TOTAL ORGANOFLUORINE (TOF) ANALYSIS BY COMBUSTION ION CHROMATOGRAPHY

A New Tool for Monitoring PFAS Impacts

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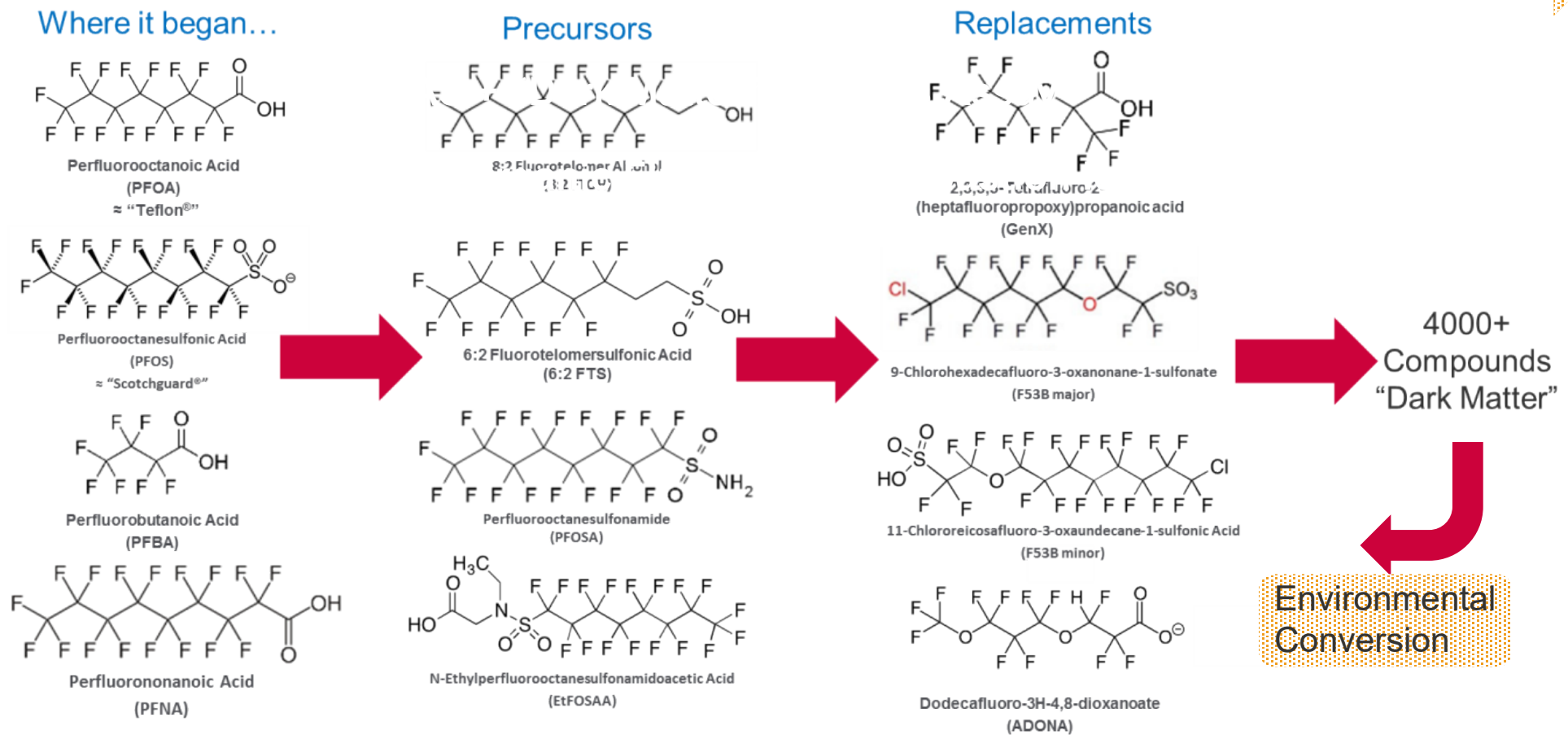
LC-MS/MS ANALYSIS TELLS PART OF THE STORY

Total Organic Fluorine (TOF)

Total Oxidizable Precursors (TOPs)



PFAS by LC-MS/MS

EPA DRAFT METHOD 1621 – PUBLISHED APRIL 2022

"Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)"

TOF vs AOF?

AOF is one of two common approaches to measuring Total Organic Fluorine by CIC

- AOF: Adsorbable Organic Fluorine
- EOF: Extractable Organic Fluorine

Note: EPA 1621 has been published in Draft, following completion of a Single Laboratory Validation study (SLV).

A multi-laboratory validation study (MLV) is planned for 2022. The Office of Water will use the results of the multi-laboratory validation study to finalize the method and add formal performance criteria. The method validation process may adjust some of the parameters listed in this draft method.

TWO CIC TOF DETERMINATION APPROACHES

Water Sample or Soil Extract = Total Fluorine

SPE – **Carbon** Cartridge

resin

Combustion

IC

AOF

EPA Method 1621 (draft)
DIN 38409-59:2020-11(draft)

SPE – **WAX** or **HLB** Cartridge

extract

Combustion

IC

EOF

EOF: no standard methods yet

ADSORBABLE ORGANIC FLUORINE-CIC ANALYSIS STEPS

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

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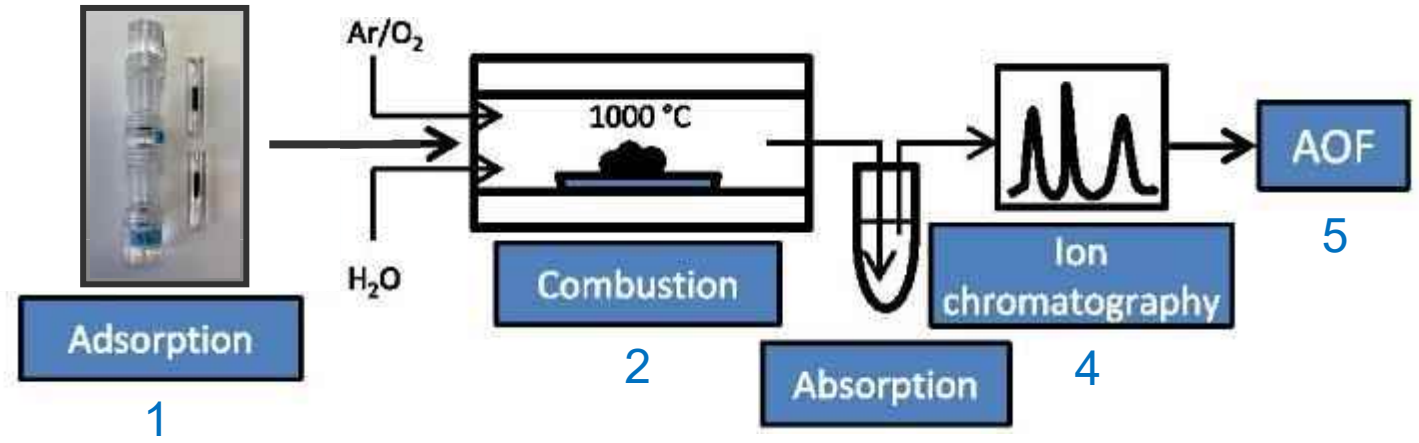
journal homepage: www.elsevier.com/locate/scitotenv

