TOTAL ORGANOFLUORINE (TOF) ANALYSIS BY COMBUSTION ION CHROMATOGRAPHY

A New Tool for Monitoring PFAS Impacts

Presented by:
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OUTLINE

- Per- and Polyfluorinated Alkyl Substances (PFAS)
  - *Why look beyond LC-MS/MS analysis?*

- Total Organic Fluorine: TOF
  - *Combustion Ion Chromatography (CIC)*
  - *AOF vs EOF*
  - *What do the results mean compared to LC-MS/MS analysis?*
- AOF-CIC: How to Interpret Results
  - *How rugged is the method?*
  - *Are there limitations?*
- Conclusions

PFAS ARE EVERYWHERE!

An overview of the uses of per- and polyfluoroalkyl substances (PFAS)†

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Environmental Sci. Processes Impacts, 2020, 22, 2345

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Industries

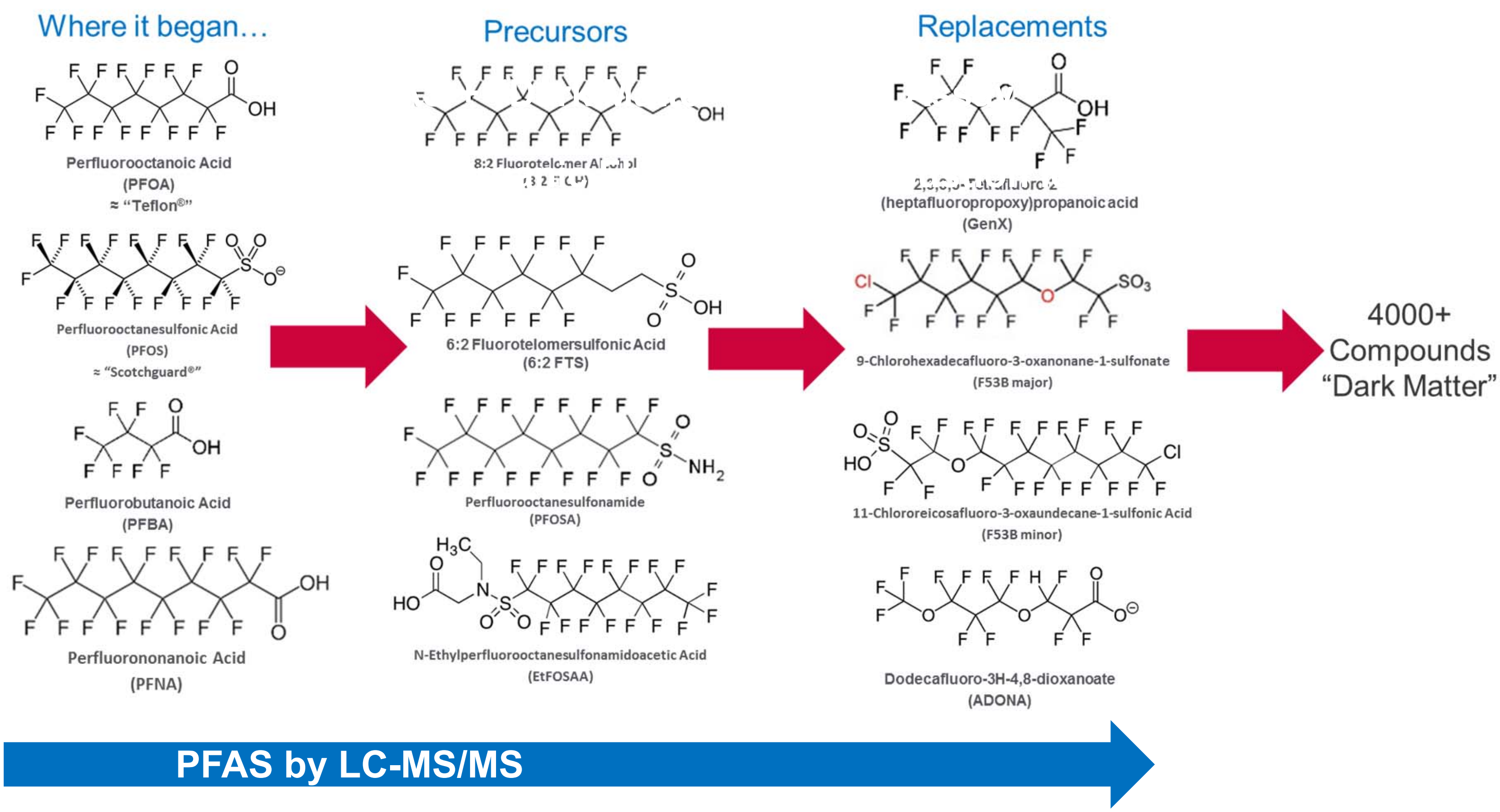
Aerospace (7)
Biotechnology (2)
Building and construction (5)
Chemical industry (8)
Electroless plating
Electroplating (2)
Electronic industry (5)
Energy sector (10)
Food production industry
Machinery and equipment
Manufacture of metal products (6)
Mining (3)
Nuclear industry
Oil & gas industry (7)
Pharmaceutical industry
Photographic industry (2)
Production of plastic and rubber (7)
Semiconductor industry (12)
Textile production (2)
Watchmaking industry
Wood industry (3)

Uses

Cook- and bakingware
Dispersions
Electronic devices (7)
Fingerprint development
Fire-fighting foam (5)
Flame retardants
Floor covering including carpets and floor polish (4)
Glass (3)
Household applications
Laboratory supplies, equipment and instrumentation (4)
Leather (4)
Lubricants and greases (2)
Medical utensils (14)
Plastic, rubber and resins (4)
Printing (4)
Refrigerant systems
Sealants and adhesives (2)
Soldering (2)
Soil remediation
Sport article (7)
Stone, concrete and tile
Textile and upholstery (2)
Tracing and tagging (5)
Water and effluent treatment
Wire and cable insulation, gaskets and hoses

The numbers in parentheses indicate the number of subcategories.

