, civilian airports, oil refineries and firefighter training centers represent a major source of contamination of water, soil and sediments with PFASs (Barzen-Hanson et al., 2017). While the initial introduction of AFFF in 1963 featured specific PFASs, (Ateia et al., 2023a) it is important to note that these formulations have since undergone changes. Presently, AFFF generally comprises perfluoroalkyl acids, such as perfluoroalkyl carboxylates and perfluoroalkyl sulfonates, alongside an assortment of anionic, cationic, and zwitterionic polyfluoroalkyl compounds (Nickerson et al., 2020). These constituents can undergo transformations through both abiotic and biotic processes, resulting in the

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formation of various other compounds, including perfluoroalkyl acids (Jin et al., 2023; Zhang et al., 2021). Consequently, AFFF-impacted sites often feature complex mixtures of PFASs, many of which currently lack analytical standards (Nickerson et al., 2020).

As part of efforts to better account for the PFASs in wastewater, PFAS-impacted solids, surface-and groundwater researchers have developed analytical methods that provide an aggregate measure of total organofluorine content. Comparison of data from these characterization methods with targeted measurement of PFASs by LC/MS-MS methods (which only include compounds for which analytical standards are available) suggest that only a fraction of the organofluorine content of AFFF-derived PFAS mixtures can be quantified directly (Pelch et al., 2023; Wellmitz et al., 2023; Hao et al., 2021). Complementary aggregate techniques, like the total oxidizable precursor (TOP) assay, suspect screening, and total organofluorine quantification have been developed to gain more information about unidentified PFASs (Getzinger et al., 2021; Charbonnet et al., 2022). These methods, however, exhibit considerably different estimates of total organofluorine compound concentrations (Rehnstam et al., 2023) when the same sample is analyzed by multiple methods. These differences are attributable to the underlying chemistry of the measurement technique.

Measuring precursors that can be oxidized to perfluoroalkyl acids is important to efforts to characterize PFAS contamination because it provides information on the concentration of compounds for which direct quantification methods are not available (Ateia et al., 2023b). Because the same kind of oxidative transformation reactions in the TOP assay occur in the environment, it also may provide insight into the potential for precursors to be converted into perfluoroalkyl acids by microbes, chemical oxidants or in vivo processes. Suspect screening is a technique that involves identifying and quantifying concentrations of compounds present in a sample by using a list of potential candidates. Quantification is considered to be semi-quantitative because surrogate standards are used that are believed to behave in a similar manner to the target compounds. In contrast, non-target analysis is used to identify compounds present in a sample without prior knowledge of its presence. It offers a broader potential for assessing the full scope of PFAS contamination but it cannot provide quantitative data for the compounds that are detected.

Methods that quantify total organofluorine content in environmental samples are not affected by individual product yields or the selection of surrogates. Such methods include detection of adsorbable organofluorine by combustion ion chromatography (AOF-CIC), detection of adsorbable organofluorine by particle-induced gamma ray emission spectroscopy (AOF-PIGE), (Tighe et al., 2021) and fluorine-19 nuclear magnetic resonance spectroscopy (^{19}F NMR) (Camdzic et al., 2023; Gauthier and Mabury, 2022). All three are inclusive methods that detect diverse PFAS (Ritter et al., 2017; Han et al., 2021). Lower detection limits compared to LC/MS-MS methods, however, require preconcentration from relatively large sample volumes. As with other methods using preconcentration, the total organofluorine methods may underestimate compounds with poor adsorbability/retention. For ^{19}F NMR, chemical shift information can distinguish among different fluorinated functional groups; (Bhat et al., 2024, 2022) in particular, most linear PFASs share a characteristic ^{19}F NMR response signal from the terminal CF_3 near -83 ppm (Camdzic et al., 2023).

Although each of the available quantification methods measure a different subset of PFASs and each method has different limitations, a direct intercomparison of the performance of all methods is not yet available (Han et al., 2021; Gehrenkemper et al., 2021; Forster et al., 2023). To address this gap, we performed a systematic inter-method evaluation of ten analytical methods using AFFF diluted into tap water and two samples of AFFF-impacted groundwater. By simultaneously analyzing samples with targeted quantification methods and aggregate methods, we provide insight into the strengths and weaknesses of available approaches as well as guidance on ways to use combinations of methods to characterize AFFF contamination.

2. Materials and methods

2.1. Description of samples

An electrochemical fluorination (ECF) derived AFFF was collected from a tank at a U.S. Air Force Facility (Hao et al., 2021) and was used to spike tap water (~10,000,000-fold diluted) collected at the University of California at Berkeley. All spiked tap water samples were used as received from the tap (without dechlorination) and were run in 5–6 experimental replicates for all the tested analytical methods. Tap water in this location typically contains residual chloramines at concentrations of 3–4 mg/L as Cl_2 (EBMUD, 2023). However, scientific studies suggests that the reaction between chloramines and PFAS precursors might be slow or inefficient under these conditions (Twight, 2019). In addition, two groundwater samples were collected from a PFAS-impacted aquifer near a military site (DOC: 1.3 – 1.9 mg C/L and pH ~ 7.0). Selection criteria for the wells that were sampled were based on 2022 groundwater monitoring data from EPA Method 1633 provided by the site managers (data not available publicly). The first monitoring well (Site 1) featured higher PFOA+PFOS concentration (1.8 ± 0.1 μg/L) and was chosen to represent contamination near the source. The second well (Site 2), located approximately 500 m downgradient, featured lower concentrations (though still above detection limits for method 1633; PFOA+PFOS, 0.07 ± 0.002 μg/L) and represented conditions likely to be encountered after sorption and biotransformation had removed the less mobile PFAS.

