**Submission to NGOs on the need to include Total Fluorine measurements in the NPRI**
**Prepared by Beverley Thorpe, May 1, 2024**

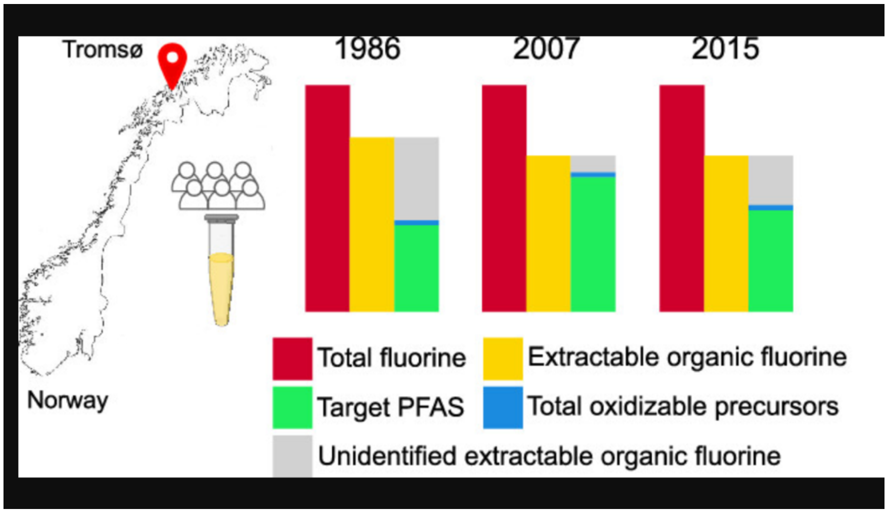
1. **Defining Total Florine as only a sum of a designated list of PFAS would be an under representation of the extent of PFAS being released into the environment.**

The two images and citations below demonstrate the limitations of not measuring Total Fluorine in the manufacturing, production, use or waste management/incineration of PFAS.

- **Fluorine Mass Balance, including Total Fluorine, Extractable Organic Fluorine, Oxidizable Precursors, and Target Per- and Polyfluoroalkyl Substances, in Pooled Human Serum from the Tromsø Population in 1986, 2007, and 2015**.

Figure 1:

Environ. Sci. Technol. 2023, 57, 40, 14849–14860. September 25, 2023. https://doi.org/10.1021/acs.est.3c03655Environ.