LC-MS/MS ANALYSIS TELLS PART OF THE STORY



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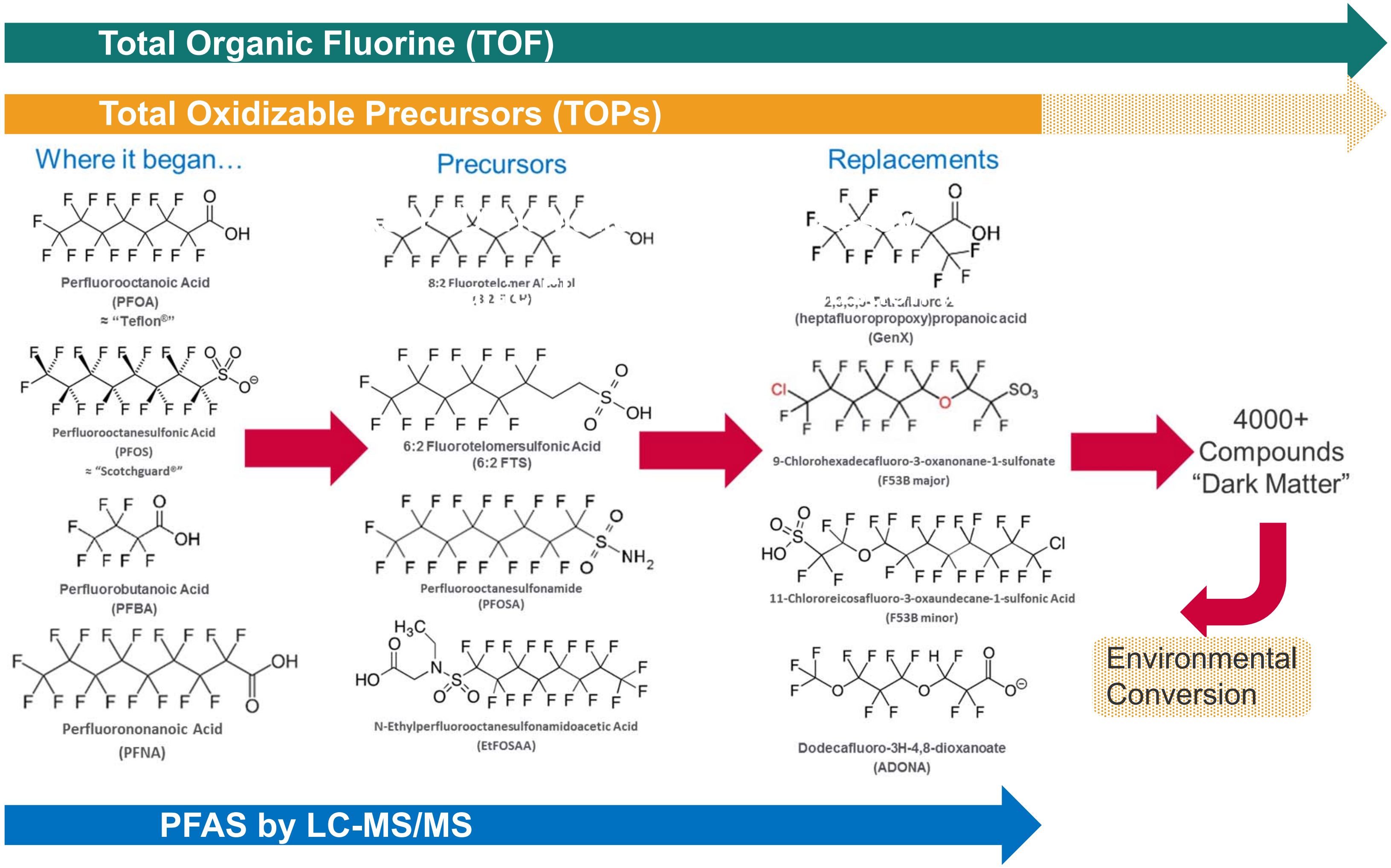
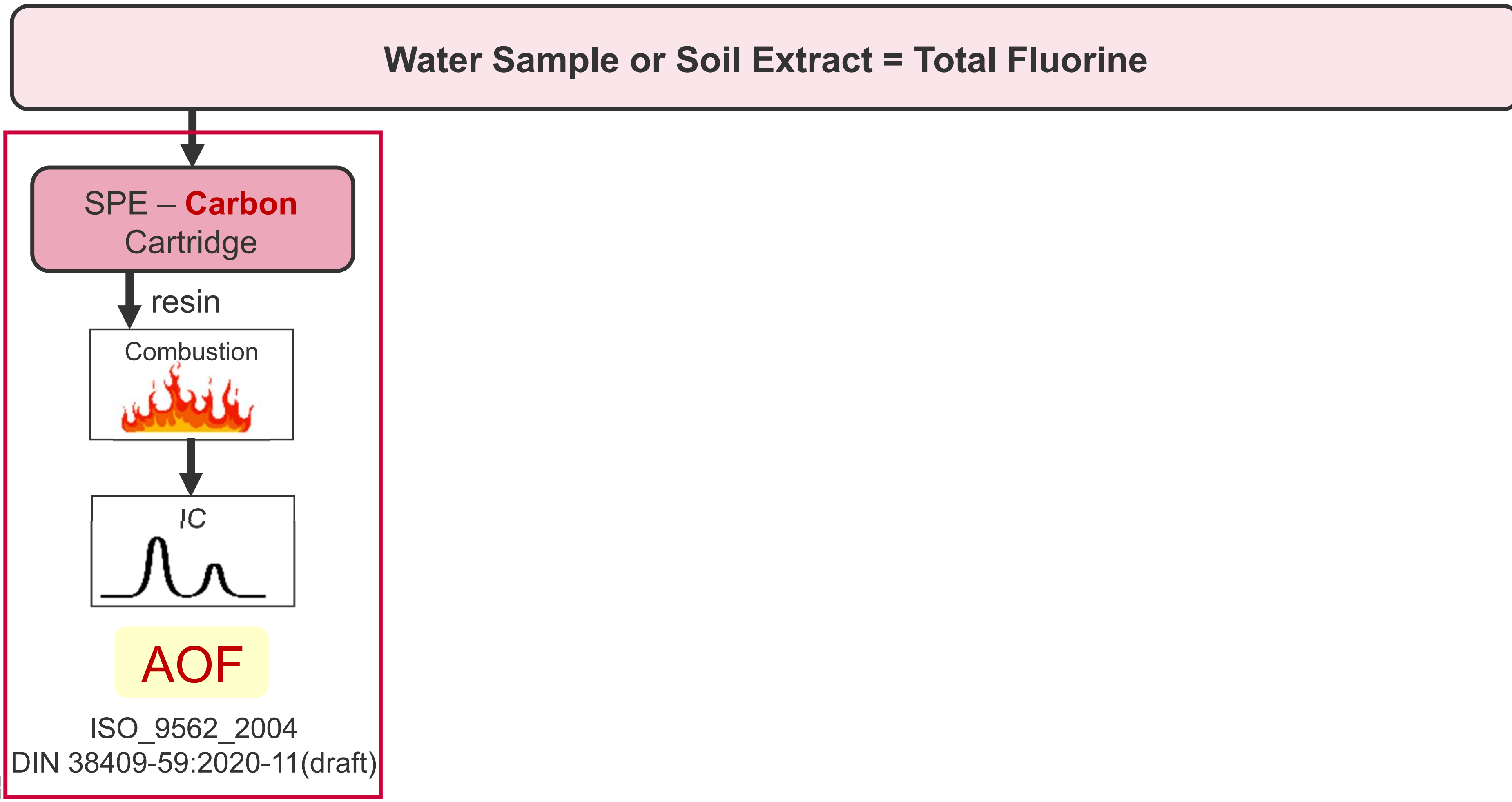
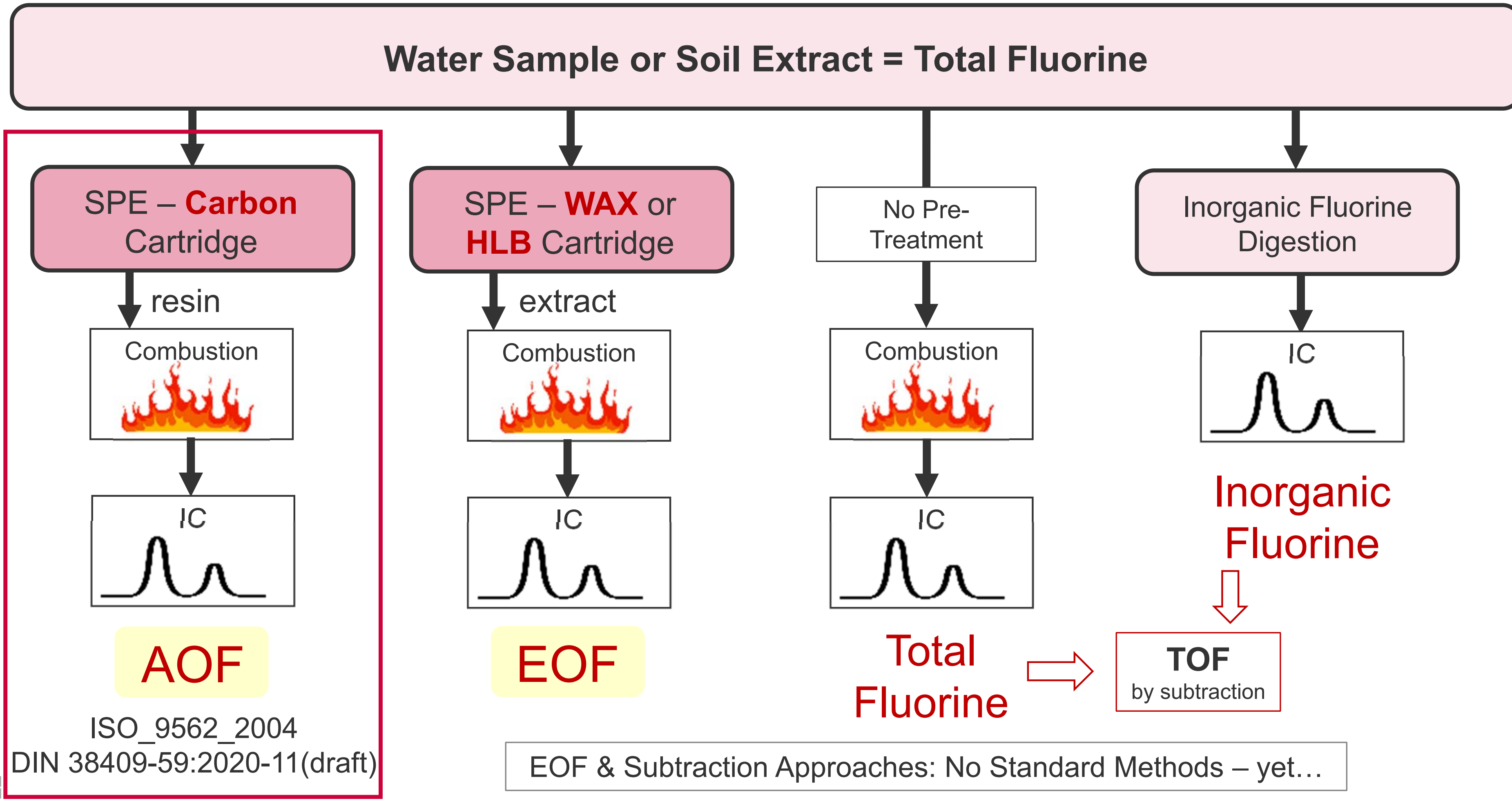


- Total Organic Fluorine: TOF
  - *Combustion Ion Chromatography (CIC)*
  - *AOF vs EOF*
  - *What do the results mean compared to LC-MS/MS analysis?*