2.2. PFAS analytical methods

Ten available analytical methods were utilized in this study. Four of the methods quantify a specific, though limited number of individual PFAS with detection by HPLC/MS-MS (i.e., EPA Method 533, (USEPA, 2019) EPA Method 537.1, (Shoemaker, 2020) EPA Method 1633, (USEPA, 2021) and modified EPA Method 1633 (similar to EPA Method 1633 without any changes to the SPE extraction technique or analytical protocols but with 21 additional analytes)) while two methods quantify select organofluorine compounds for which standard methods are not available (i.e., suspect screening (see details in S.1.4), TOP assay (total concentration of fluorine in PFCAs + PFSAs after oxidation; ultrashort compounds (e.g., TFA and PFPrA) were not measured (Houtz and Sedlak, 2012). Three methods were used to quantify total organofluorine compounds (i.e., AOF-CIC, (USEPA, 2022) ^{19}F NMR, and AOF-PIGE (Tighe et al., 2021) as an estimate of total PFAS (i.e., providing no measurement of concentration of individual PFAS). Finally, a GC-MS/MS method targeting semi-volatile PFASs, fluorotelomer alcohols and acrylates was included. Specific details on these methods are listed in Section S.1 of the SI and related documentation cited in that section. Lists of analytes and limits of quantifications for specific methods are in sections S.2 and S.3.

3. Results

3.1. AFFF-spiked tap water

As an initial investigation, nine techniques were evaluated for measuring total organofluorine in AFFF-spiked tap water (see total organofluorine calculation in Section S.6 in SI). The two most commonly used targeted quantification methods (i.e., EPA Method 533 and EPA Method 1633) yielded similar total organofluorine values (i.e., 107.8 ± 6.4 nM and 120.5 ± 2.3 nM, respectively; Fig. 1). This similarity is notable given that PFOS (~3 μg/L) and PFHxS (~0.3 μg/L), the two PFAS detected at the highest concentrations in these samples, were identified by both methods. Two other methods yielded similar results to those obtained by the targeted quantification method: AOF-PIGE (110.1 ± 9.6 nM) and ^{19}F NMR (110.0 ± 11.9 nM). The modified version of EPA Method 1633, which included 61 PFASs for which reference

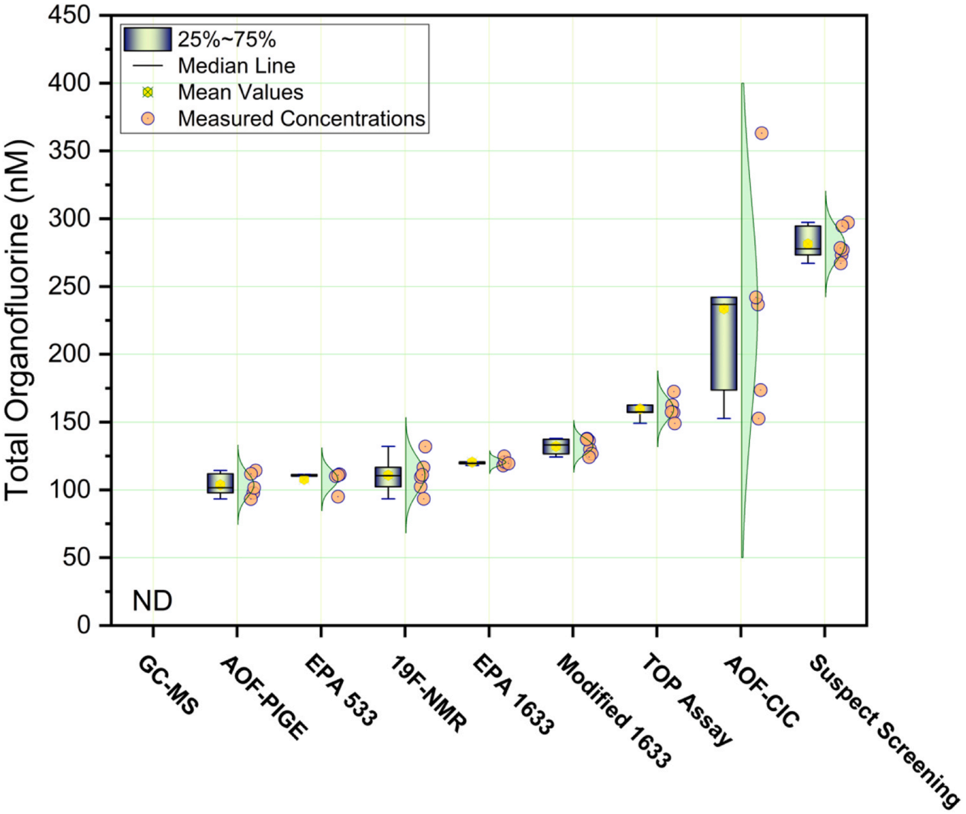

Fig. 1. Total organofluorine concentrations measured by nine methods in spiked tap waters (n=5 except ^{19}F NMR, modified EPA Method 1633 and suspect screening (n=6). ND: Not Detected. Green areas are density curves, where the width of each curve corresponds with the approximate frequency of data points in each region. *Uncertainty is represented as standard deviation of replicate samples and does not represent uncertainty in the quantitative method used for suspect screening.

standards are available (Table S.2) yielded a total concentration that was about 10 % higher than those obtained with EPA Method 1633, which included 40 PFASs ($p<0.05$). About 10 % of the increase in PFASs for the modified EPA Method 1633 was attributable to the presence of PFPrS, Cl-PFOS, FHxSA and PFEtCHxS which were not monitored by any other method (see Figure S.3).

