Comparative Evaluation of Analytical Techniques for PFAS Quantification

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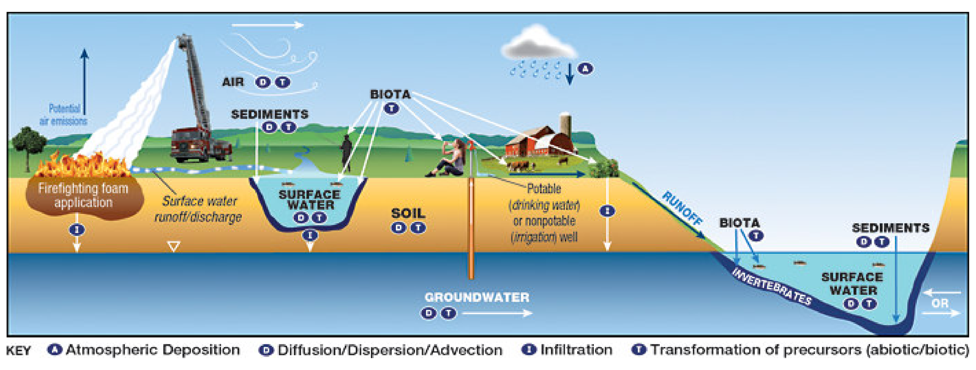
1. Background



- PFAS in aqueous film forming foam (AFFF) are highly persistent ("forever chemicals") and contaminate soil, water bodies, and drinking water, making them a long-term environmental concern.
- Accurate detection and quantification of PFAS in the environment are critical; however, several analytical challenges remain.

1.1 Challenges in PFAS detection and quantitation

- Diverse Chemical Structures
- Limitations of Standardized Methods
- Low Environmental Concentrations
- Variability in Measurement Techniques
- Complex Environmental Matrices

1.2 Study Objectives

- To measure PFAS (and organic fluorine content) using multiple analytical techniques (USEPA 1633, 537.1m, 1621, ISO 21675, Japan Ministry of Environment (MoE) Notification, Ultrashort chain (USC) PFAS)
- To compare the analytical techniques employed and identify their respective limitations
- To propose a comprehensive assessment strategy

2. Methodology

2.1 Sample description

Undiluted fire-extinguishing agent (liquid waste) was diluted and analyzed using several methods (n=3 for each method, except AOF (n=1)).

2.2 Method description

① TOP Assay + USEPA 1633

1. Add 20 mL of 400 mM NaOH + 150 mM $K_2S_2O_8$ mixed solution to 20 mL of sample
2. Digest at 85° C for 12 h
3. Adjust the pH (pH: 6-7) and spike EIS
4. SPE (Strata-WAX GCB (200/ 50 mg), Phenomenex)
5. Elute with 5 mL of 1% NH3 in methanol
6. Add NIS and acidify the sample with acetic acid
7. LC-MS/MS Analysis

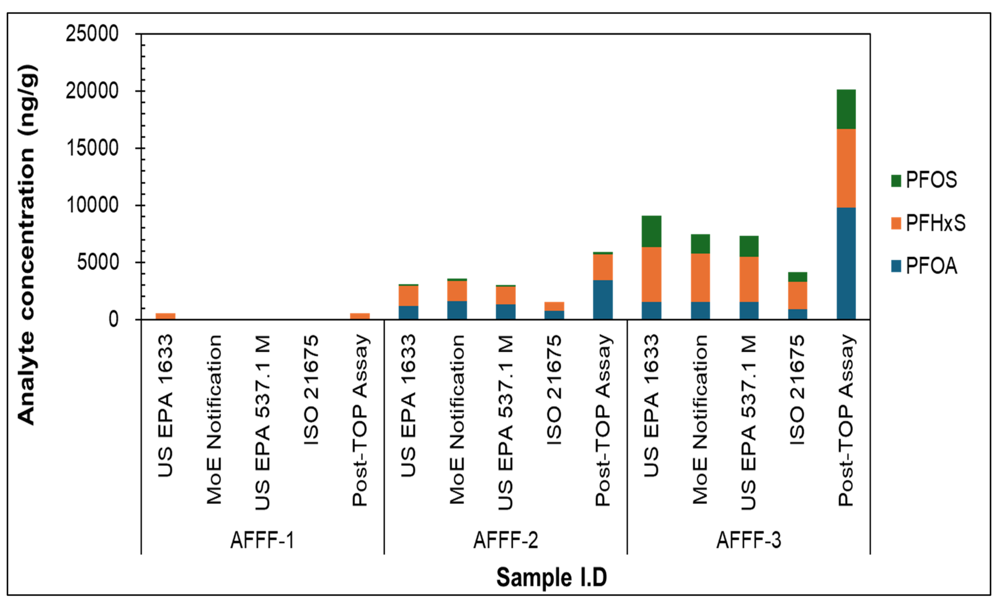
② AOF (USEPA 1621)