CIC TOF DETERMINATION APPROACHES



CIC TOF DETERMINATION APPROACHES



TOTAL ORGANOFLUORINE ANALYSIS BY COMBUSTION IC

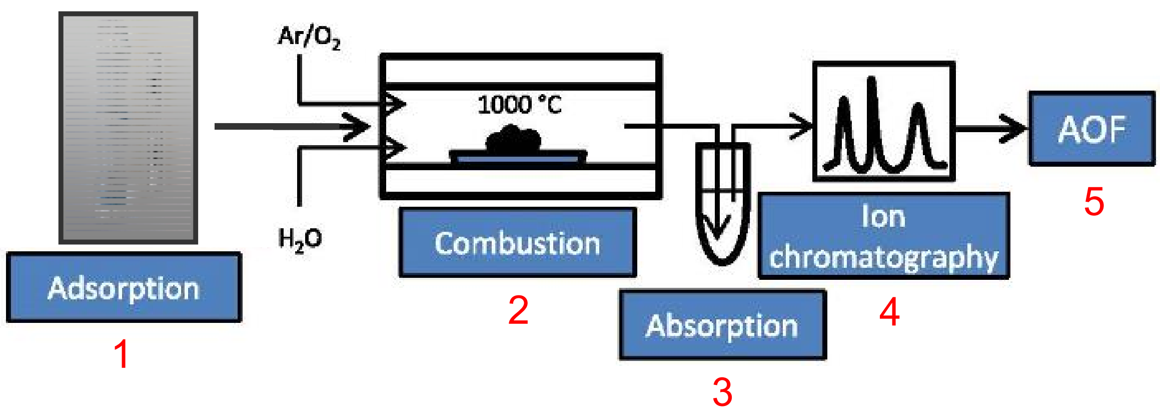
Science of the Total Environment 673 (2019) 384–391

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Determination of adsorbable organically bound fluorine (AOF) and adsorbable organically bound halogens as sum parameters in aqueous environmental samples using combustion ion chromatography (CIC)

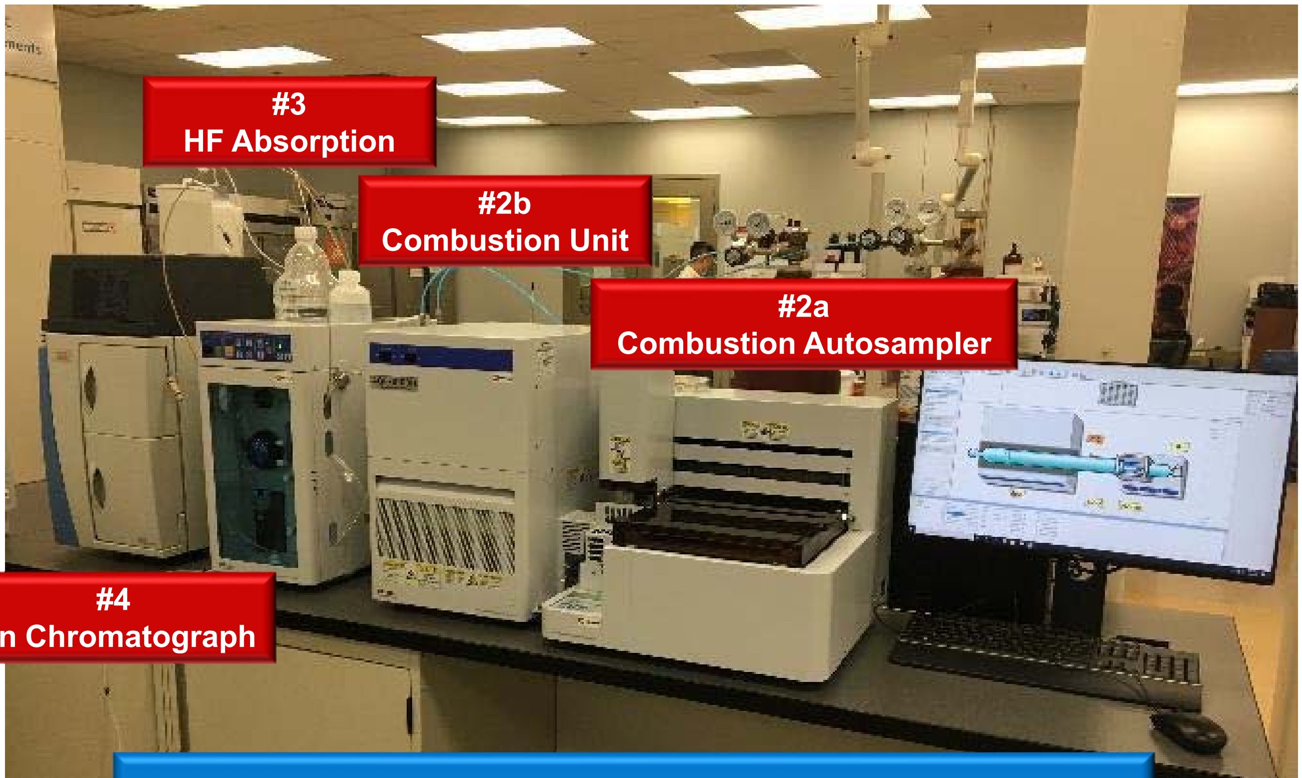


1. Water sample or soil extract diluted in water adsorbed in carbon cartridges
2. Carbon resin transferred to boat and combusted.
3. Hydrogen fluoride (HF) in combustion gasses trapped in water.
4. Water with HF injected to Ion Chromatography
5. Fluorine signal reported as Total Adsorbed Organic Fluorine

Method described in Thermo Scientific Application Note 73481

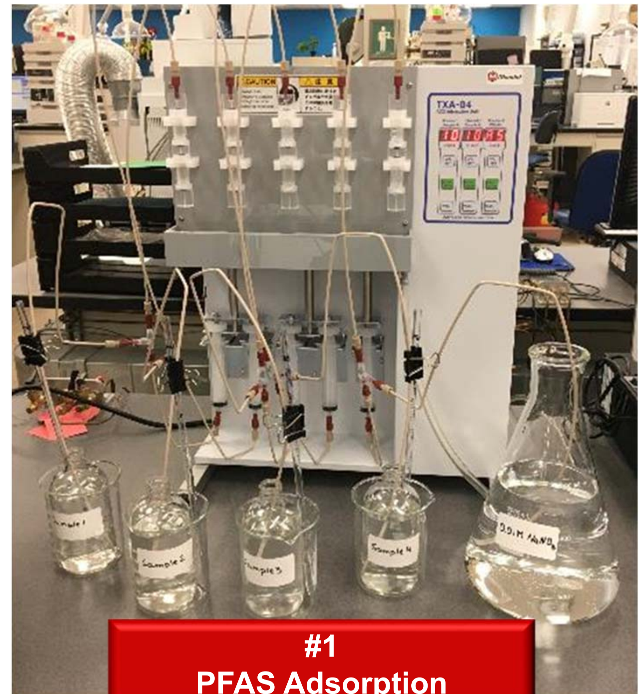
Reference: von Abercron *et.al.*: *Sci. Tot. Environ.*, 2019, 673, 384-391

BUREAU VERITAS LABORATORIES' TOF-CIC SYSTEM



Reporting Limits: 1 µg/L waters; 200 µg/kg soils

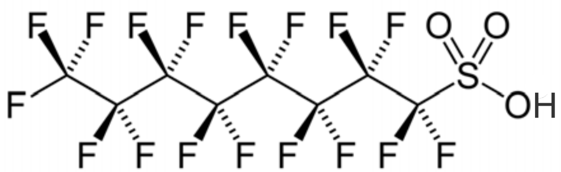
AOF Sample Pre-Treatment



WHAT DO TOF RESULTS MEAN?

Remember…

TOF by CIC is measuring the fluorine contribution from all of the fluorine-containing compounds in the sample



PFOS
($C_8F_{17}SO_3^-$)

PFOS Mol. Wt.	= 500 g/mol	
F Mol Wt. = 19 g/mol	17x F = 323 g/mol	
Fluorine Contribution:	$\frac{323}{500}$	= 64.6 %