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



Combustion: Mitsubishi AQF-2100H

IC: Thermo Integrion

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 (IC).
5. Fluorine signal reported as Total Adsorbed Organic Fluorine.

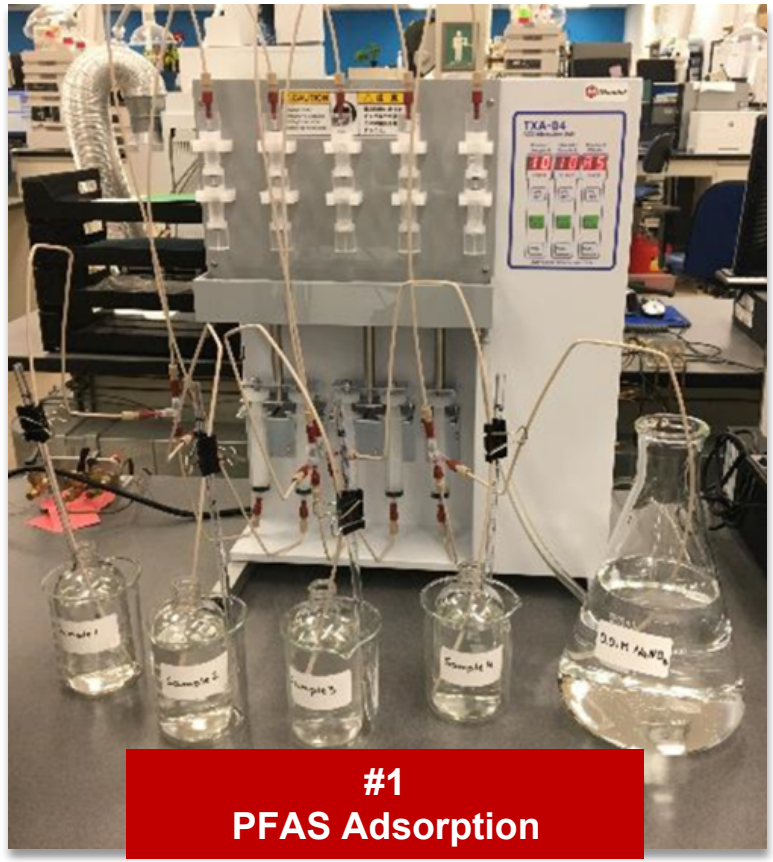
Procedures are very similar to EPA 1621

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

BUREAU VERITAS AOF-CIC SYSTEM

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

AOF Sample Pre-Treatment



WHAT ABOUT INORGANIC FLUORINE?

EPA 1621 Single Laboratory Validation Data (SLV)

"The nitrate wash employed in the method is capable of removing up to 8 mg/L of inorganic fluorine that may be adsorbed in conjunction with organofluorines, reducing the positive bias from inorganic fluoride."

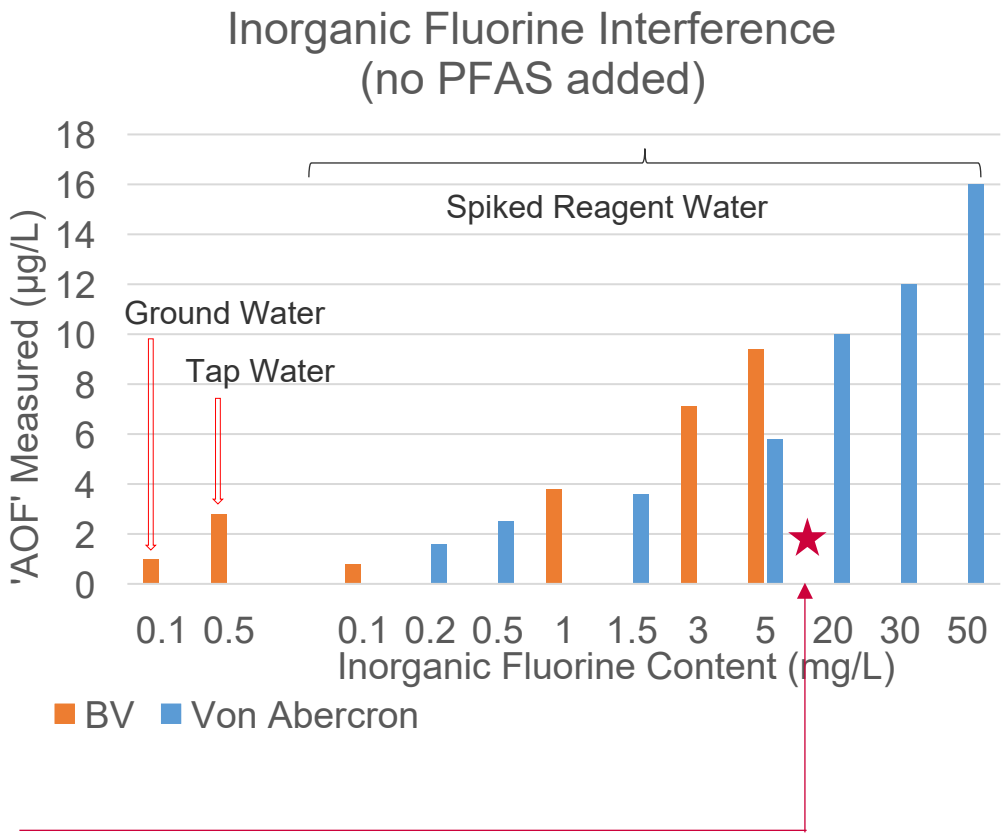
Table 4-9 Inorganic Fluorine Interference on GAC Adsorption

	4 mg F^-/L				8 mg F^-/L			
	% Recovery			RSD	% Recovery			RSD
Compound	Rep 1	Rep 2	Rep 3	(%)	Rep 1	Rep 2	Rep 3	(%)
PFHxS	99	94	102	4.1	118	140	132	8.5

6.2 µg/L F^- from PFHxS per sample

Suggests ~2 µg/L interference from 8 mg/L inorganic fluorine.