Three of the aggregate analysis methods yielded considerably higher concentrations. The TOP assay coupled with solid phase extraction and LC-MS/MS analysis, yielded estimates of total organofluorine concentration that were about 50 % higher than the targeted quantification techniques (160 ± 8 nM), likely due to the presence of polyfluoroalkyl compounds in 3 M AFFF for which analytical standards are not available (Edmiston et al., 2023). The AOF-CIC method yielded estimated total organofluorine concentrations that were about twice as high as the targeted quantification methods (234 ± 73 nM), while semiquantitative analysis using the suspect screening approach yielded even higher organofluorine concentrations (281 ± 13 nM). Although the semi-quantitative suspect screening method captured the highest concentrations of total organofluorine compounds, its use is limited to laboratories with high resolution mass spectrometry (HRMS) and trained analysts, while the TOP assay and AOF-CIC can be run in most commercial or research labs. It should also be noted that the GC/MS-based method failed to yield any data above the limit of detection of this method (50–250 ng/L depending on the analyte).

Among the widely accessible methods, AOF-CIC yielded the highest estimates of total organofluorine compounds in AFFF-contaminated waters. However, the AOF-CIC method exhibited substantial variability among replicate analyses. This may be because the method detection limit for AOF-CIC is 50 nM (or 1 μg F/L), which is close to the amount of targeted PFASs that was added to the sample ($C_0 \sim 150$ nM or 3 μg/L), which is comparable to the range of concentrations reported for environmental samples (e.g., 10–400 nM as in Figs. 2 and 3). As a result, AOF-CIC exhibited lower precision in these samples. Less commonly used aggregate methods such as AOF-PIGE and ^{19}F NMR have somewhat higher sample volume requirements for preconcentration (e.g., at least 1 L sample for ^{19}F NMR; 1.5 L sample for AOF-PIGE) and yielded estimates of total organofluorine compounds that were lower than those obtained by AOF-CIC and the TOP assay. The ^{19}F NMR spectra are in Section S.7.

3.2. PFAS-impacted groundwater

Results from analysis of the two samples from PFAS-impacted groundwater provide further insights into the performance of the aggregate characterization methods under conditions encountered in less contaminated samples near source zones and at downgradient locations. According to results from the targeted quantification methods (Fig. 2), the sample collected from Site 1 contained concentrations of targeted PFASs that were about twice as high as those in the diluted AFFF depicted in Fig. 1. However, the downgradient groundwater sample (Site 2) contained PFAS concentrations that were about one order of magnitude lower than those detected at Site 1 (Fig. 3).

The Site 1 sample which was collected in source zone is believed to be impacted by similar AFFF types as those used for the AFFF-spiked tap water samples described in the previous section. PFAS concentrations from modified EPA Method 1633 and the suspect screening method were about twice as high as the values obtained by the standard targeted quantification methods (i.e., EPA Method 533 and EPA Method 1633), whereas the TOP assay yielded results that were about 50 % higher than the targeted quantification methods. The ^{19}F NMR method yielded results that were about 25 % higher than the targeted quantification methods. This sample was only analyzed once due to limited remaining sample volume being available, and additional volume may have improved the result (Camdzic et al., 2023; Gauthier and Mabury, 2022).