Measured amounts…

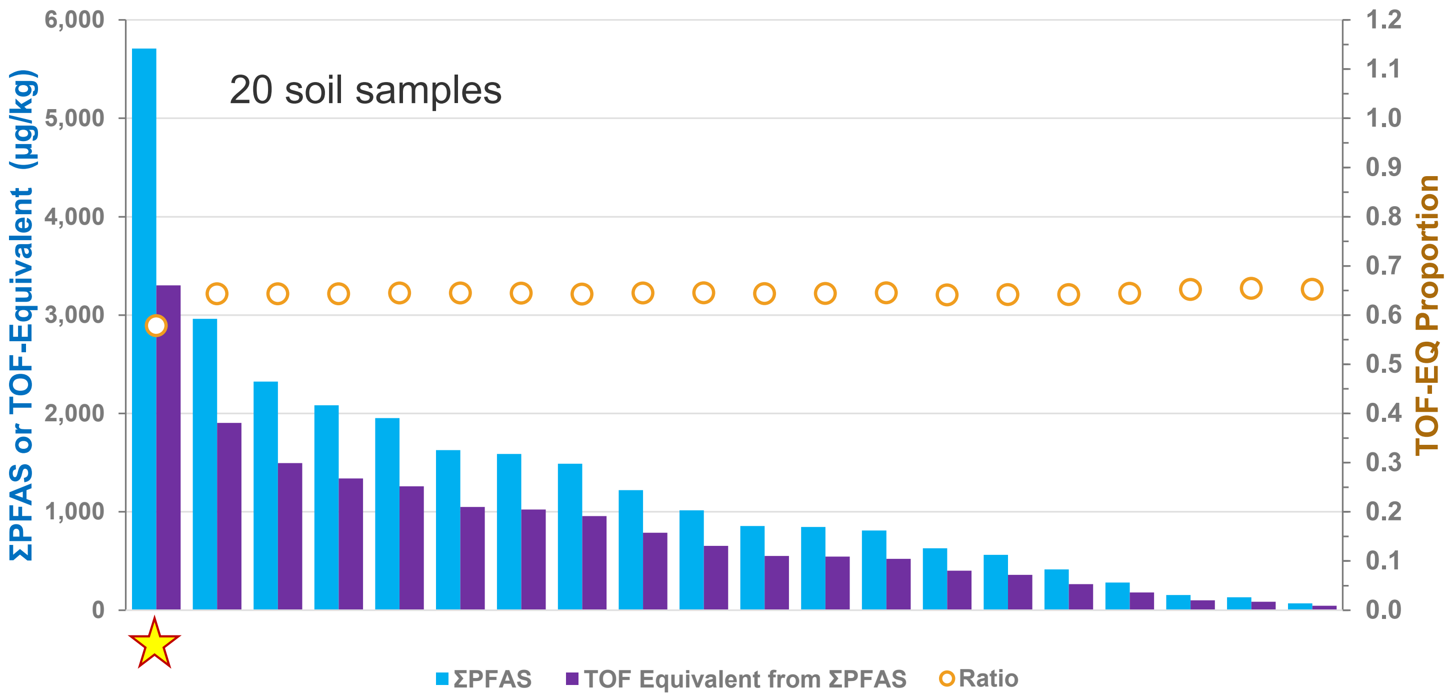
PFOS (by LC/MS/MS) = **250 ng/L PFOS**

F_{total} (by CIC) = 0.646 x 250 ng/L

= **162 ng/L F**

PFOS TOF equivalent (TOF-EQ) ~65%

LC-MS/MS ΣPFAS vs. TOF-EQ

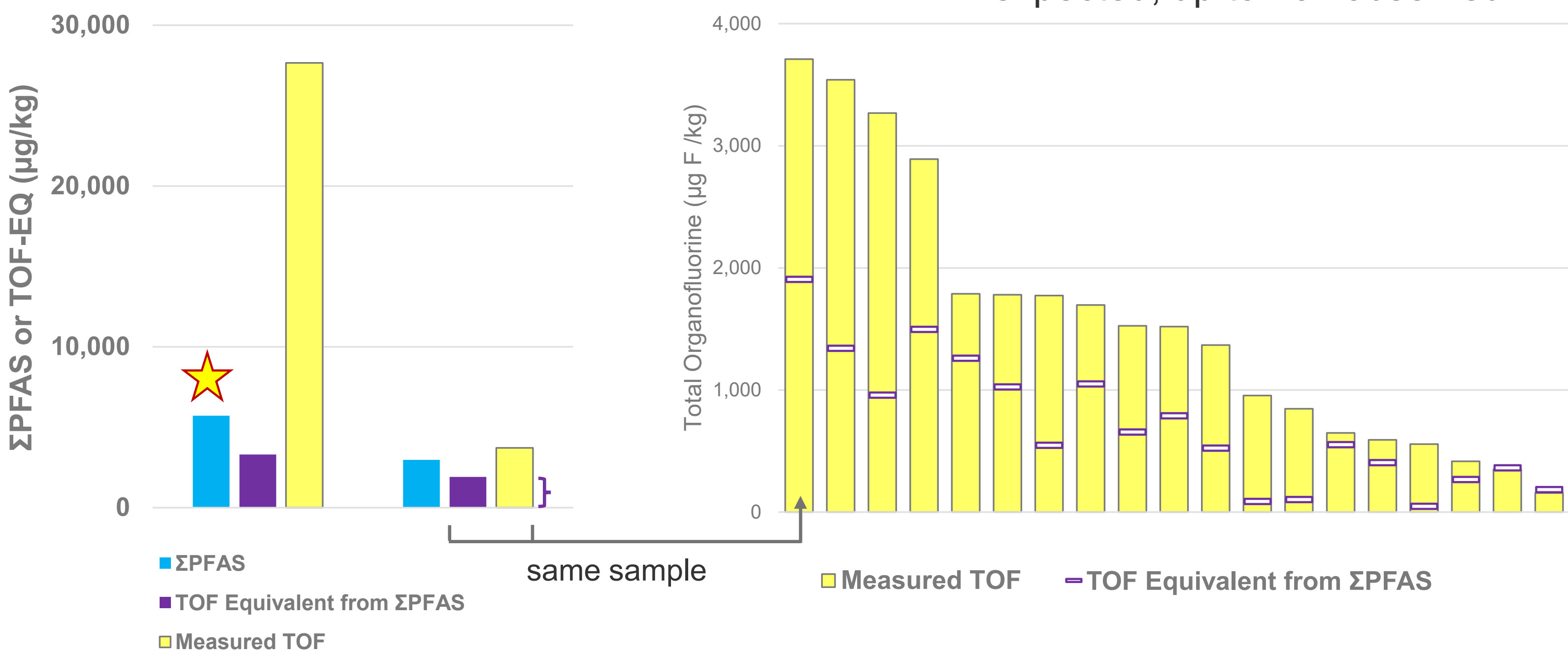


TOF Equivalent from ΣPFAS is ~65%
-calculated for each PFAS individually and summed

If you want ΣPFAS and TOF-EQ reported with your PFAS data just ask!

LC-MS/MS vs. TOF/AOF-CIC: SOIL SAMPLES

Measured TOF/AOF range typically 1x to 2x of expected, up to 10x observed.



★ Sample was primarily 6:2 fluorotelomer sulfonate
6:2 FTS = 58% F

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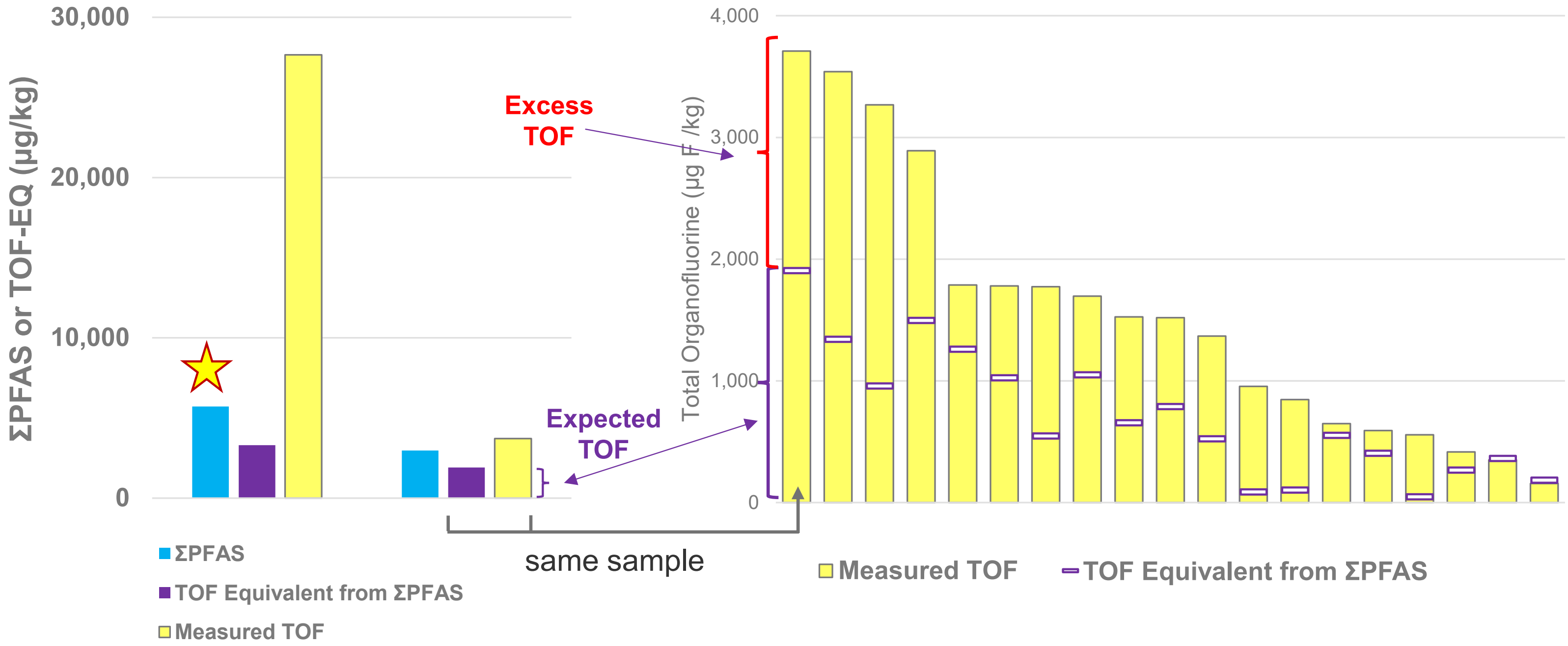