BV Study vs Literature Data



SLV data indicates EPA 1621 has lower levels of interference than the literature method.

COMPARISON: BV METHOD VS EPA 1621

Similarities

- Equipment
- Sample preparation – carbon adsorption
- Combustion procedure
- IC procedure
- QA/QC
- Reporting Limit

COMPARISON: BV METHOD VS EPA 1621

Differences

	BV	EPA 1621	Comment
Sample Volume	250 mL	100 mL	BV method allows for reduced sample volume submission.
SPE surface adsorption mitigation	Yes	No	BV method: surfaces passivated prior to extraction with additional sample volume.
Hold time	28 d	90d	BV will switch to 90d hold time now that we have the SLV data.
Sample pH	pH < 2	pH ≥ 5	BV will switch to pH ≥ 5 now that we have the SLV data.
Instrument run time	30 min	15 min	Longer run time allows good separation between fluoride & chloride, no chloride interferences seen to date.
Instrument Runs	One	Two or three	SPE sorbents combusted separately. Beneficial for MLV but limited practical value afterwards. Added cost and TAT.
Matrices	Water, soil, AFFF	Water only	EPA method developed through EPA Office of Water.
Chloride/Fluoride checks	On request	Each sample	Beneficial for MLV, afterwards will delay turnaround as checks need to be done prior to extraction.

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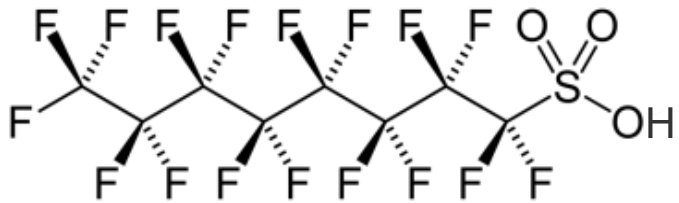
WHAT DO TOF RESULTS MEAN?