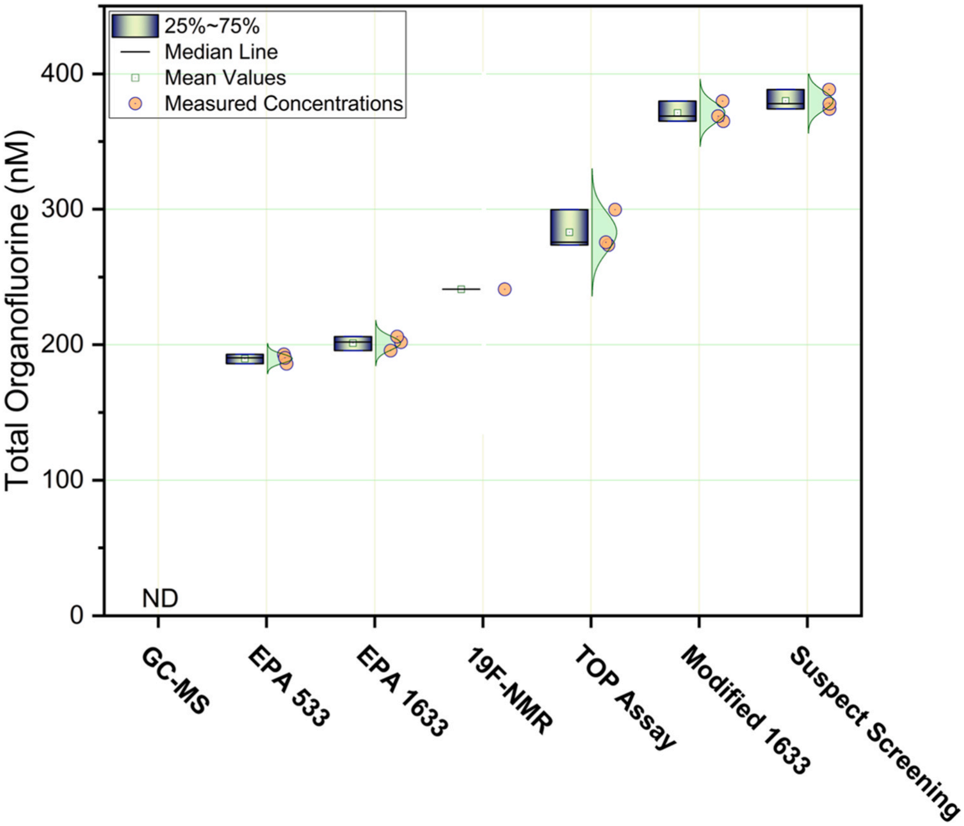

Fig. 2. Total organofluorine concentrations measured by seven methods in a groundwater sample from a field site (Site 1) with high PFAS concentration (n=3) except for ^{19}F NMR, (n = 1). Green areas are density curves, where the width of each curve corresponds with the approximate frequency of data points in each region. ND: Not Detected. *Uncertainty is represented as standard deviation of replicate samples and does not represent uncertainty in the quantitative method used for suspect screening. * AOF-CIC was not selected for this analysis because results from analysis of spiked spiked tap waters indicated high variability under these conditions.

No PFASs were detected by GC-MS analysis.

Results from analysis of samples collected downgradient of the source (Site 2) yielded lower PFAS concentrations but indicated a trend similar to Site 1, where the TOP assay (10.1 ± 2.3 nM) yielded a higher estimate of total organofluorine concentration compared to the EPA Method 1633 (2.2 ± 1.6 nM), EPA Method 533 (7.0 ± 0.03 nM) and modified EPA Method 1633 (8.5 ± 0.3 nM) and suspect screening (modified EPA Method 1633 + semiquantitative analysis of the suspect analytes (8.7 ± 0.3 nM)). AOF-PIGE and AOF-CIC were not employed for these samples due to the need for high sample volumes (>250 mL per analysis) and the low sensitivity of the methods.

4. Discussion

4.1. Impacts of concentrating extracts during sample preparation

Results from the sample associated with Site 1 suggest that the three sulfonamides (FBSA, FPeSA and FHxSA; see attached excel sheets and Figure S.4 in SI) explain some of the differences between the reported total organofluorine concentration between EPA Method 533, EPA Method 1633, the TOP assay, modified EPA Method 1633 and the suspect screening analysis. For this sample, these three compounds accounted for about 35 % of the total mass of F. Incorporation of sulfonamides into the targeted PFAS lists would require method modification to mitigate losses, as was done for the modified EPA Method 1633. For instance, results from the TOP Assay indicate that compounds like FHxSA undergo volatilization when the sample is heated or are lost when samples are blown to dryness (unpublished data). Therefore, enhancements in the methodology are essential to minimize sulfonamide losses.

4.2. Discrepancies between TOP assay, modified EPA method 1633 and suspect screening

The observation that total organofluorine concentrations obtained by the TOP assay are sometimes lower than those obtained from the modified EPA Method 1633 or suspect screening is consistent with our understanding of the way that the oxidation process works. Estimates of total organic fluorine by the TOP assay are based on an assumption of quantitative conversion (i.e., 100 % yield) to measurable target PFAS, despite the observation of conversions in the range of 70—90 % for compounds like perfluoroalkyl sulfonamides (Houtz and Sedlak, 2012). Although it might be possible to adjust organofluorine compound concentrations by correcting for incomplete conversion of the compounds, such approaches would require assumptions that would be difficult to justify or correct among samples. It should also be noted that trifluoroacetic acid (TFA) and perfluoropropanoic acid (PFPrA) were not measured by the TOP assay implemented here. This omission could be significant, as these ultrashort compounds account for about 20–50 % (molar fluorine) of the perfluorocarboxylates produced when certain AFFF are subjected to the TOP assay (Tsou et al., 2023; Martin et al., 2019). Additionally, the TOP assay may generate unknowns beyond these ultrashorts, including non-traditional endpoints such as oxa-unsaturated perfluoroalkyl acids (UPFECAs), perfluoro cyclopentane carboxylic acids (PFCPeCAs) and H-PFCAs for AFFFs (Shojaei et al., 2022; Liu et al., 2024). Incorporating these non-traditional endpoints presents challenges, such as the need for new analytical methods or standards.

