Environmental Measurement Symposium

Characterization of PFAS in Wastewater Using Multiple Target Analytical Methods

August 4th, 2025

Jonathan Thorn

Technical Director & PFAS Practice Leader

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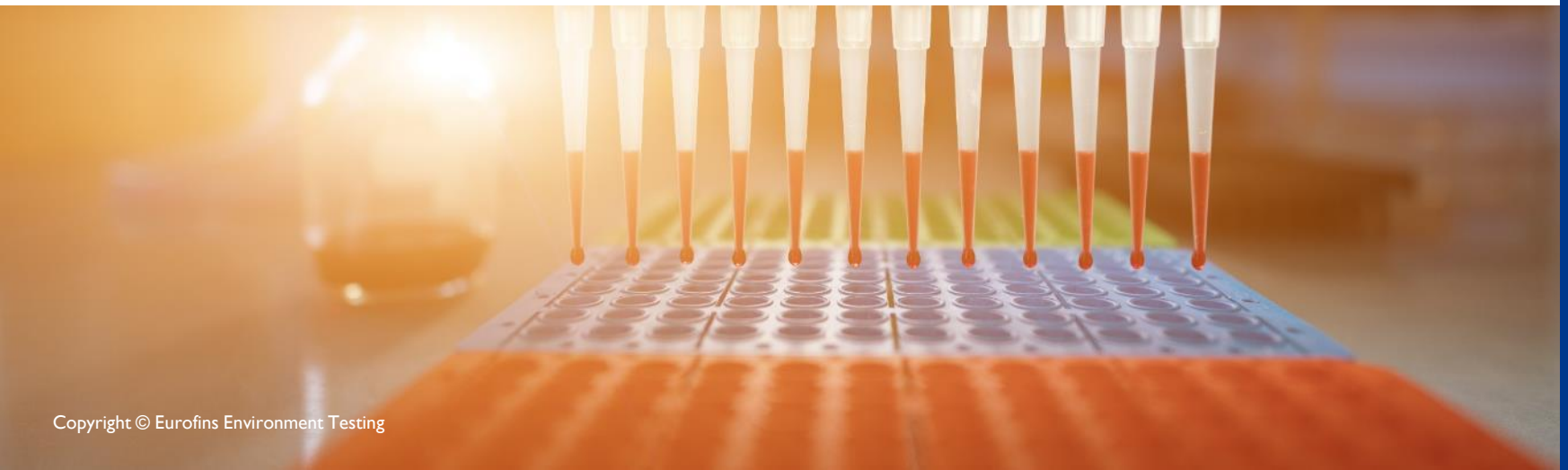
Presentation Topics

- EPA 1633A
- Other targeted and proxy methods
- Real world data



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Thank You!

- Hannah Kruelle – Principal Chemist
- Joseph Anderson – Technical Director
- Toby Barnhart – Chemist

The Published Method: EPA 1633A

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EPA 1633A (December 2024)

- CWA method
- Multi-lab validated for surface water, groundwater, wastewater, landfill leachate, soil, sediment, biosolids, fish, and shellfish tissue
- Solid Phase Extraction - aqueous
- Solvent extraction followed by SPE – all other matrices
- Carbon cleanup
- LC/MS/MS
- Isotope Dilution quantification
- 40 target analytes

EPA 1633A Multi-Lab Validation Study

- 8 Commercial / 2 state laboratories
- Tested in real world matrices
  - No fortifications
  - Low-level fortification
  - High-level fortification
  - Each in triplicate
- Four method drafts, two final versions
- Announced for promulgation December 2024
- MUR 22 posted 1/21/2025

Links to MLV Study Reports:

- Wastewater, Surface Water, and Groundwater
- Soild and Sediment
- Biosolids and Landfill Leachate
- Tissue

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EPA 1633A – Target Analytes

PFCA	PFSA	FTS	PFOSA	PFECA
•PFBA	•PFBS	•4:2 FTS	•PFOSA	•HFPO-DA
•PFPeA	•PFPeS	•6:2 FTS	•NMeFOSA	•ADONA
•PFHxA	•PFHxS	•8:2 FTS	•NEtFOSA	•PFMPA
•PFHpA	•PFHpS	**FTCA**	**FOSAA**	•PFMBA
•PFOA	•PFOS	•3:3 FTCA	•NMeFOSAA	•NFDHA
•PFNA	•PFNS	•5:3 FTCA	•NEtFOSAA	**PFESA**
•PFDA	•PFDS	•7:3 FTCA	**FOSE**	•9Cl-PF3ONS
•PFUnA	•PFDoS		•NMeFOSE	•11Cl-PF3OUdS
•PFDoA			•NEtFOSE	•PFEESA
•PFTrDA				
•PFTeDA				

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EPA 1633A – Section 9.1.2

In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements.