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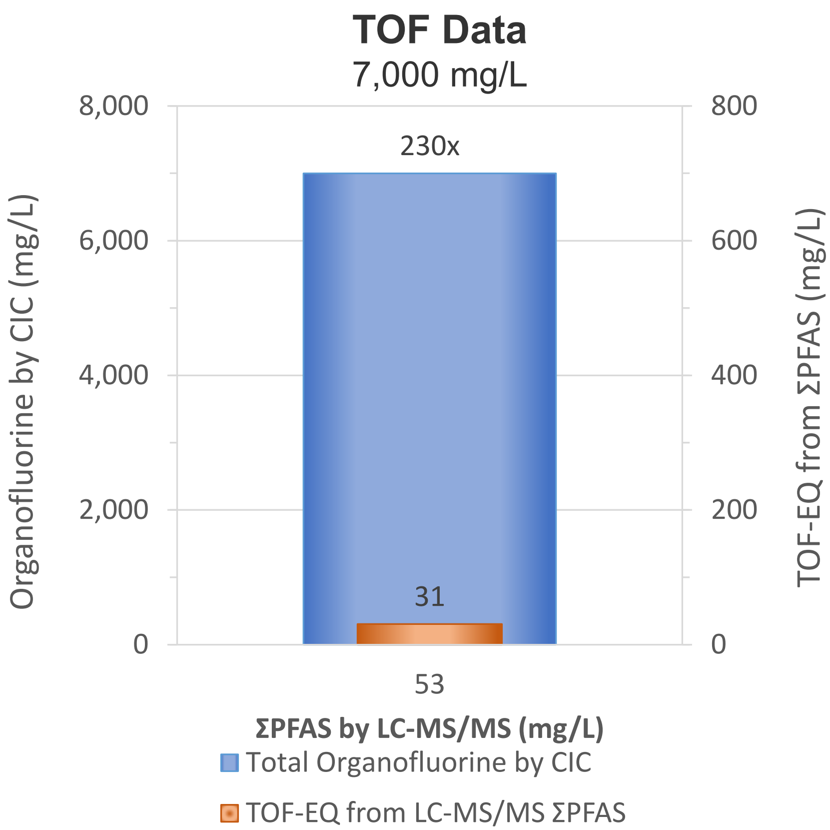
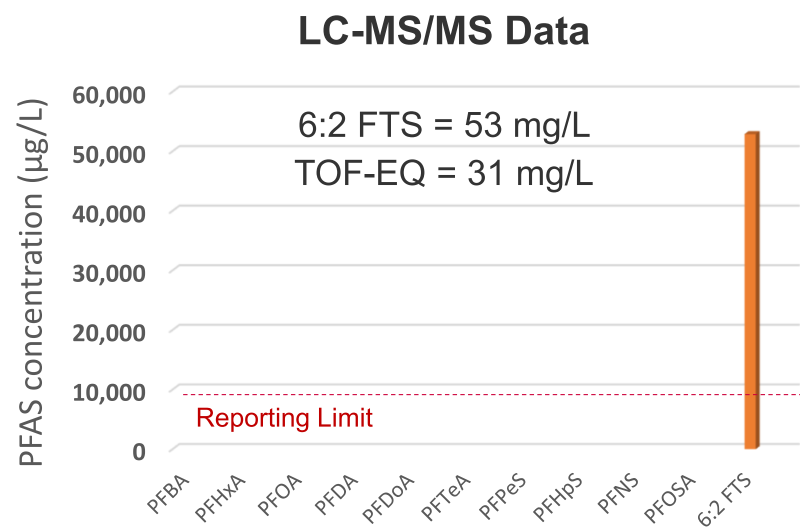
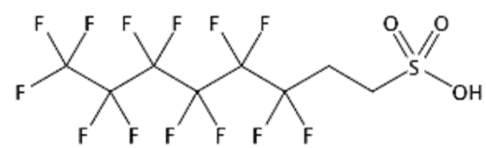
6:2 FTS = 58% F

LC-MS/MS vs. TOF-CIC: AFFF SAMPLE



CIC DL: 200 mg/L (due to sample dilution)





6:2 FTS
58% Fluorine

Supplier Information:
"…readily biodegradable and virtually nontoxic to aquatic organisms. It is based on a natural protein foaming agent and contains no harmful synthetic detergent… can be successfully treated in biological wastewater treatment systems."

- AOF-CIC: How to Interpret Results
  - *How rugged is the method?*
  - *Are there limitations?*

APPLICATION OF AOF-CIC TO SOILS

AOF-CIC reference method does not provide for soil analysis

Approach:

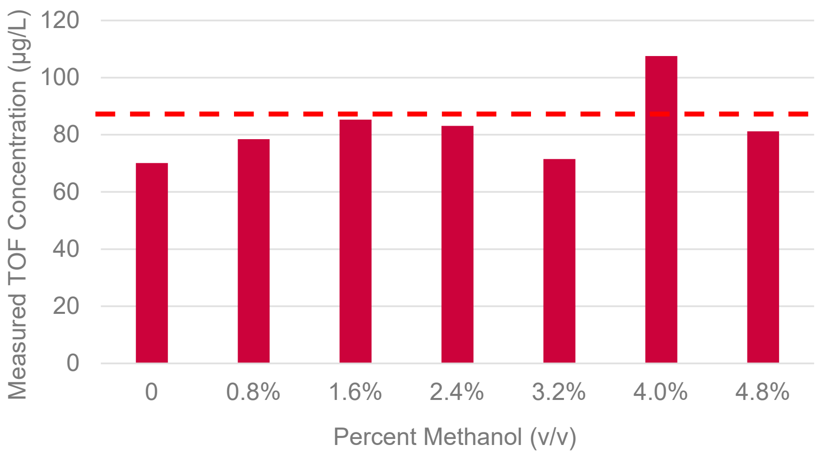
- Extract soils following the typical method for PFAS by LC-MS/MS
- Dilute soil extracts in water – How Much Methanol?
- Process as per reference method for water samples

Question:

- What is the soil extraction recovery?
- Note: not relevant for PFAS by LC-MS/MS due to isotope dilution calibration.