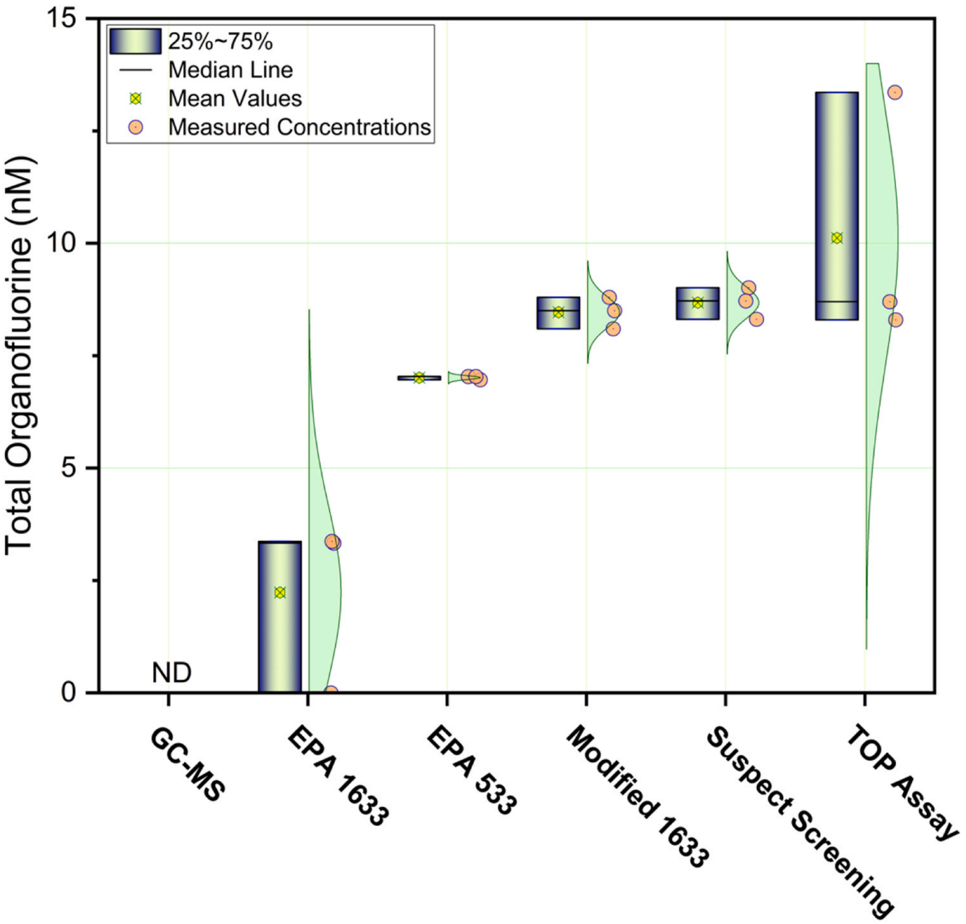

Fig. 3. Total organofluorine concentrations measured by five methods in a groundwater sample from a field site (Site 2) with low PFAS concentration (n=3). Green areas are density curves, where the width of each curve corresponds with the approximate frequency of data points in each region. ND: Not Detected. *Uncertainty is represented as standard deviation of replicate samples and does not represent uncertainty in the quantitative method used for suspect screening.

4.3. Detection and recovery issues with total fluorine methods

Results for the total organofluorine methods suggest a tradeoff between greater analytical inclusivity compared to LC-MS/MS methods and analyte losses during preconcentration steps required to accommodate higher detection limits. For ^{19}F NMR, the lower total organofluorine concentrations detected compared to the TOP assay and suspect screening may be attributable to volatile losses during extract dry down/concentration, incomplete elution from the mixed bed cartridges, and/or poor retention of ultrashort chain PFAS on the mixed bed cartridges. Increasing the signal-to-noise ratio for more accurate measurements can be achieved by increasing the ^{19}F NMR scan count. However, a four-fold increase in scan count, which doubles the signal-to-noise ratio, yielded an increase of only 10.6 nM in the overall fluorine detection for one AFFF-spiked tap water sample (Figure S.1). Consequently, it is improbable that the higher limits of detection for ^{19}F NMR are the cause of the differences in detection between ^{19}F NMR and the methods that yielded higher results.

Quantification using AOF-CIC exhibited relatively high variability in total organofluorine measurements (Fig. 1), indicative of apparent precision issues specific to AOF-CIC when applied to AFFF-impacted waters. Although AOF-PIGE exhibited a lower variability, the reported concentrations were 1.5 – 3 fold lower than the TOP assay and semi-quantitative analysis. It should be noted that the limit of quantification (LOQ) for AOF-CIC and AOF-PIGE was 1 μg F/L (or 52.6 nM). Several factors may contribute to the low precision, such as variability in inorganic fluorine content of carbon adsorption tubes, poor and/or inconsistent retention of shorter chain PFASs, inconsistent separation of inorganic fluorine during column washing, or contamination of the wash solutions, combustion chamber and/or condensation tubing (Pan and Helbling, 2023).

4.4. Discrepancies observed for EPA Method 1633 in field samples

Results from the sample associated with Site 2 suggest that EPA Method 1633 exhibited a high level of variability. For this sample, no perfluorocarboxylic acids (PFCAs) were detected in any of the three replicates, which contradicted the modified EPA Method 1633, TOP Assay and EPA Method 533 results where PFCAs accounted for about 45 % of the total mass of F (SI Section S.8, Figure S.5). The high EPA Method 1633 LOQ (40–400 ng/L, see Table S.4) resulted in the reporting of all concentrations as ‘non-detect’, while the results from TOP Assay, modified EPA Method 1633 and EPA 533 confirm that multiple PFCAs were present in Site 2 with concentrations ranging from 1–30 ng/L. This discrepancy was not evident in Site 1 samples where PFCAs concentrations ranged between 80–720 ng/L. Therefore, method quantification limits should also be monitored along with PFASs concentrations to identify organofluorine content in environmental samples.