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…

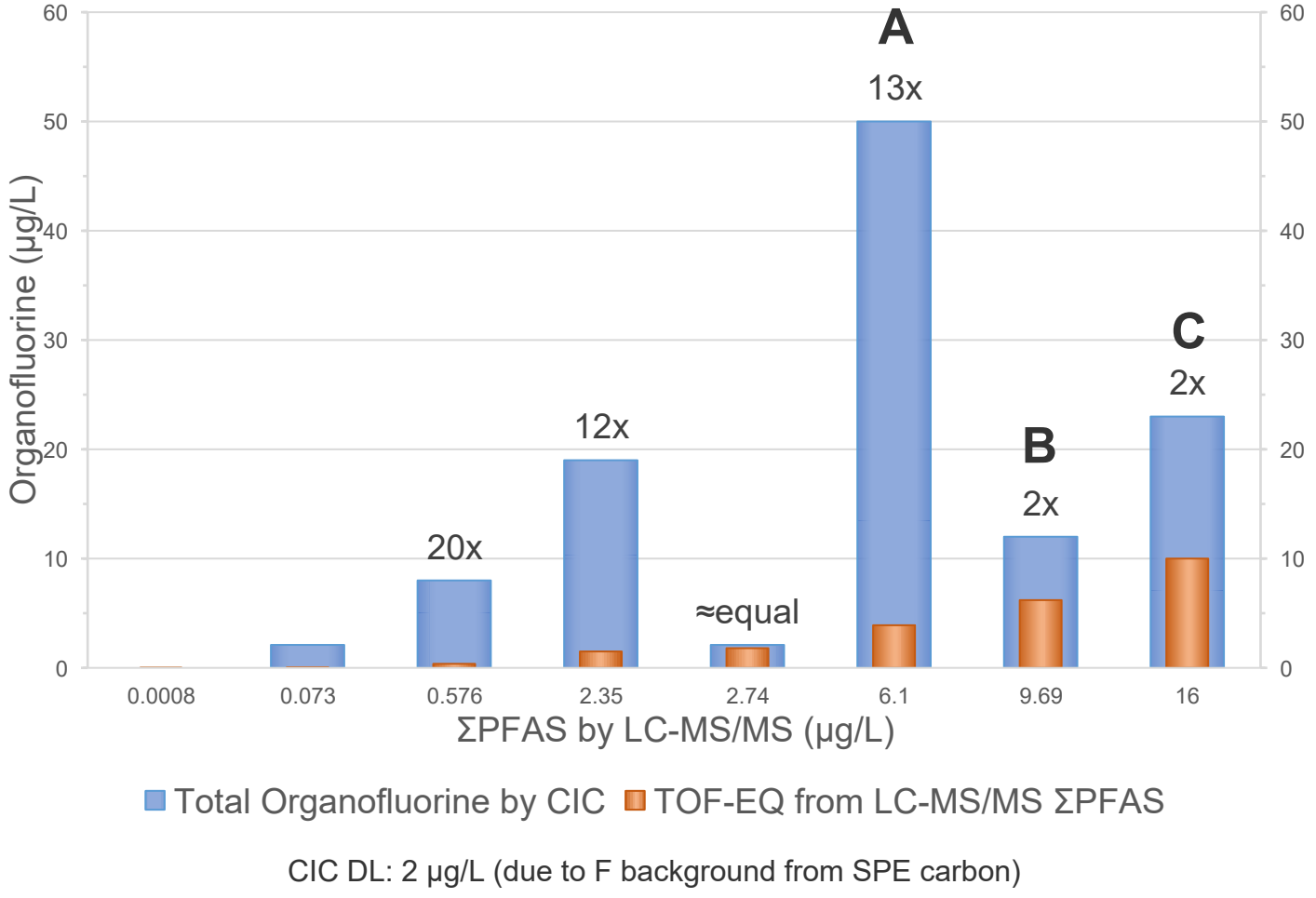
PFOS (by LC/MS/MS) = **250 ng/L PFOS**

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

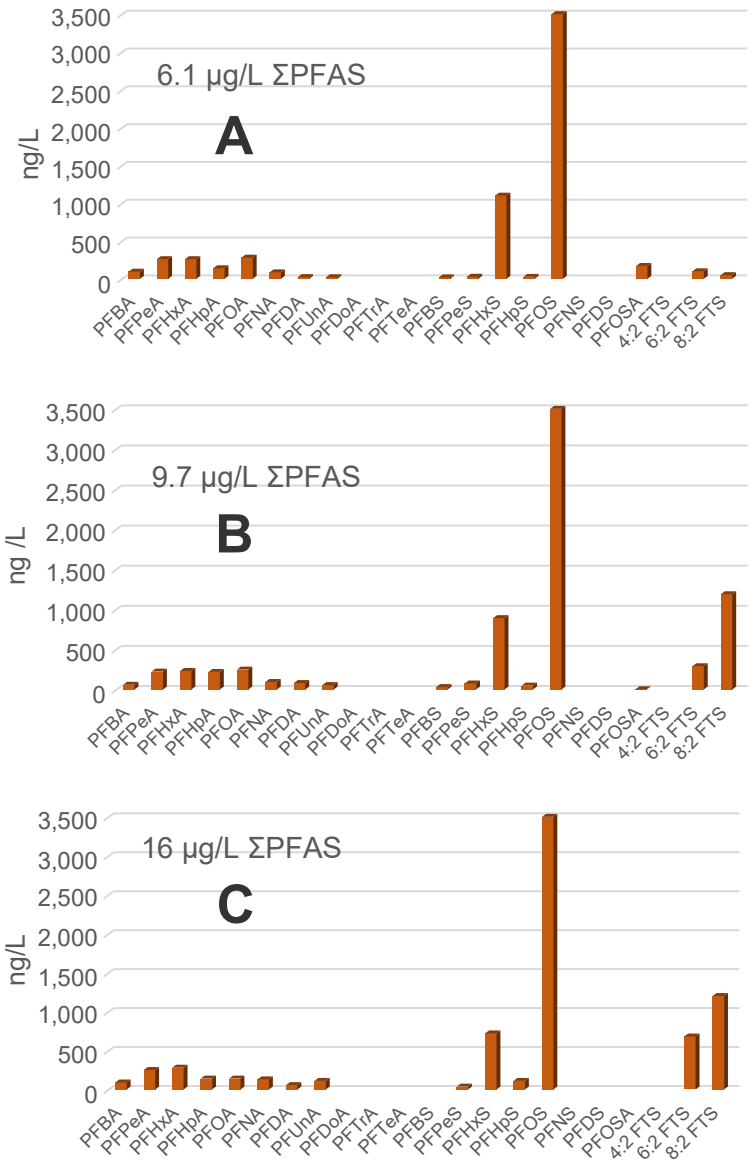
= **162 ng/L F**

PFOS TOF equivalent (TOF-EQ) ~65%

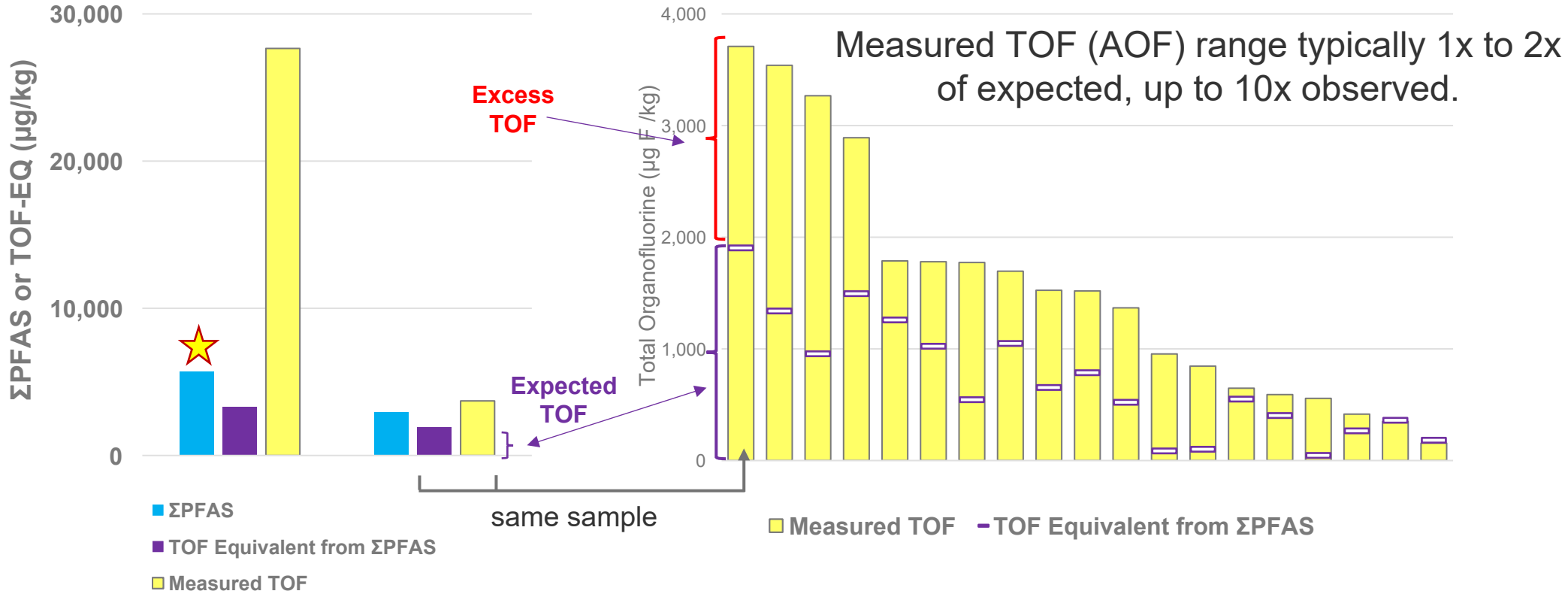
LC-MS/MS vs. AOF-CIC: WATER SAMPLES



CIC DL: 2 µg/L (due to F background from SPE carbon)