Methanol Concentration Study

Spike: 144 µg/L PFBS, 15% RSD

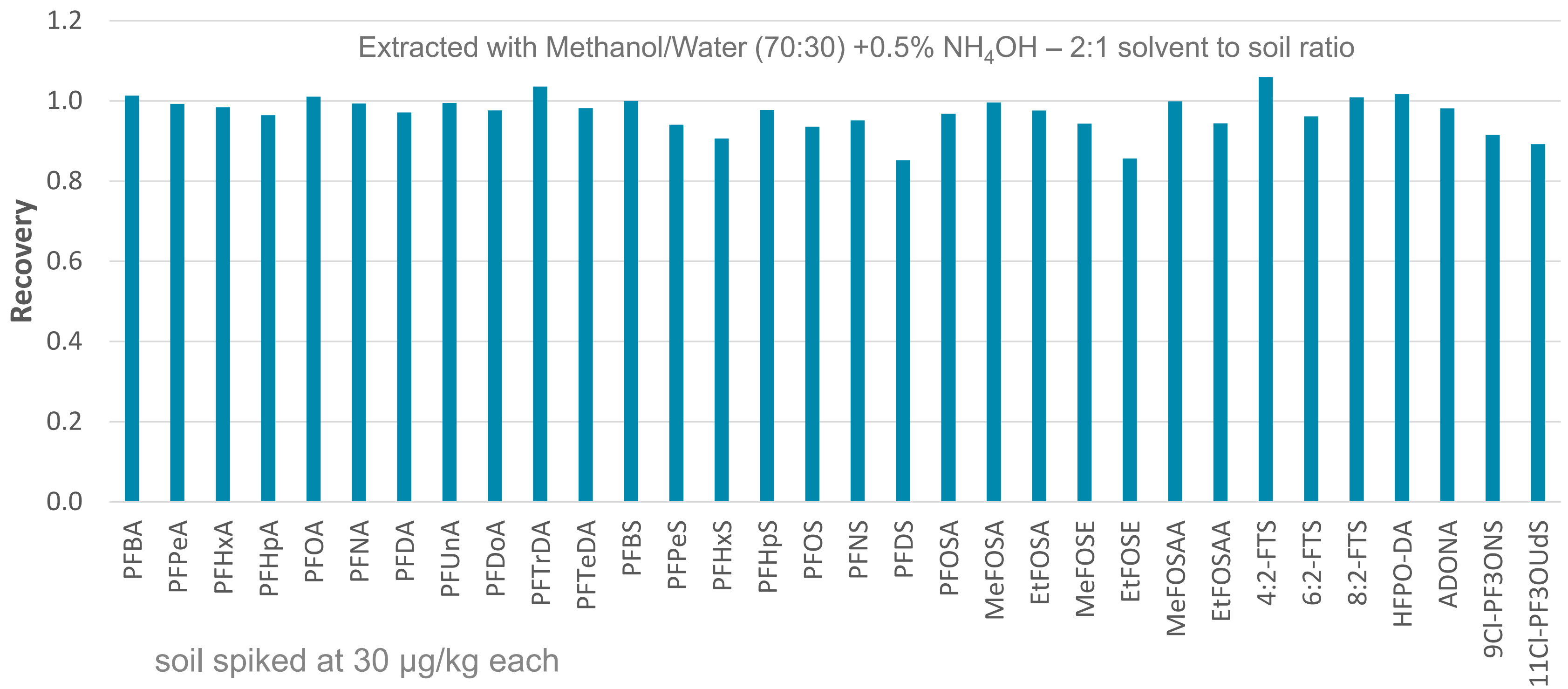


BUREAU VERITAS

RESULTS: AOF-CIC RECOVERY INVESTIGATION

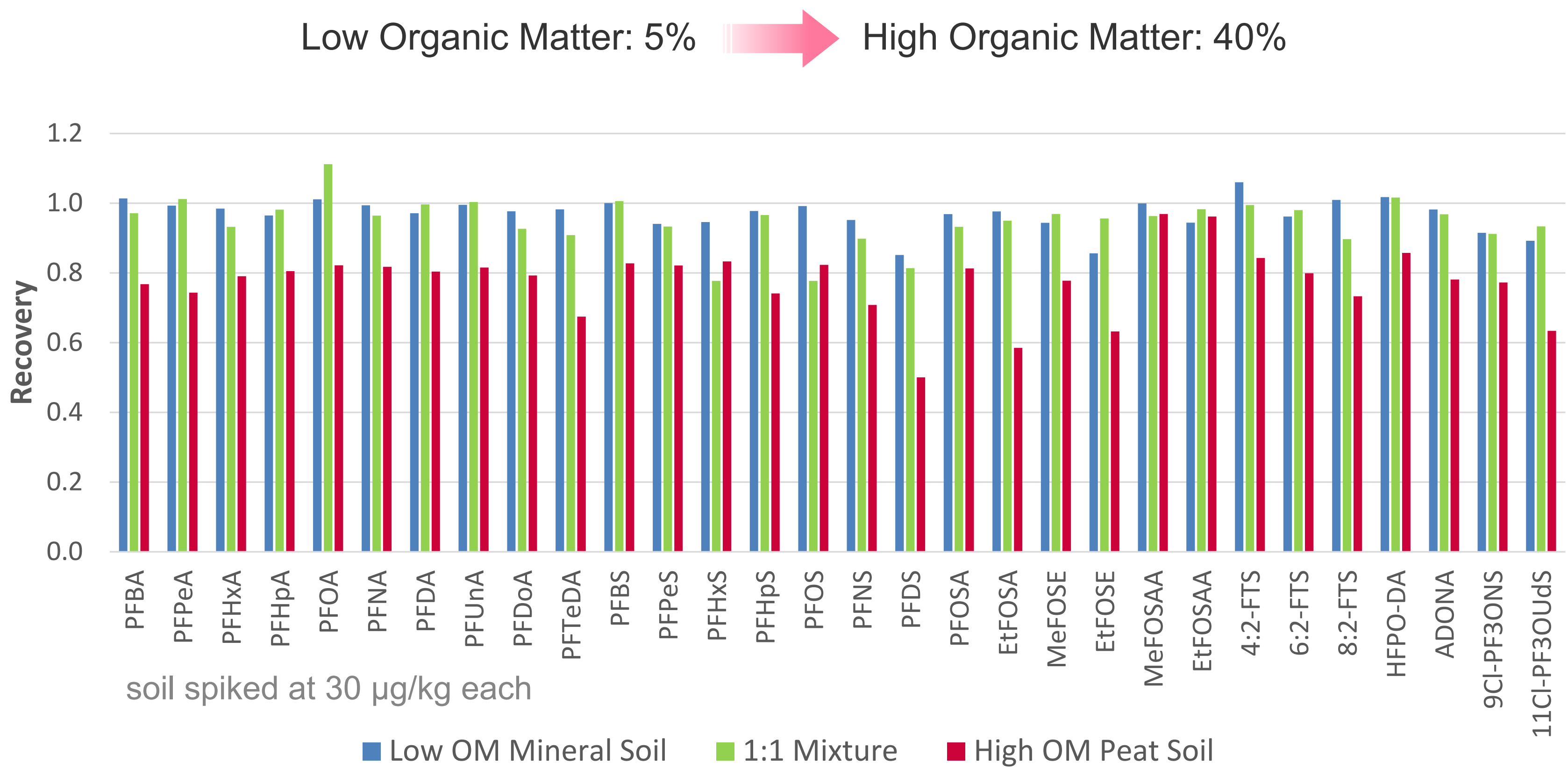
Soil extraction efficiency:

- PFAS standards spiked to real soil sample, extracted by **Accelerated Solvent Extraction**, and processed by **LC-MS/MS** by isotope dilution mass spectrometry.



soil spiked at 30 µg/kg each

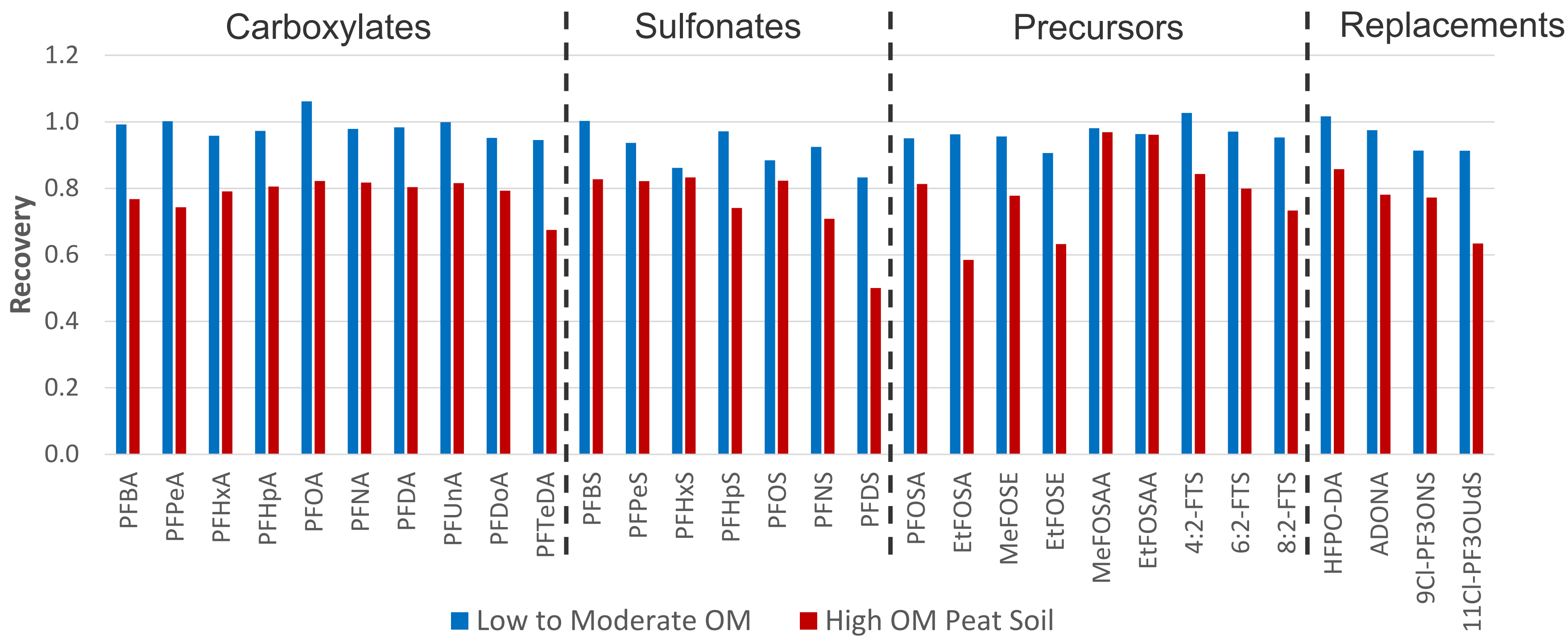
RECOVERY vs SOIL ORGANIC MATTER



Only very high OM soil has significant impact on recovery.