5. Conclusions

In summary, several approaches have been identified that could be useful for further development of the methods evaluated in this study (Table 1).

For methods that rely upon LC/MS-MS and the ^{19}F NMR, eliminating the need of nitrogen drying during extract concentration could prevent

Table 1
Suggestions to consider when examining total organofluorine with different methods.

Method	Current Practice	Better Practice
^{19}F NMR	• Mixed bed cartridges are used for PFASs extraction. • Extract concentration is performed by concentrating organic eluent under nitrogen gas which may result in loss of volatile precursors.	• Drying under nitrogen gas should be evaluated for loss of volatile precursors. • Cartridge composition and elution protocol should be optimized for PFAS retention and elution. • Lower detection limits.
AOF-CIC and AOF-PIGE	• Both AOF-CIC and AOF-PIGE use carbon-based adsorbent used for PFASs sorption. • AOF-PIGE is a screening tool to measure total organofluorine in a water sample. • AOF-PIGE needs pH adjustment to an acidic pH to reduce binding potential of inorganic F on carbon. • Proprietary wash solution used to remove inorganic fluorine for AOF-CIC. • Relatively high variability in total organofluorine observed with AOF-CIC.	• Alternative adsorbents for PFASs sorption. • Protocols to minimize variability are warranted. • Include ultra-short chain target analytes.
TOP	• ^{13}C FOSA used as oxidation surrogate	• Avoid losses of volatile compounds during sample blowdown.
EPA 533	• Examines 25 analytes. • Extract concentration is performed under nitrogen gas. • Does not analyze precursor compounds such as FBSA, FPeSA and FHxSA. • Does not include ultra-short chain target analytes.	• Adopt EPA 1633 protocols for PFASs analysis (avoid nitrogen drying). • Analyze additional precursor compounds with commercially available standards (e.g., FBSA, FPeSA and FHxSA). • Include ultra-short chain target analytes.
EPA 537.1	• Adopted for drinking water. • Extract concentration is performed under nitrogen gas. • Fails in high turbidity samples (>1 NTU).	• Filtration prior to analysis for field samples may be warranted.
EPA 1633	• Examines 40 analytes. • Does not involve extract concentration under nitrogen gas. • Does not analyze precursor compounds such as FBSA, FPeSA and FHxSA. • Does not include ultra-short chain target analytes.	• Analyze additional precursor compounds with commercially available standards (e.g., FBSA, FPeSA and FHxSA). • Include ultra-short chain target analytes.
Modified 1633	• Examines 61 analytes. • Does not involve extract concentration under nitrogen gas. • Includes precursor compounds such as FBSA, FPeSA and FHxSA.	• Inclusion of additional analytes may be warranted considering the suspect screening analysis with spiked tap waters. • In LC-MS, higher injection volumes can increase signal intensity but may also introduce noise and matrix effects, while lower volumes improve resolution but reduce signal. • Water quality parameters like pH, TDS, and organic content can affect detection accuracy.
GC-MS/MS	• Only limited to FTOHs and FTACs.	• Method amendment to include other volatile and semi-volatile (non-fluorotelomer) AFFF precursors is warranted. • Lower detection limits.

evaporative loss of volatile compounds. Methods such as EPA Method 533 and EPA Method 1633 could significantly benefit by the incorporation of additional standards as illustrated by application of the modified Method EPA Method 1633 in the groundwater samples. The widespread availability of additional analytical standards for PFASs known to be present in AFFF could improve total organofluorine recovery by targeted quantification methods. Further research on the transformation of polyfluorinated AFFF analytes may provide a basis for targeting the inclusion of transformation products in standard methods.

The GC-MS protocol was ineffective in this study. This may be attributable to its relatively low sensitivity and limited analyte list (i.e., it currently examines fluorotelomer alcohols and fluorotelomer acrylates). Protocols to incorporate perfluoroalkyl sulfonamides and other polyfluoroalkyl precursors might make this method more useful.

The TOP assay could be improved by developing approaches that avoid nitrogen drying from extracts. Inclusion of a wider range of target analytes, including ultrashorts and transformation products from ether compounds, could increase total organofluorine recovery.

For AOF-CIC, results indicate that protocols to minimize variability are warranted. This could potentially involve examination of background contamination in the carbon adsorbents and during combustion process, development of more reliable adsorbents for PFASs capture, and identification of steps to optimize the organofluorine recovery during eluent extraction protocols. Protocols to lower the detection limit of AOF-CIC and ^{19}F NMR would also be helpful. AOF-PIGE and ^{19}F NMR, although more precise than AOF-CIC, still need improvements with the sample preconcentration methods. Options include processing larger volumes, further optimization of cartridge composition and extraction/elution protocol (for ^{19}F NMR), using more than one carbon felts (AOF-PIGE) and/or using lyophilization (^{19}F NMR) as an alternate preconcentration method (Camdzic et al., 2023; Gauthier and Mabury, 2022).