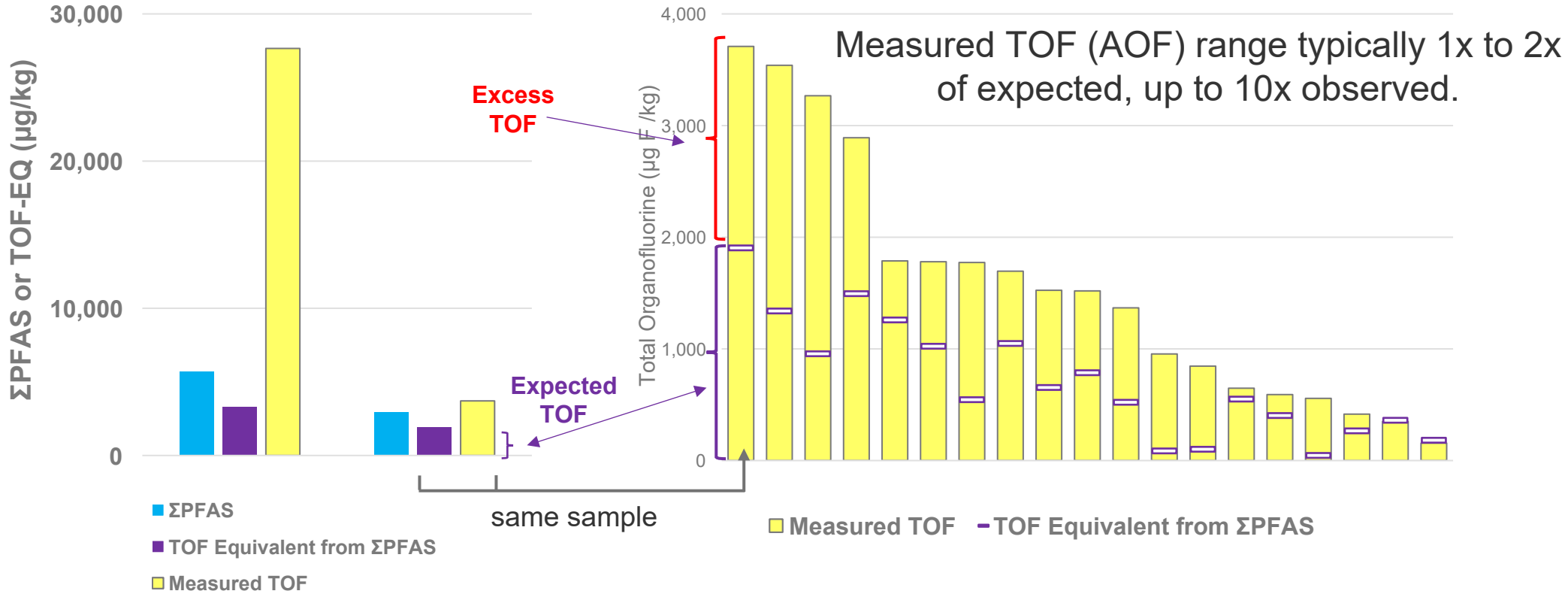


LC-MS/MS vs. AOF-CIC: SOIL SAMPLES



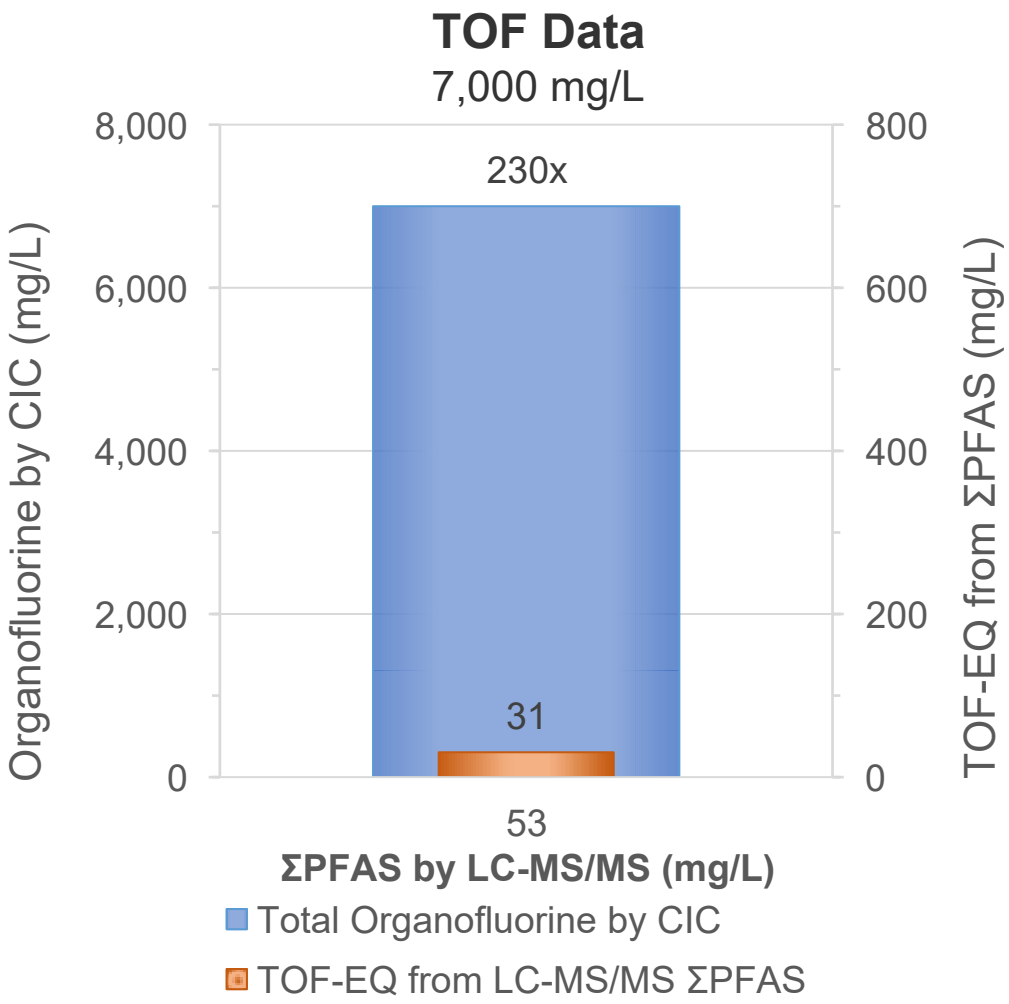
★ Sample was primarily 6:2 fluorotelomer sulfonate