These options include alternative extraction, concentration, and cleanup procedures, and changes in sample volumes, columns, and detectors.

Alternative determinative techniques and changes that degrade method performance are not allowed without prior review and approval (see 40 CFR 136.4 and 136.5).

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1633A Expanded...

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1633A EXP… What is that??

- Section 1.6: In addition, under the allowance for flexibility and method modifications described at 40 CFR 136.6, laboratories may include additional PFAS compounds as target analytes and/or alternative labeled PFAS compounds as authentic standards become commercially available without the need for the EPA review and approval, provided that they complete the requirements in Section 9 for those new analytes.
- 1633A EXP – 59 additional analytes, 15 new EIS

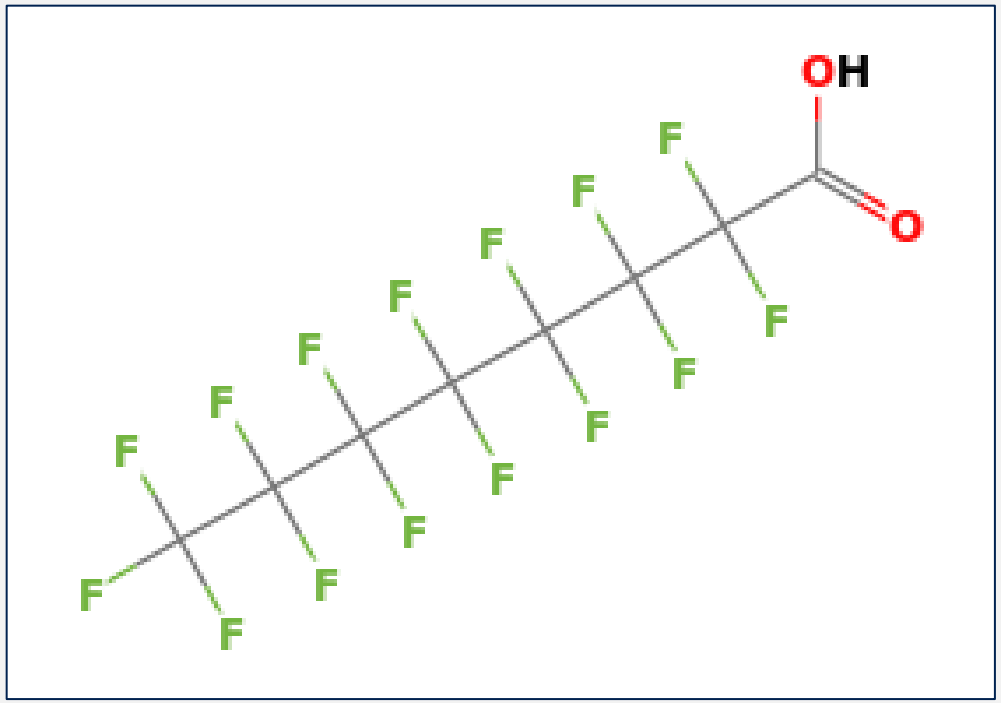
1633A EXP - Analytes

	EPA 1633A
Perfluoroalkyl carboxylic acids (PFCA)	11
Perfluoroalkyl sulfonic acids (PFSA)	8
Fluorotelomer sulfonic acids (FTSA)	3
Perfluorooctane sulfonamides (PFOSA)	3
Perfluorooctane sulfonamidoacetic acids (FOSAA)	2
Perfluorooctane sulfonamide ethanols (FOSE)	2
Per- and Polyfluoroether carboxylic acids (PFECA)	5
Perfluoroalkyl ether sulfonic acids (PFESA)	3
Fluorotelomer carboxylic acids (FTCA)	3