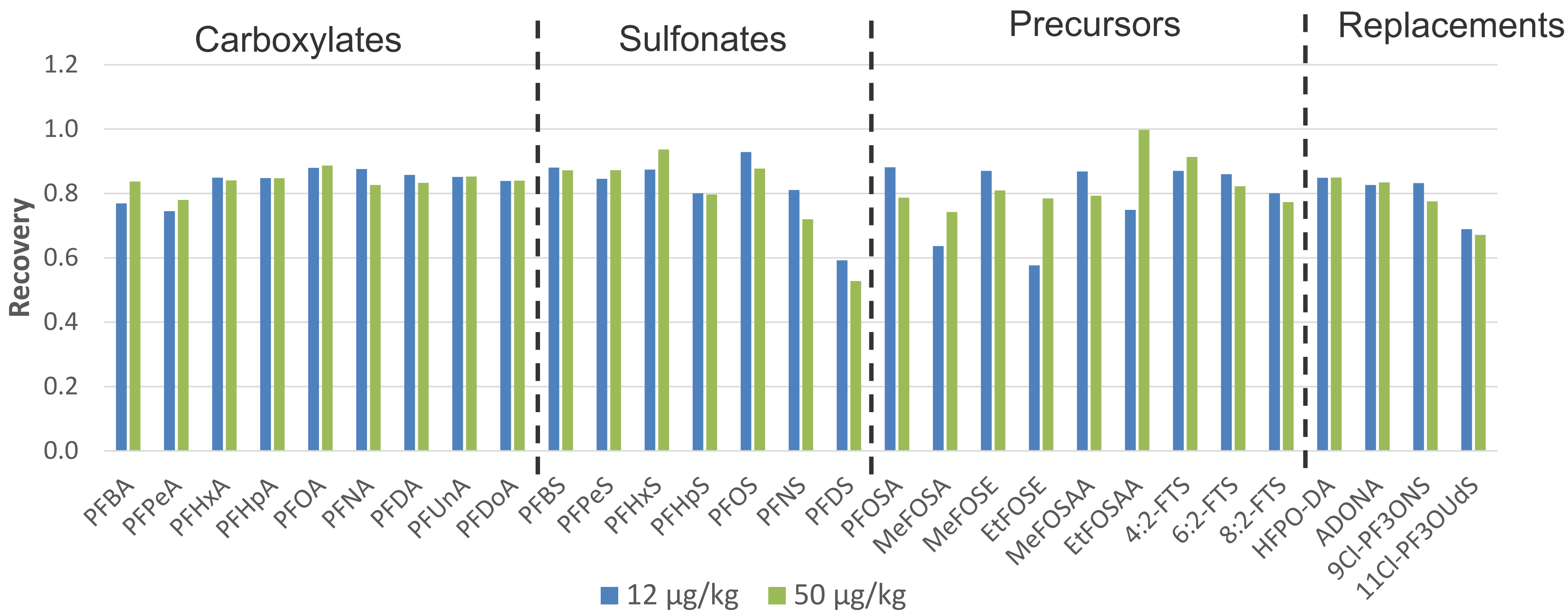
RECOVERY vs SOIL ORGANIC MATTER

Low-Moderate Organic Matter: 5% to 20% → High Organic Matter: 40%



Spike level 30 µg/kg

HIGH OM SOIL RECOVERY vs SPIKE LEVEL



No significant impact of spike level on high OM soil recovery

HOW WELL DOES AOF-CIC COMPARE TO TOF-EQ?

thermoscientific

Thermo Scientific Application Note 73481

AOF by combustion IC – non-targeted complemental determination of PFAS in aqueous samples

Carboxylic Acids	Acronym	% Recovery
Trifluoroacetic acid	TFA	**<2**
Pentafluoropropionic acid	PFPrA	**<2**
Perfluorobutanoic acid	PFBA	**52**
Perfluoropentanoic acid	PFPeA	95
Perfluorohexanoic acid	PFHxA	84
Perfluoroheptanoic acid	PFHpA	82
Perfluorooctanoic acid	PFOA	**64**
Perfluorononanoic acid	PFNA	**47**
Perfluorodecanoic acid	PFDA	**41**
Sulfonic Acids		
Trifluoromethanesulfonic acid	TMSA	**<2**
Perfluoropropanesulfonic acid	PFPrSA	99
Perfluorobutanesulfonic acid	PFBS	100
Perfluoropentanesulfonic acid	PFPeSA	91
Perfluorohexane sulfonic acid	PFHxS	94
Perfluorooctane sulfonic acid	PFOS	**64**
Other		
6:2-fluorotelomer sulfonic acid	6:2 FTS	**63**
Hexafluoropropyleneoxide Dimer Acid	HFPO-DA	87

Tabular data adapted from App. Note

Authors noted some AOF-CIC recoveries are quite low.

Authors only evaluated at water analysis.

PFAS SOPs typically require minimum recoveries 60% to 70%.

Possible Sources for Low Recoveries:

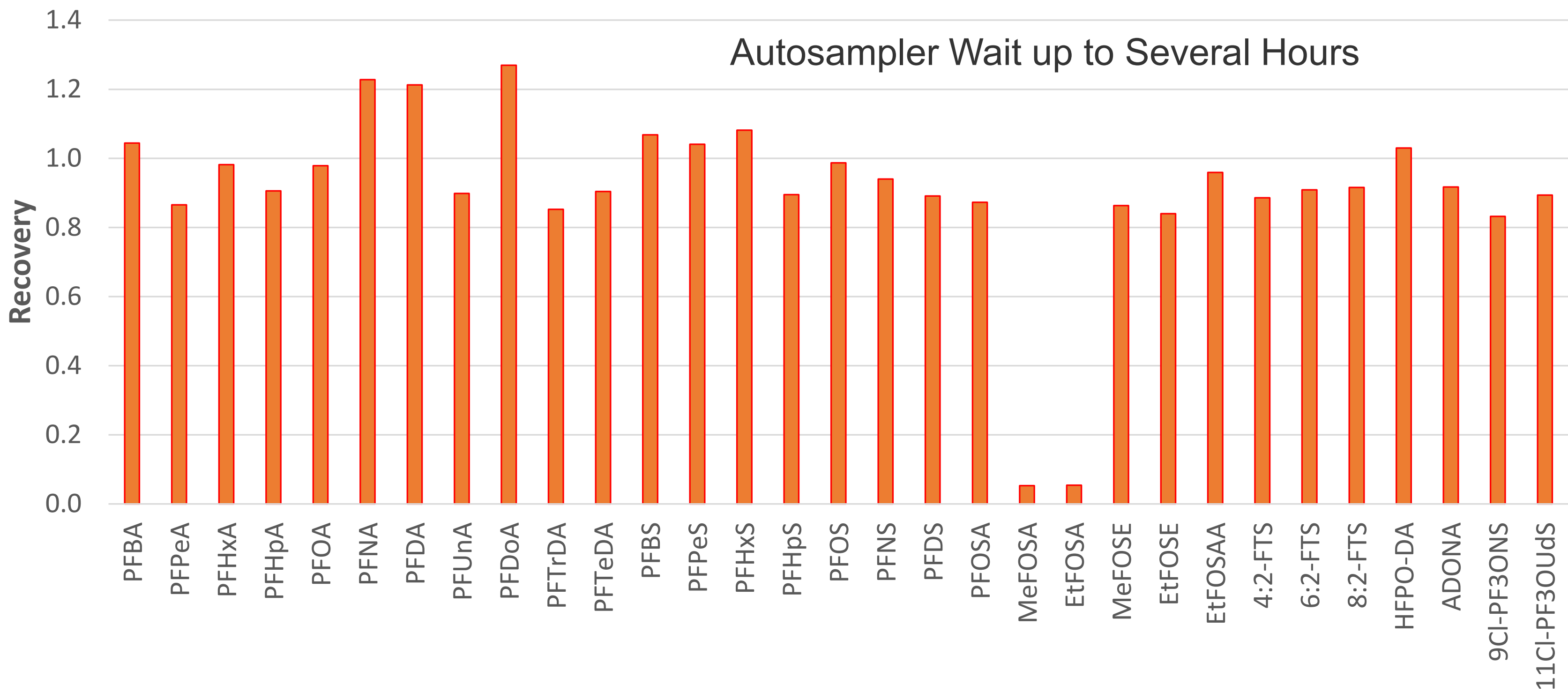
- Combustion efficiency?
- Carbon adsorption efficiency?

Note: High variability in PFAS recoveries is often seen in LC-MS/MS analysis as well, but is corrected for using isotope dilution mass spectrometry.

RESULTS: AOF-CIC RECOVERY INVESTIGATION

Combustion efficiency:

- Individual PFAS standards transferred to ceramic boats and combusted directly.