**Fluorine Mass Balance Approach**

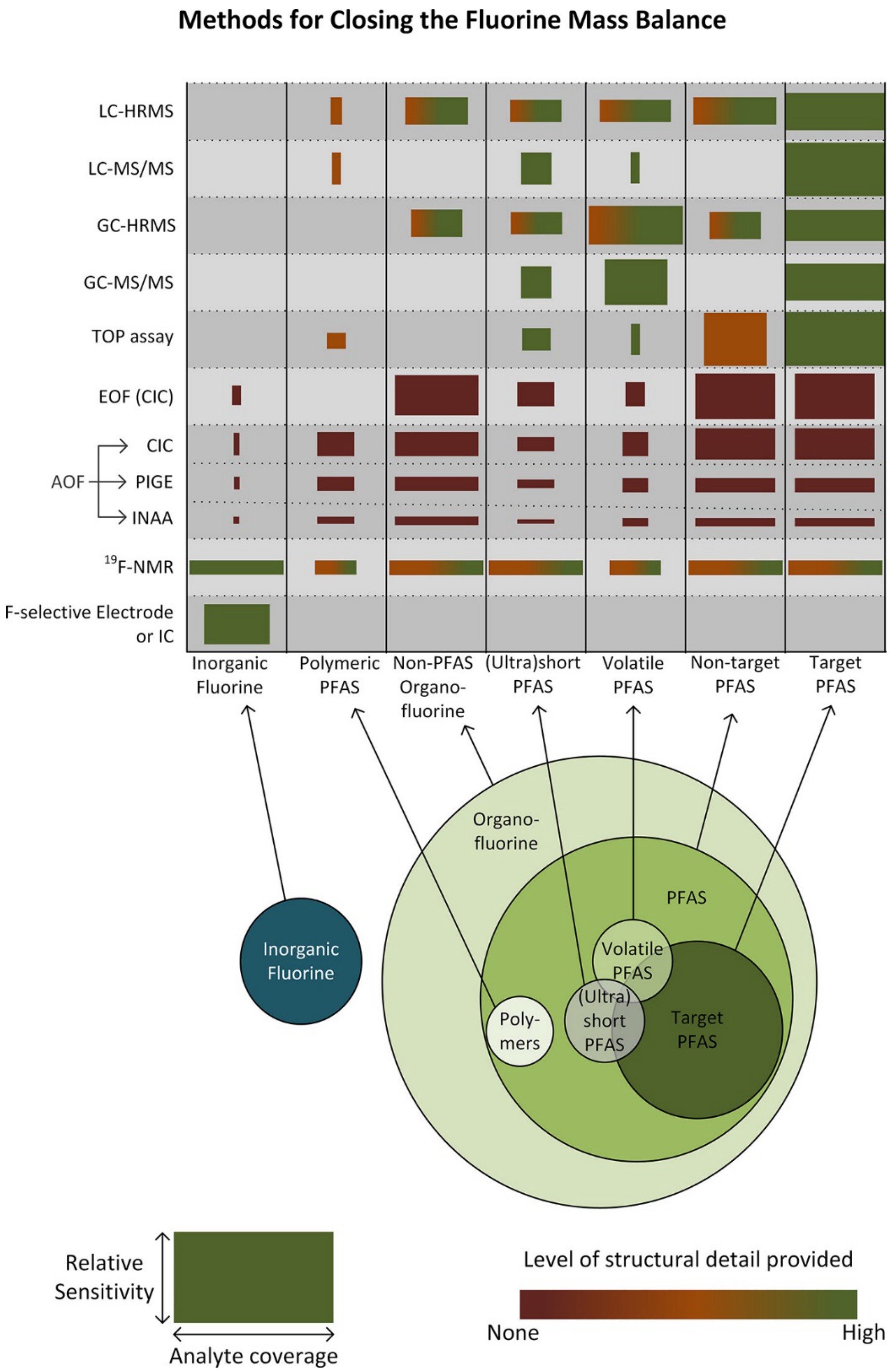
Of the thousands of per- and polyfluoroalkyl substances (PFAS) known to exist, only a small fraction (≤1%) are commonly monitored in humans. This discrepancy has led to concerns that human exposure may be underestimated. Here, we address this problem by applying a comprehensive fluorine mass balance (FMB) approach, including total fluorine (TF), extractable organic fluorine (EOF), total oxidizable precursors (TOP), and selected target PFAS, to human serum samples collected over a period of 28 years (1986, 2007, and 2015) in Tromsø, Norway.

EOF values were subtracted from TF concentrations to estimate the amount of inorganic and nonextractable organic fluorine. The comparison of EOF and target PFAS concentrations revealed the presence of unidentified organofluorine at all time-points.

- **The Need to Include a Fluorine Mass Balance in the Development of Effective Technologies for PFAS Destruction**

Figure 2:

Environ. Sci. Technol. 2024, 58, 6, 2587–2590. February 5, 2024
https://doi.org/10.1021/acs.est.3c10617



Overview of the relative potential of analytical methods to complete the fluorine mass balance in PFAS destruction, for different types of fluorinated substances potentially found in environmental samples. "Target PFAS" are the typically <100 specific PFAS included in a GC- or LC-MS analyte list, for which standards are available. "Polymeric PFAS" include fluoropolymers, perfluoropolyethers, and side-chain fluorinated polymers and may be present in environmental samples as micro- or nanoparticles. The heights of the boxes represent the general sensitivity of the method as typically employed, and the widths the general coverage of the method within the corresponding group of fluorinated substances. These parameters also strongly depend on the sample types (air, water, soil, etc.), sample collection (grab vs integrated and whole air vs sorbents), and preparation methods (extraction and concentration), which are not included in the figure and can vary significantly depending on the practitioner. Ideally, EOF and AOF methods detect only organic fluorine, but because the extent of fluoride removal is often slightly below 100%, these methods are shown to include some inorganic fluorine.

**2. Total Fluorine measurements should be made publicly available.**

In terms of analytical testing, it is recommended to test for total fluorine (rather than total organic fluorine) to capture as much PFAS as possible. While total fluorine is measured by burning the whole sample, total organic fluorine is typically measured by either 1) extracting fluorinated chemicals from the sample into a solvent and then burning the extract, or 2) adsorbing the fluorinated chemicals onto a substrate like activated charcoal and then burning the substrate. No matter what you do, you will miss some PFAS.