LC-MS/MS vs. AOF-CIC: RISK ASSESSMENT STRATEGY

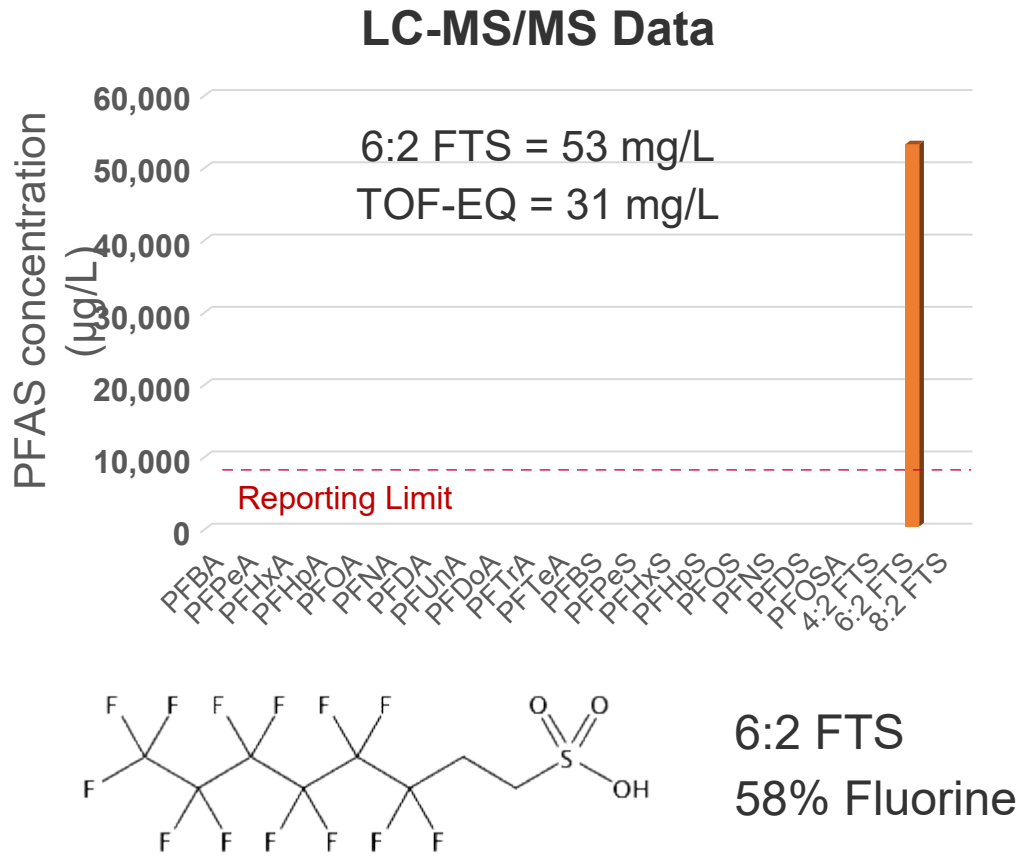


The closer the **Expected TOF (TOF-EQ)** and the **Observed TOF** results are, the more confident you can be that targeted analysis results will accurately estimate risk.

LC-MS/MS vs. AOF-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."

WATER RECOVERIES?

Thermo Scientific Application Note 73481

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

- Follows von Abercron method
- Investigated individual PFAS recoveries

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

Some reported recoveries are quite low.

PFAS SOPs typically require minimum recoveries ~50%

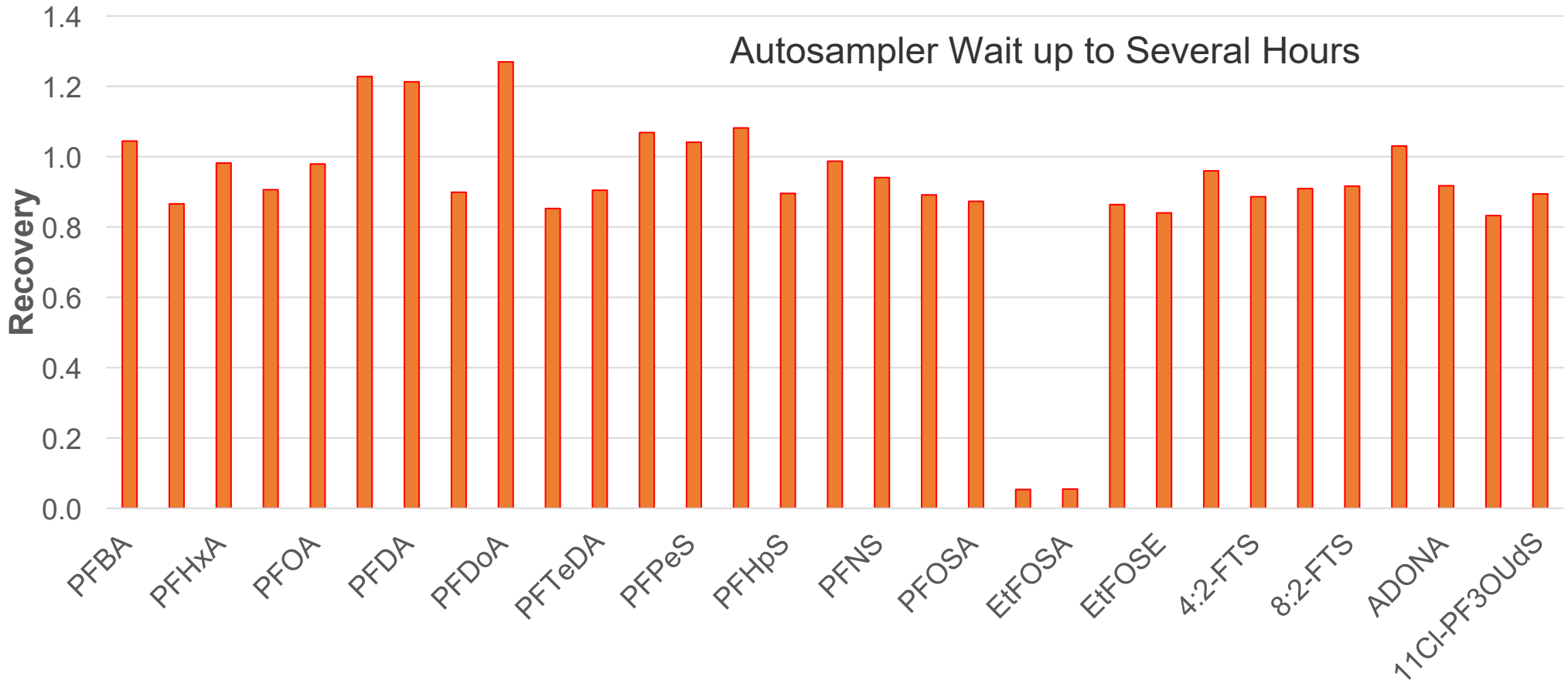
Possible Sources for Low Recoveries:

- Combustion efficiency?
- Carbon adsorption efficiency?