Disclaimer

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Writing – review & editing, Funding acquisition, Formal analysis, Data curation. **FUHAR DIXIT:** Writing – review & editing, Writing – original draft, Validation, Project administration, Methodology, Formal analysis, Data curation. **Lisa Alvarez-Cohen:** Writing – review & editing, Supervision, Funding acquisition. **Edmund H. Antell:** Writing – review & editing, Methodology, Formal analysis. **David L. Sedlak:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis. **Katharine A. Faber:** Writing – review & editing, Methodology, Data curation. **Mohamed Ateia:** Writing – review & editing, Validation, Project administration, Investigation, Funding acquisition, Formal analysis. **Chuhui Zhang:** Writing – review & editing, Methodology, Data curation. **Manmeet W. Pannu:** Writing – review & editing, Data curation. **Megan H. Plumlee:** Writing – review & editing, Funding acquisition. **Jean Van Buren:** Writing – review & editing, Validation, Methodology, Formal analysis, Data curation. **Abraham Doroshow:** Methodology, Data curation. **William C.K. Pomerantz:** Writing – review & editing, Validation, Formal analysis, Data curation. **William A. Arnold:** Writing – review & editing, Funding acquisition, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data attached in SI as a locked excel sheet

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2024.100122.

References

Ateia, M., Buren, J.V., Barrett, W., Martin, T., Back, G.G., 2023a. Sunrise of pfas replacements: a perspective on fluorine-free foams. ACS Sustain. Chem. Eng. 11, 7986–7996.

Ateia, M., Chiang, D., Cashman, M., Acheson, C., 2023b. Total oxidizable precursor (TOP) assay— best practices, capabilities and limitations for PFAS site investigation and remediation. Environ. Sci. Technol. Lett. 10, 292–301.

Barzen-Hanson, K.A., Roberts, S.C., Choyke, S., Oetjen, K., McAlees, A., Riddell, N., McCrindle, R., Ferguson, P.L., Higgins, C.P., Field, J.A., 2017. Discovery of 40 classes of per-and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. Environ. Sci. Technol. 51, 2047–2057.

Bhat, A.P., Pomerantz, W.C., Arnold, W.A., 2024. Fluorinated pharmaceutical and pesticide photolysis: investigating reactivity and identifying fluorinated products by combining computational chemistry, ^{19}F NMR, and mass spectrometry. Environ. Sci. Technol.

Bhat, A.P., Pomerantz, W.C., Arnold, W.A., 2022. Finding fluorine: photoproduct formation during the photolysis of fluorinated pesticides. Environ. Sci. Technol. 56, 12336–12346.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., De Voogt, P., Jensen, A. A., Kannan, K., Mabury, S.A., van Leeuwen, S.P., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr. Environ. Assess. Manag. 7, 513–541.

Camdzic, D., Dickman, R.A., Joyce, A.S., Wallace, J.S., Ferguson, P.L., Aga, D.S., 2023. Quantitation of total PFAS including trifluoroacetic acid with fluorine nuclear magnetic resonance spectroscopy. Anal. Chem. 95, 5484–5488.

Charbonnet, J.A., McDonough, C.A., Xiao, F., Schwichtenberg, T., Cao, D., Kaserzon, S., Thomas, K.V., Dewapriya, P., Place, B.J., Schymanski, E.L., 2022. Communicating confidence of per-and polyfluoroalkyl substance identification via high-resolution mass spectrometry. Environ. Sci. Technol. Lett. 9, 473–481.

EBMUD, Water Quality Data, https://www.ebmud.com/water/about-your-water/water-quality/water-quality-data, (2023).

Edmiston, P.L., Carter, E., Toth, K., Hershberger, R., Hill, N., Versluis, P., Hollinden, P., 2023. C. Divine, Field evaluation of the sentinel™ integrative passive sampler for the measurement of perfluoroalkyl and polyfluoroalkyl substances in water using a modified organosilica adsorbent. Groundw. Monit. Remediat. 43, 38–54.

Evich, M.G., Davis, M.J., McCord, J.P., Acrey, B., Awkerman, J.A., Knappe, D.R., Lindstrom, A.B., Speth, T.F., Tebes-Stevens, C., Strynar, M.J., 2022. Per-and polyfluoroalkyl substances in the environment. Science 375, eabg9065.

Forster, A.L., Zhang, Y., Westerman, D.C., Richardson, S.D., 2023. Improved total organic fluorine methods for more comprehensive measurement of PFAS in industrial wastewater, river water, and air. Water Res. 235, 119859.

Gauthier, J.R., Mabury, S.A., 2022. Noise-reduced quantitative fluorine NMR spectroscopy reveals the presence of additional per-and polyfluorinated alkyl substances in environmental and biological samples when compared with routine mass spectrometry methods. Anal. Chem. 94, 3278–3286.

Gehrenkemper, L., Simon, F., Roesch, P., Fischer, E., von der Au, M., Pfeifer, J., Cossmer, A., Wittwer, P., Vogel, C., Simon, F.-G., 2021. Determination of organically bound fluorine sum parameters in river water samples—comparison of combustion ion chromatography (CIC) and high resolution-continuum source-graphite furnace molecular absorption spectrometry (HR-CS-GFMAS). Anal. Bioanal. Chem. 413, 103–115.