To ensure only PFAS are measured (and not inorganic fluorine) companies can do a second test for inorganic fluorine and then subtract that from the total fluorine to get the total organic fluorine.

In the proposed EU Restriction on PFAS, a concentration threshold of 50ppm for the sum of all PFASs applies. The ppm value is derived from the total fluorine, measured in milligrams of fluorine per kilogram (mg F/kg), according to an approach outlined in the restriction's annexes. This conversion accounts for how the fluorine content varies from one PFAS to the next. The EU further clarifies that: "Fluorine can be present in non-PFAS compounds, meaning it is possible for the total fluorine content to be high without there being any PFAS. However, under such circumstances, companies should be prepared to prove to authorities that they are compliant. Specifically, if during enforcement activity total fluorine is found to exceed 50mg F/kg, companies will need to provide proof of compliance in the form of either supply chain information or analytical data."

**3. Any analytical method must include ultra-short chain PFAS. Trifluoroacetic Acid (TFA) needs to be a priority focus.**

Note that ultra-short chain PFAS are highly persistent and also highly mobile. Short chain PFAS are a dominant form of PFAS in human blood, urine, and the environment (water, soil, air, dust). **The increase of Trifluoroacetic acid (TFA) – a super short chain PFAS, is worrying.**

- ***Rapidly rising levels of TFA 'forever chemical' alarm experts:*** *Trifluoroacetic acid found in drinking water and rain is thought to damage fertility and child development****. The Guardian. 1 May 2024.***

  https://www.theguardian.com/environment/2024/may/01/rapidly-rising-levels-of-tfa-forever-chemical-alarm-experts
  *Studies from across the world are reporting sharp rises in TFA. A major source is F-gases, which were brought in to replace ozone-depleting CFCs in refrigeration, air conditioning, aerosol sprays and heat pumps. Pesticides, dyes and pharmaceuticals can also be sources.*

> TFA is also a product of thermal decomposition (360-382°C) of several fluoropolymers. As far back as 1999, fluoropolymers thermolysis was known to explain 40% of TFA wet deposition in Europe and over 80% of TFA observed in the rainwater of Toronto. (Ref: Jia'nan Cui et al. The contribution of fluoropolymer thermolysis to trifluoroacetic acid (TFA) in environmental media. Chemosphere. 2019 doi: 10.1016/j.chemosphere.2019.01.174)
> Moreover, studies of Arctic ice cores show TFA levels have been rising sharply since F-gases replaced CFCs in the 1990s. The result is that no other substance has been found in so many environmental media, in these high concentrations and with such a fast increase. The bad news is that it is almost technically impossible and too costly to remove TFA from drinking and wastewater which is why time is of the essence to measure the release of TFA to the Canadian environment and stop TFA's rapid buildup.

A 2023 publication demonstrates the evolution of analytical methods to capture short-chain PFAS:-

**Quantitation of Total PFAS Including Trifluoroacetic Acid with Fluorine Nuclear Magnetic Resonance Spectroscopy.**
Anal Chem. 2023 Apr 4; 95(13): 5484–5488. 2023 Mar 22. doi: 10.1021/acs.analchem.2c05354.
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC10601338/

> "Monitoring short chain analytes is critical because they have replaced long chain PFAS in commercial formulations, can be produced as a result of long chain PFAS degradation, are not adsorbed or removed by traditional sorbent materials, and may have similar negative health effects as longer chain PFAS. Specifically, trifluoroacetic acid (TFA) is not retained by common SPE sorbents and reversed-phase columns for LC-MS. TFA is an environmental contaminant of growing importance, as PFAS become more widely studied due to its ubiquity in the environment, extreme water solubility, and uptake in plants. Further, TFA contamination in the environment is predicted to increase because of new PFAS alternatives. These issues exemplify the need for more comprehensive analyses of PFAS.
> Fluorine nuclear magnetic resonance (19F-NMR) spectroscopy has been shown to be a powerful tool capable of quantifying the total per- and polyfluoroalkyl substances (PFAS) in a complex sample. Traditional quantitative analytical techniques for PFAS, such as liquid chromatography–mass spectrometry (LC-MS) and combustion ion chromatography (CIC), contain inherent limitations that make total fluorine analysis challenging. The use of 19F-NMR to quantify the total PFAS in highly complex samples can be used to complement classic TOP or LC-MS approaches for more accurate reporting of PFAS contamination in the environment."