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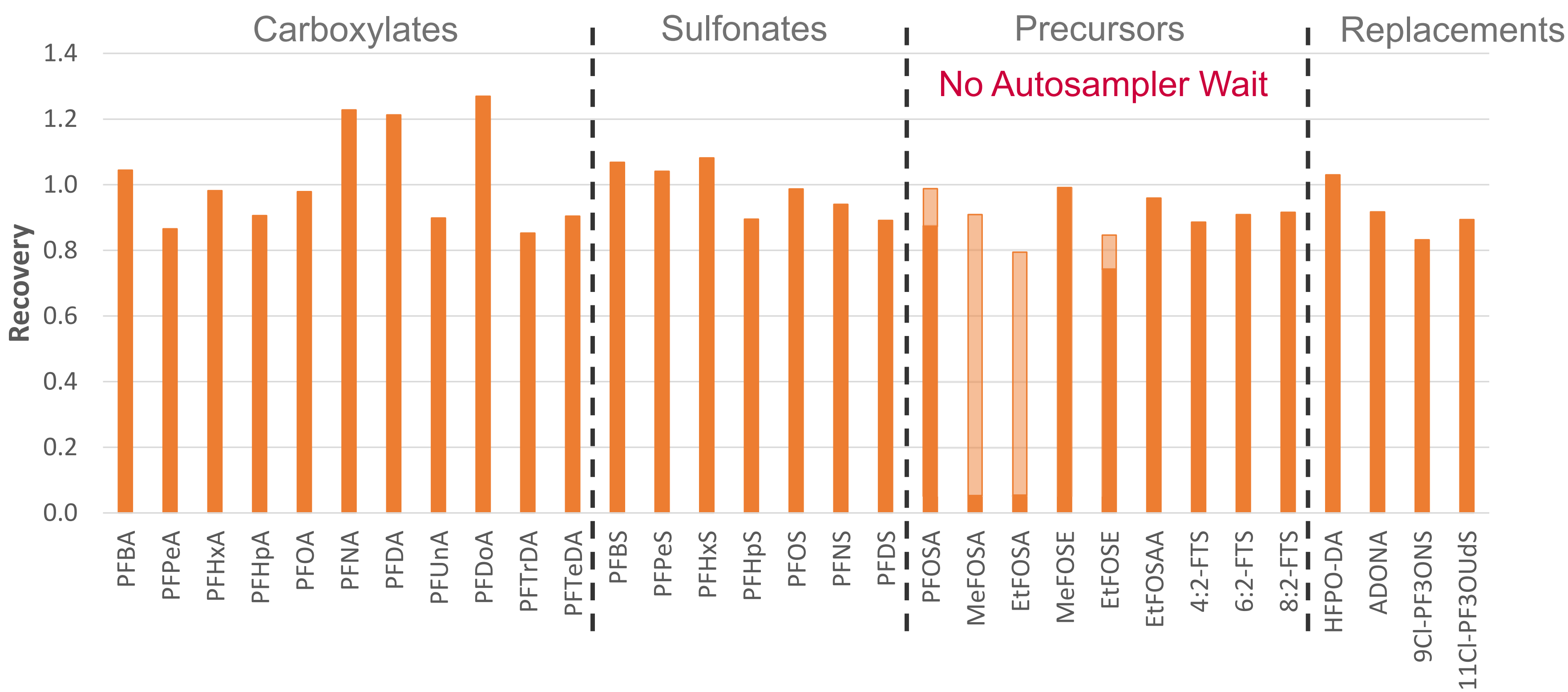
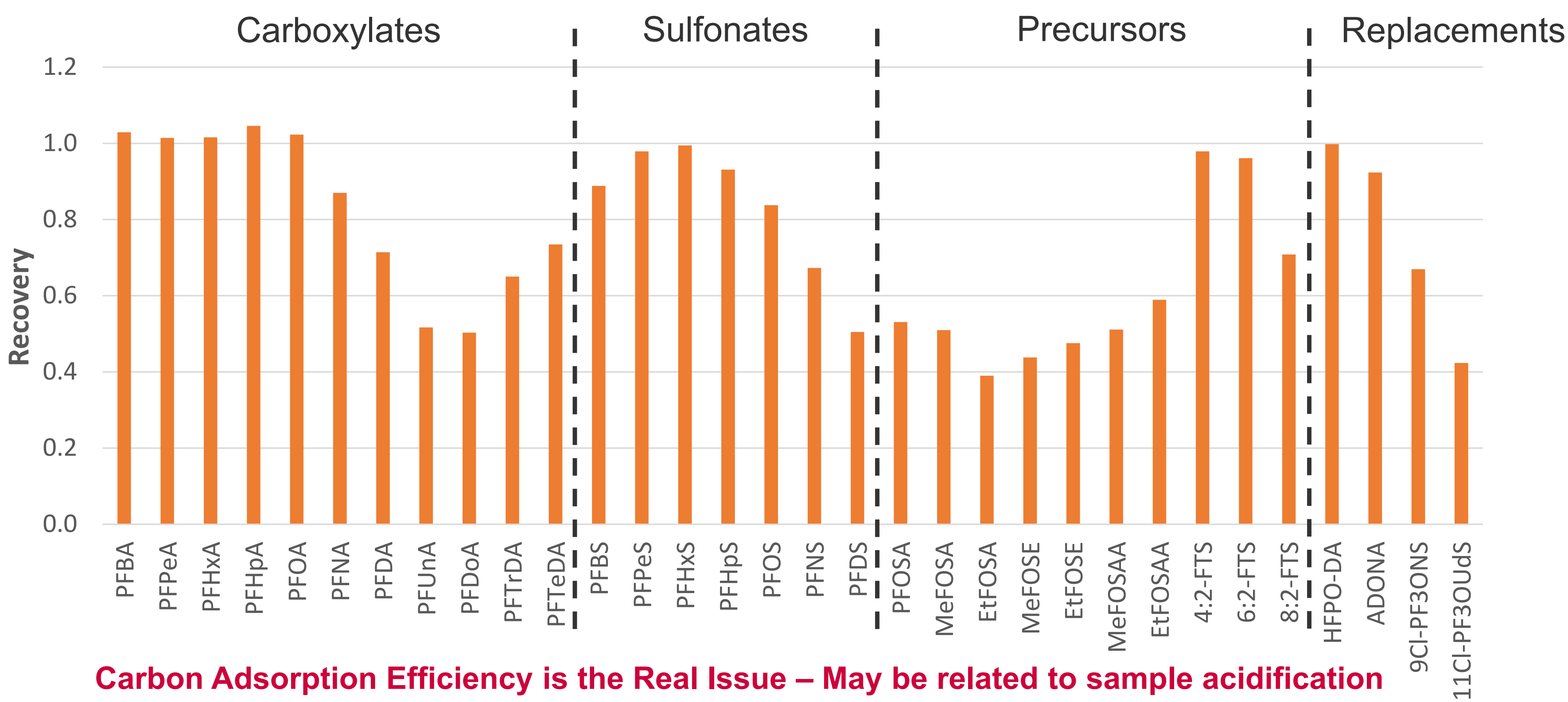


Highly volatile PFAS may be lost during AOF-CIC

RESULTS: AOF-CIC RECOVERY INVESTIGATION

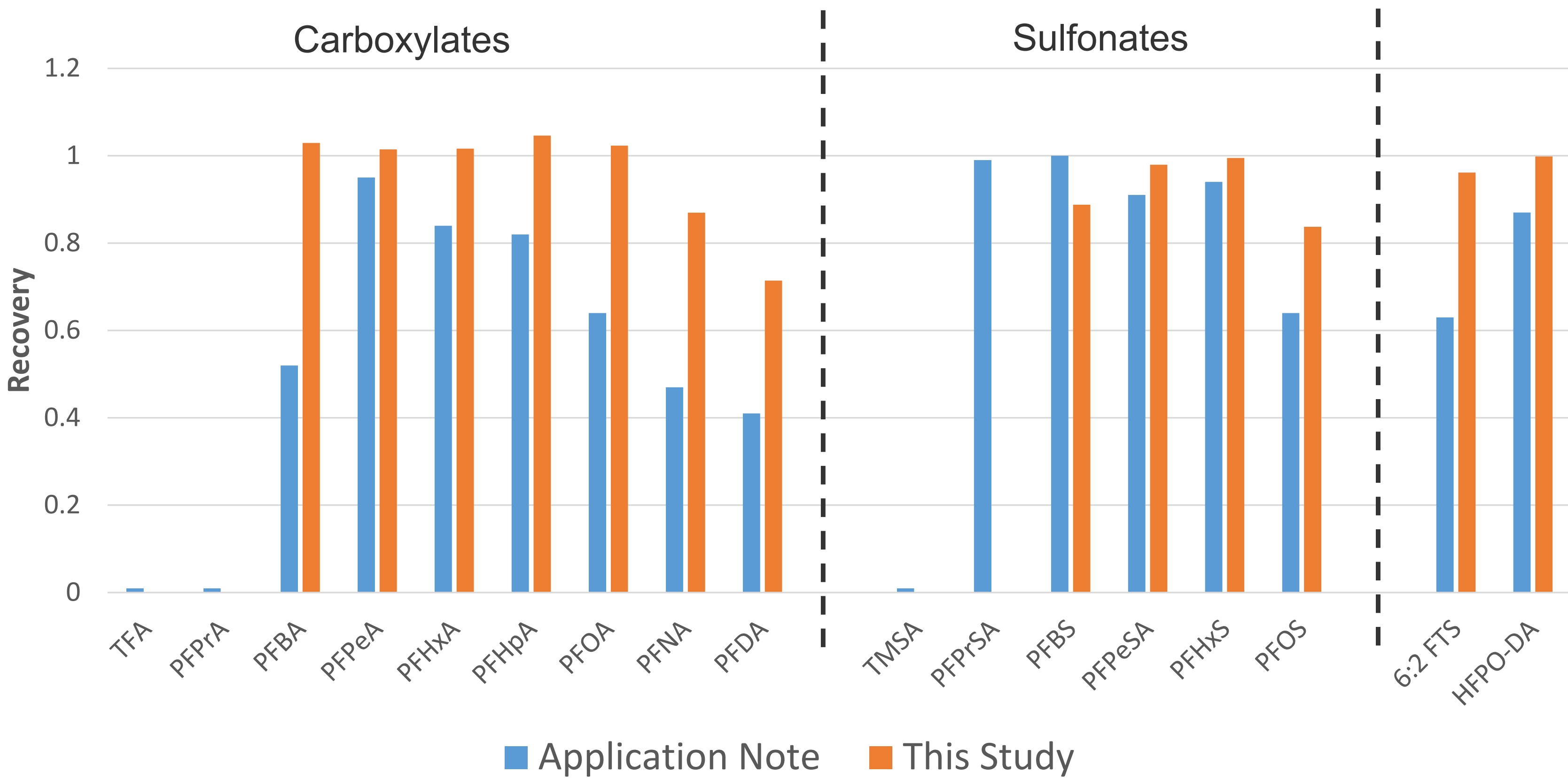
Carbon adsorption efficiency:

- Individual PFAS standards spiked to blank water and processed by TOF/AOF-CIC



Carbon Adsorption Efficiency is the Real Issue – May be related to sample acidification

RECOVERY COMPARISON: APP NOTE VS THIS INVESTIGATION



Our recoveries generally higher than the Application Note
PFAS <C4 not evaluated

CONCLUSIONS

1. Carboxylates and Sulfonates C4-C9 recovered with good efficiency.
2. Some lower recoveries for high OM soils & highly volatile PFAS. AOF carbon adsorption efficiency could be improved.
3. Applicability to soil extract analysis is demonstrated.
4. Reduced cost & faster turn-around
5. Improved monitoring of remedial progress
6. Method improvements are under investigation.

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COMMENTS AND QUESTIONS

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