Getzinger, G.J., Higgins, C.P., Ferguson, P.L., 2021. Structure database and in silico spectral library for comprehensive suspect screening of per-and polyfluoroalkyl substances (PFASs) in environmental media by high-resolution mass spectrometry. Anal. Chem. 93, 2820–2827.

Han, Y., Pulikkal, V.F., Sun, M., 2021. Comprehensive validation of the adsorbable organic fluorine analysis and performance comparison of current methods for total per-and polyfluoroalkyl substances in water samples, ACS ES&T. Water 1, 1474–1482.

Hao, S., Choi, Y.-J., Wu, B., Higgins, C.P., Deeb, R., Strathmann, T.J., 2021. Hydrothermal alkaline treatment for destruction of per-and polyfluoroalkyl substances in aqueous film-forming foam. Environ. Sci. Technol. 55, 3283–3295.

Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ. Sci. Technol. 46, 9342–9349.

Jin, B., Zhu, Y., Zhao, W., Liu, Z., Che, S., Chen, K., Lin, Y.-H., Liu, J., Men, Y., 2023. Aerobic biotransformation and defluorination of fluoroalkylether substances (ether PFAS): substrate specificity, pathways, and applications. Environ. Sci. Technol. Lett. 10, 755–761.

Liu, M., Glover, C.M., Munoz, G., Duy, S.V., Sauvé, S., Liu, J., 2024. Hunting the missing fluorine in aqueous film-forming foams containing per-and polyfluoroalkyl substances. J. Hazard. Mater. 464, 133006.

Martin, D., Munoz, G., Mejia-Avendaño, S., Duy, S.V., Yao, Y., Volchek, K., Brown, C.E., Liu, J., Sauvé, S., 2019. Zwitterionic, cationic, and anionic perfluoroalkyl and polyfluoroalkyl substances integrated into total oxidizable precursor assay of contaminated groundwater. Talanta 195, 533–542.

Nickerson, A., Rodowa, A.E., Adamson, D.T., Field, J.A., Kulkarni, P.R., Kornuc, J.J., Higgins, C.P., 2020. Spatial trends of anionic, zwitterionic, and cationic PFASs at an AFFF-impacted site. Environ. Sci. Technol. 55, 313–323.

Pan, Y., Helbling, D.E., 2023. Revealing the factors resulting in incomplete recovery of perfluoroalkyl acids (PFAAs) when implementing the adsorbable and extractable organic fluorine methods. Water Res. 244, 120497.

Pelch, K.E., McKnight, T., Reade, A., 2023. 70 analyte PFAS test method highlights need for expanded testing of PFAS in drinking water. Sci. Total Environ. 876, 162978.

Rehnstam, S., Czeschka, M.-B., Ahrens, L., 2023. Suspect screening and total oxidizable precursor (TOP) assay as tools for characterization of per-and polyfluoroalkyl substance (PFAS)-contaminated groundwater and treated landfill leachate. Chemosphere 334, 138925.

Ritter, E.E., Dickinson, M.E., Harron, J.P., Lunderberg, D.M., DeYoung, P.A., Robel, A.E., Field, J.A., Peaslee, G.F., 2017. PIGE as a screening tool for Per-and polyfluorinated substances in papers and textiles. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 407, 47–54.

J. Shoemaker, DT Method 537.1 Determination of Selected Per-and Polyflourinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography, Tandem Mass Spectrometry (LC/MS/MS), (2020).

Shojaei, M., Kumar, N., Guelfo, J.L., 2022. An integrated approach for determination of total per-and polyfluoroalkyl substances (PFAS). Environ. Sci. Technol. 56, 14517–14527.

Tighe, M., Jin, Y., Whitehead, H.D., Hayes, K., Lieberman, M., Pannu, M., Plumlee, M.H., Peaslee, G.F., 2021. Screening for per-and polyfluoroalkyl substances in water with particle induced gamma-ray emission spectroscopy, ACS ES&T. Water 1, 2477–2484.

Tsou, K., Antell, E., Duan, Y., Olivares, C.I., Yi, S., Alvarez-Cohen, L., Sedlak, D.L., 2023. Improved total oxidizable precursor assay for quantifying polyfluorinated compounds amenable to oxidative conversion to perfluoroalkyl carboxylic acids, ACS ES&T. Water 3, 2996–3003.

L. Twight, Photolytic Quantum Yields of Chloramines and Kinetics of Perfluorinated Compounds Under Advanced Water Treatment Conditions, (2019).

USEPA, Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry, https://www.epa.gov/sites/default/files/2019-12/documents/method-533-815b19020.pdf, (2019).

USEPA, Draft Method 1633 - Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf, (2021).

USEPA, Draft Method 1621 - Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC), https://www.epa.gov/system/files/documents/2022-04/draft-method-1621-for-screening-aof-in-aqueous-matrices-by-cic_0.pdf, (2022).

Wellmitz, J., Bandow, N., Koschorreck, J., 2023. Long-term trend data for PFAS in soils from German ecosystems, including TOP assay. Sci. Total Environ., 164586

Zhang, W., Pang, S., Lin, Z., Mishra, S., Bhatt, P., Chen, S., 2021. Biotransformation of perfluoroalkyl acid precursors from various environmental systems: advances and perspectives. Environ. Pollut. 272, 115908.