1. Add 0.5 mL of 2M NaNO3 to 100 mL of sample
2. Pass it through a GAC column to adsorb AOF
3. Wash the GAC column with 0.01M NaNO3 and water
4. Combust the GAC column in the CIC system then capture in the absorption
5. AOF – CIC Analysis

- The analytical protocols described in ISO 21675, and Japan MoE Notification, were followed
- USC PFAS: 500 µL of the diluted fire extinguishing agent was diluted with 500 µL of MeOH. 20 µL of USC PFAS mixed surrogate was added, after which the sample was filtered and analyzed on the LC-MS/MS.

3. Results and Discussions ①

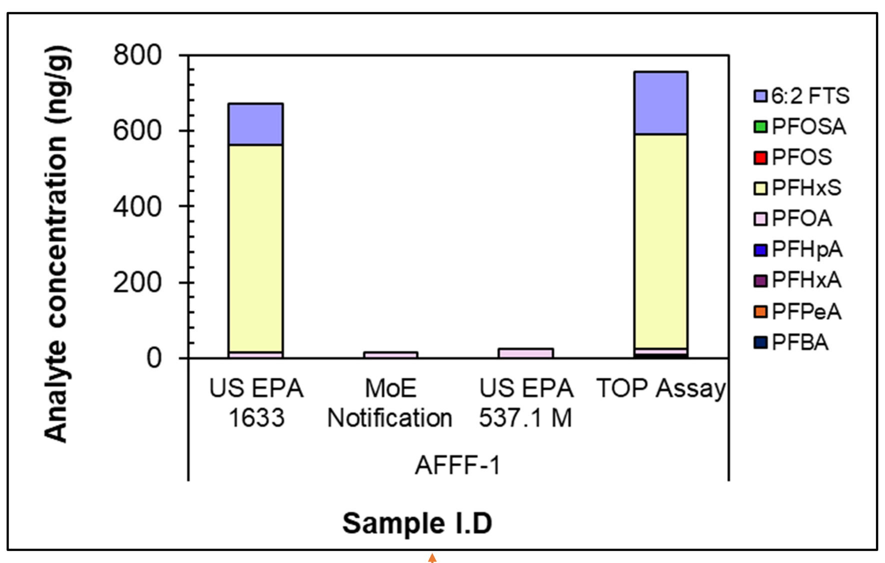
1. PFOS, PFOA and PFHxS

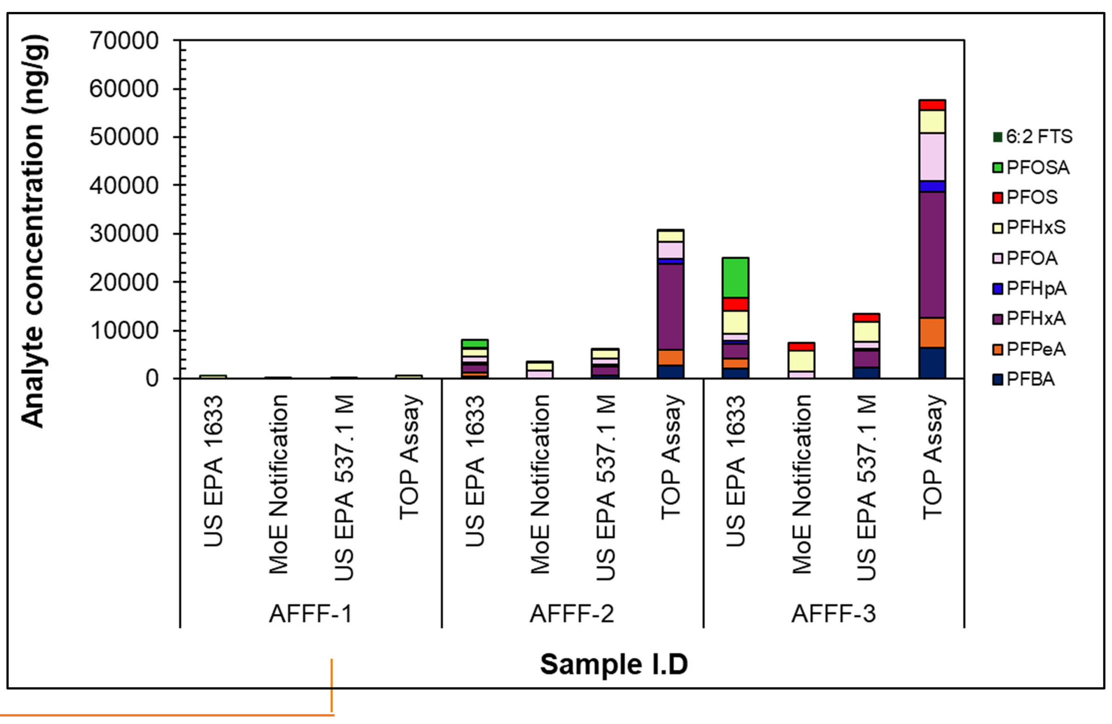


- AFFF-3 had the highest detected PFOS, PFOA and PFHxS concentration followed by AFFF-2 and AFFF-1 had the least
- Better results were obtained when using USEPA 1633, compared to USEPA 537.1 M because of its ability to handle complex samples and carbon clean-up which removes interferences while USEPA 537.1 M is optimized for clean drinking water samples and incapable of removing interferences.
- Post TOP-Assay, PFOA molar yield in AFFF-3 exceeded 500% suggesting the presence of undetected precursors
- Generally, the surrogate recovery was within the acceptable range, except for AFFF-1, PFOS could not be detected likely due to matrix interference that suppressed the internal standard signal, thus, it was eliminated from the final results.