RESULTS: AOF-CIC RECOVERY INVESTIGATION

Combustion efficiency:

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



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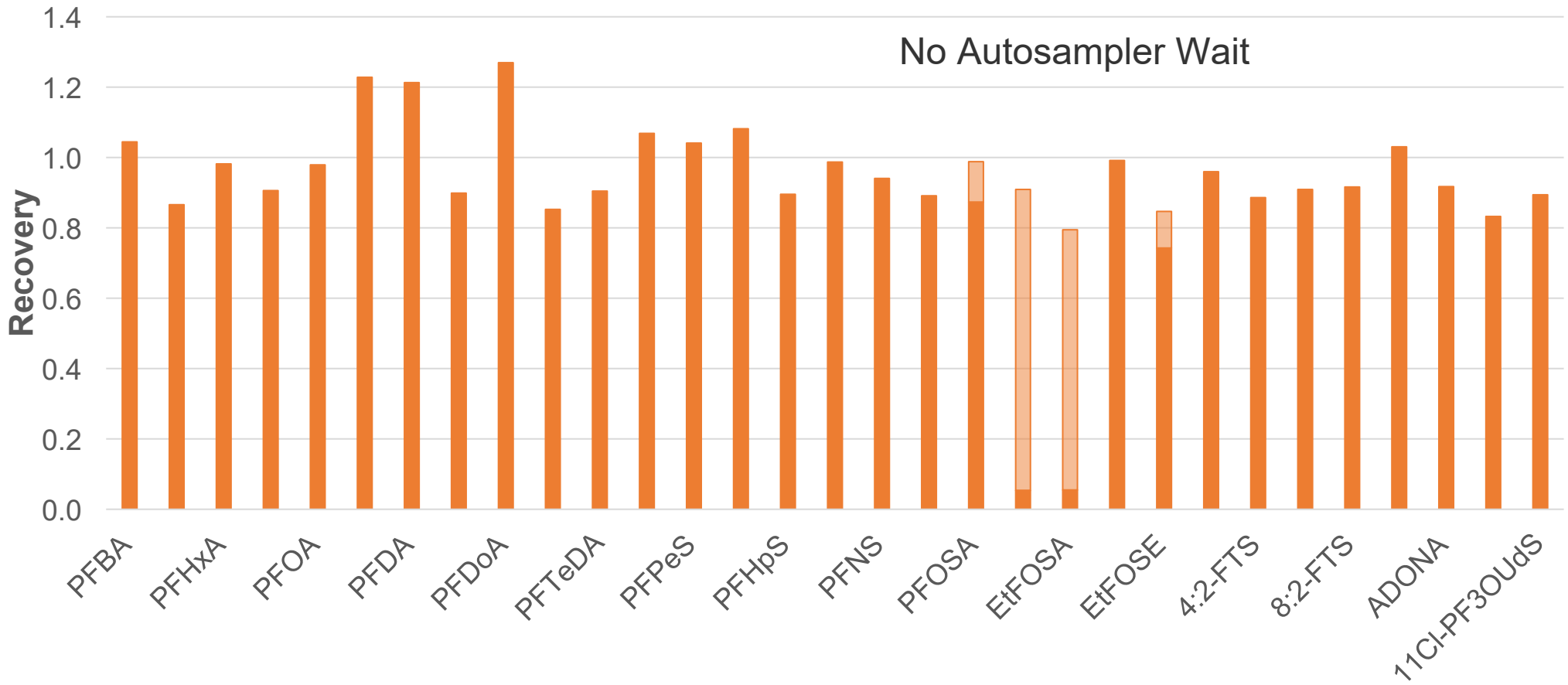
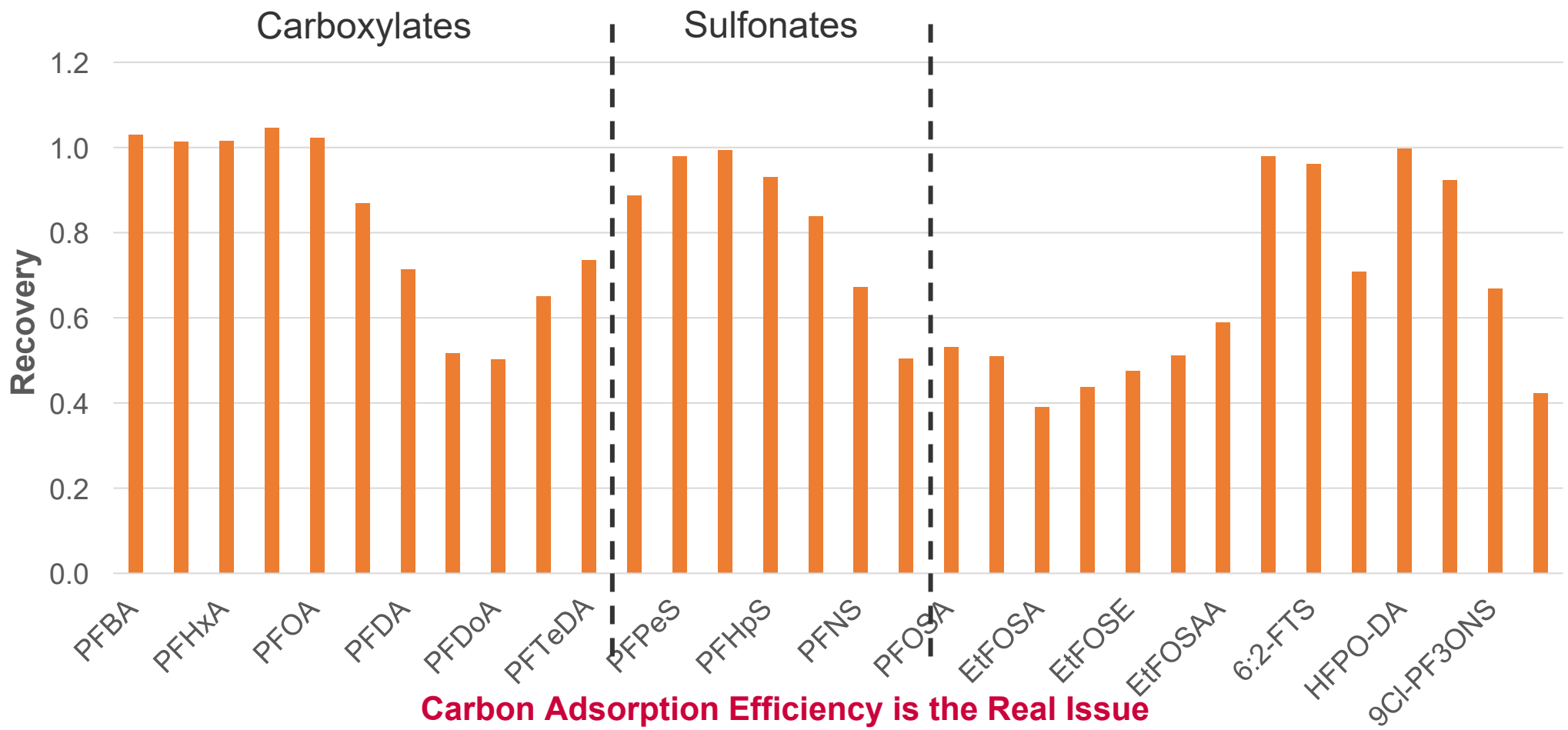