Results and Discussions ②

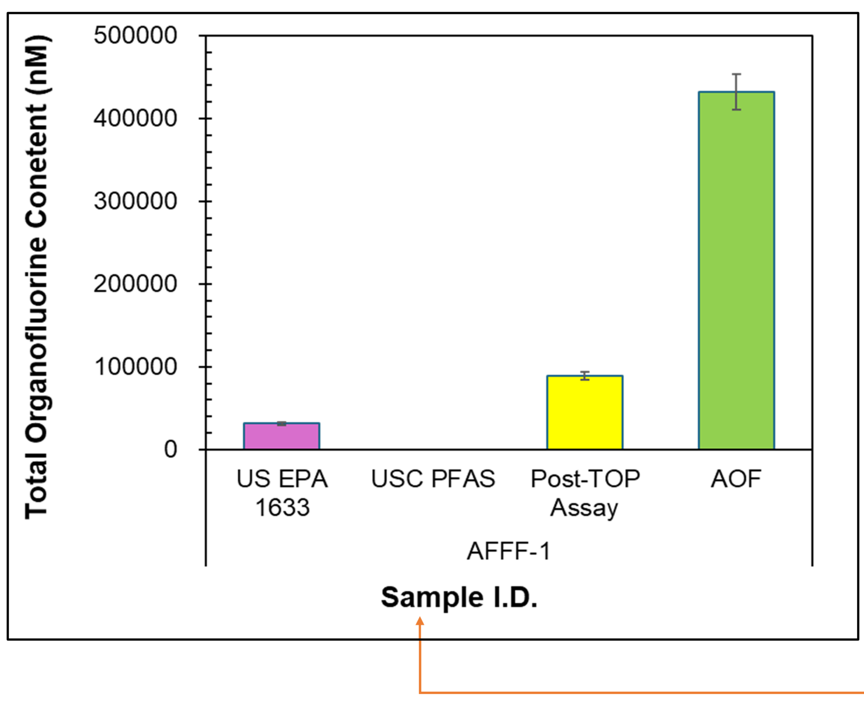
2. Other PFAS Concentrations

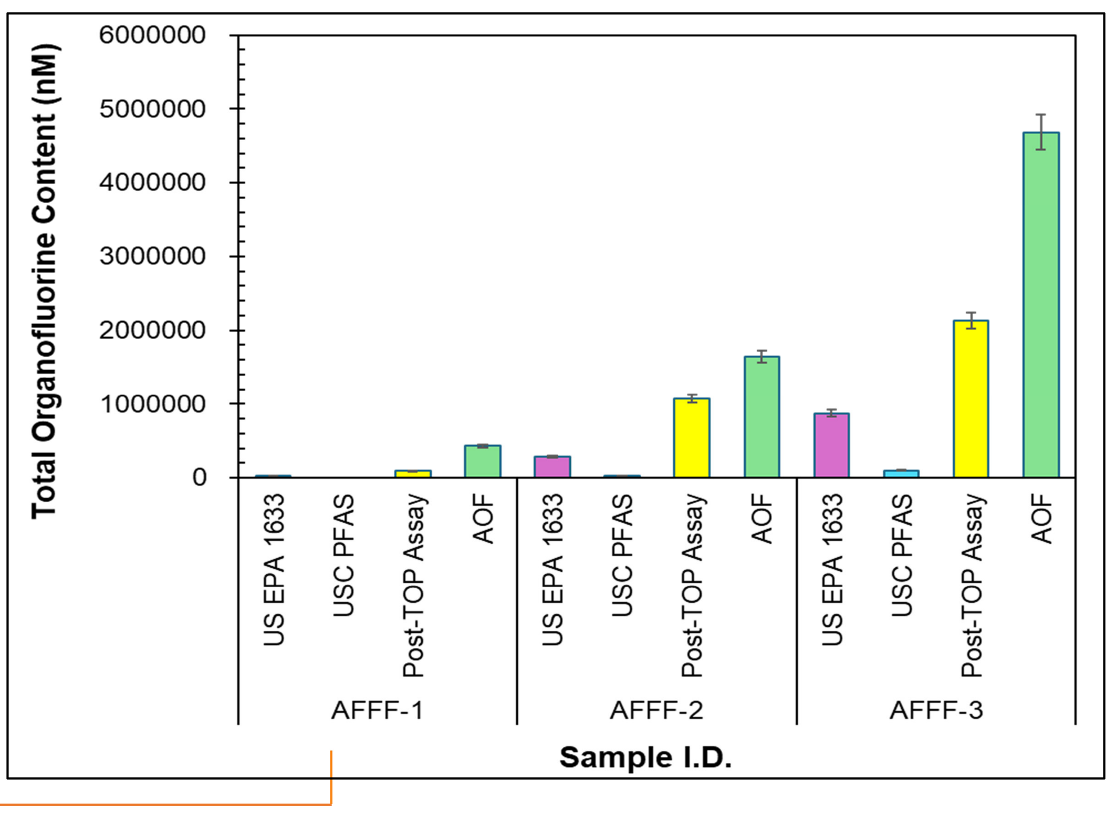




- PFHxS was the most abundant compound in all three samples ranging from 548 ng/g in AFFF-1 to 4840 ng/g in AFFF-3.
- Post-TOP assay analysis revealed analyte concentrations approximately 2–10 times higher than those obtained via targeted analytical methods, achieving at least 99% oxidation for PFOSA and complete oxidation for other PFCA precursors.
- An unexpected increase in 6:2 FTS was observed in AFFF-1. This increase in 6:2 FTS concentration may be attributed to the presence of 6:2 Fluorotelomer Thioether AmidoSulfonate (trade name: Lodyne), a common AFFF component known to degrade into 6:2 FTS under biological conditions. However, further investigation is needed to determine its behavior during the TOP assay.

3. Total Organofluorine Content





- As expected, the following trend was observed: AOF > Post-TOP Assay > USEPA 1633> USC PFAS for all sample investigated.
- AOF results were the highest because AOF measures the total adsorbable organically bound fluorine, capturing both known and unknown PFAS, precursors, and other fluorinated organics that are retained on activated carbon and combusted
- The following PFAS groups likely contributed to AOF: Long-chain PFCAs (e.g., PFOA, PFNA, PFDA); Long-chain PFSAs (e.g., PFOS, PFHxS) and 6:2 FTS.
- However, ultrashort- and short-chain PFCAs (C<4) were not converted to AOF due to low adsorption to granular activated carbon (GAC).

Proposed comprehensive assessment strategy