Highly volatile PFAS may be lost during AOF-CIC

RESULTS: AOF-CIC RECOVERY INVESTIGATION

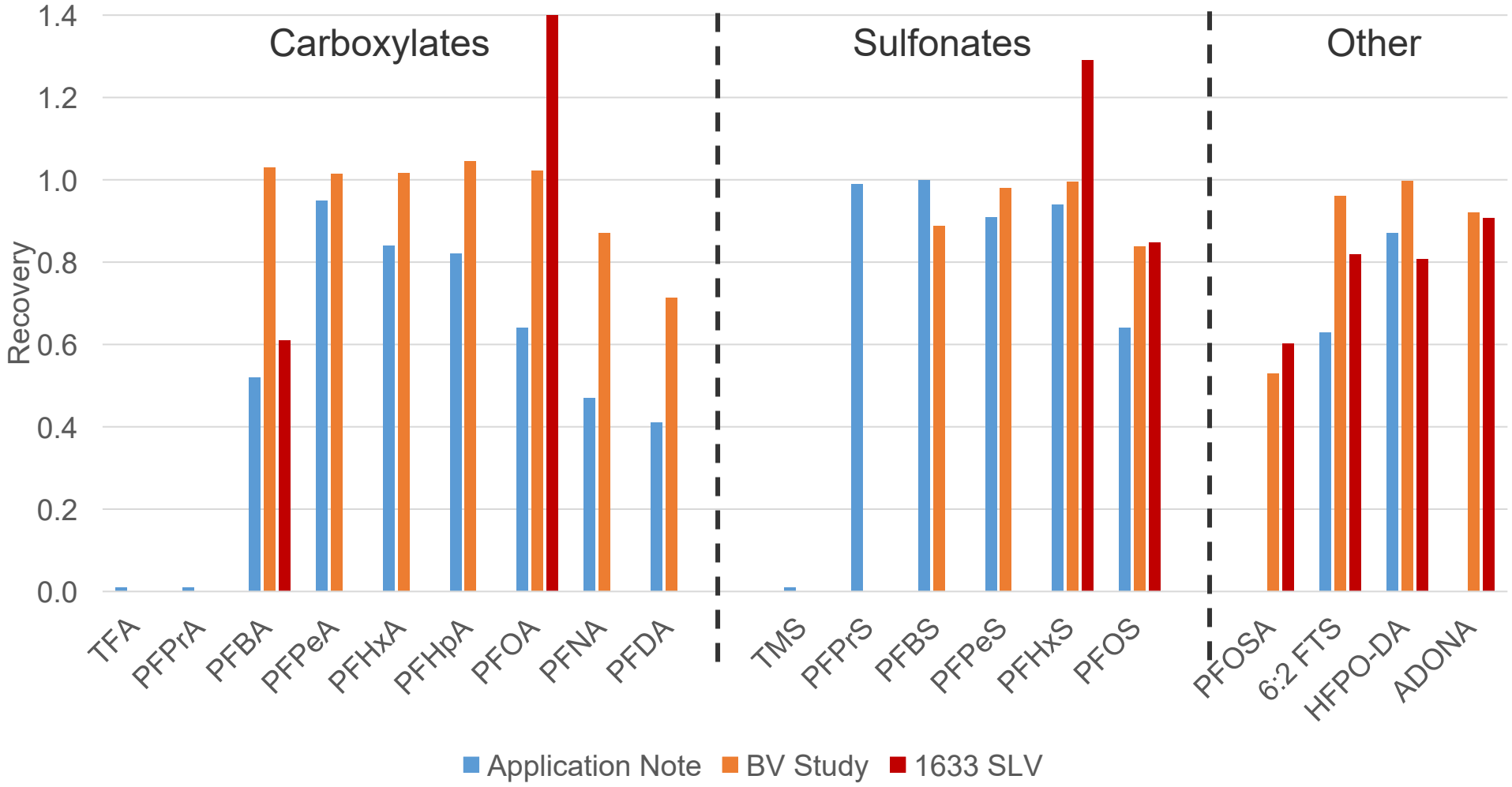
Carbon adsorption efficiency:

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



Carbon Adsorption Efficiency is the Real Issue

RECOVERY COMPARISON: BV INVESTIGATION VS APP NOTE & SLV



BV study recoveries generally higher than the Application Note & consistent with SLV

CONCLUSIONS – AOF-CIC

1. Total organofluorine provides an inexpensive alternative for PFAS screening.
2. Should verify inorganic fluorine is excluded from TOF results.
3. Comprehensive evaluation of carbon adsorption efficiency is warranted.
4. Introduction of EPA 1621 will reduce inter-laboratory variability.
5. Where TOF >> TOF-EQ (calculated from targeted analysis) further analysis is warranted.

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COMMENTS AND QUESTIONS

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