- Pre-treatment steps involving granular activated carbon, as used in Method 1633, can be used to reduce matrix interference and improve analyte detection.
- Use of highly sensitive instruments with lower detection limits
- Expand analyte target lists, incorporating USC PFAS, and precursors such as 6:2 FTAB, known to be present in AFFF samples .
- Incorporating TOP assay and total fluorine methods such as AOF to existing target methods will reveal hidden, undetected precursors that are not measured by conventional targeted methods and will also be important for mass balance analysis in order to calculate the total environmental PFAS load

Conclusions

- This study highlights the limitations of currently available analytical methods and emphasizes the need for improved or complementary approaches.
- For screening and target analytical methods, the following trend was observed: TOP Assay>M1633>ISO 21675>USEPA 537.1 M > MoE Notification> USC PFAS
- When AOF was incorporated into the investigation, the following trend was observed: AOF > Post-TOP Assay > USEPA 1633 > ISO 21675 > USEPA 537.1 M > MoE Notification > USC PFAS
- The method-specific detection patterns observed reinforce the importance of using multiple analytical techniques to achieve a more comprehensive PFAS profile in complex matrices such as AFFF.
- Incorporating sample pre-treatment steps such as the use of carbon clean-up in USEPA 1633, is essential for removing matrix interferences, thus, improved analyte detections

References

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2. Shoemaker, J. (2009). Method 537. Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS).
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