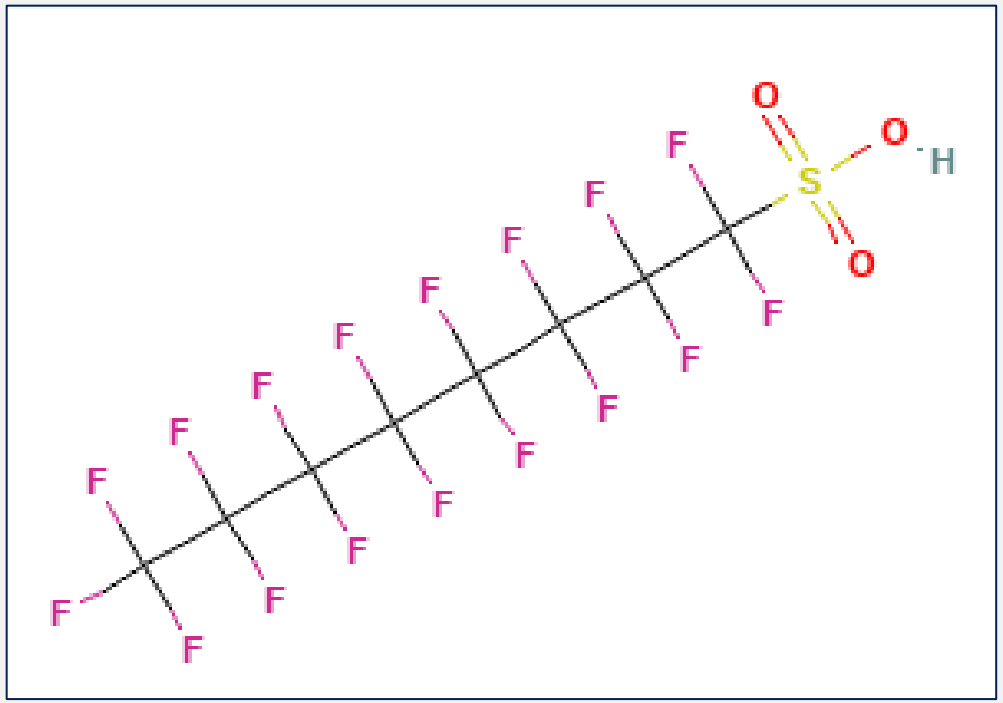
1633A EXP - Analytes

	EPA 1633A	1633A EXP	Combined
Perfluoroalkyl carboxylic acids (PFCA)	11	3	14
Perfluoroalkyl sulfonic acids (PFSA)	8	4	12
Fluorotelomer sulfonic acids (FTSA)	3	1	4
Perfluorooctane sulfonamides (PFOSA)	3	6	9
Perfluorooctane sulfonamidoacetic acids (FOSAA)	2	0	2
Perfluorooctane sulfonamide ethanols (FOSE)	2	0	2
Per- and Polyfluoroether carboxylic acids (PFECA)	5	15	20
Perfluoroalkyl ether sulfonic acids (PFESA)	3	6	9
Fluorotelomer carboxylic acids (FTCA)	3	3	6
Perfluoroalkyl Phosphinates (PFPIA)	0	4	4
Polyfluoroalkyl Phosphate di-esters (diPAP)	0	4	4
Perfluoroalkyl phosphonic acids (PFPA)	0	5	5
Fluorotelomer unsaturated carboxylic acids (FTUCA)	0	3	3
Diprotic	0	3	3
perfluorinated sulfonylimides (PFSI)	0	2	2

1633A EXP - Analytes

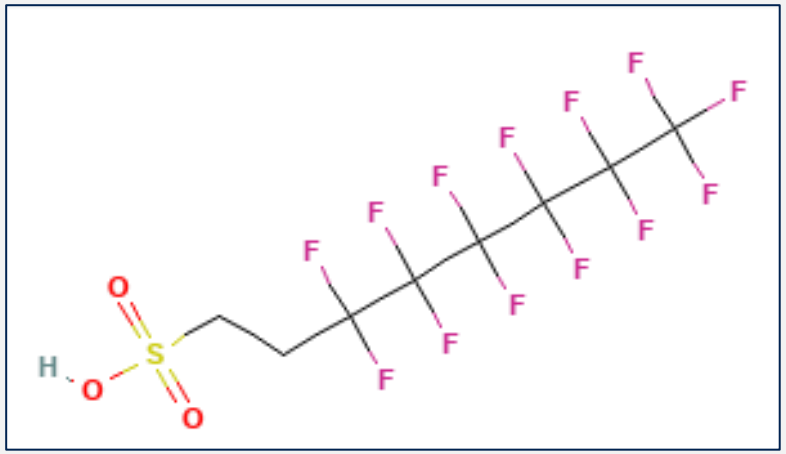


PFOA (PFCA)

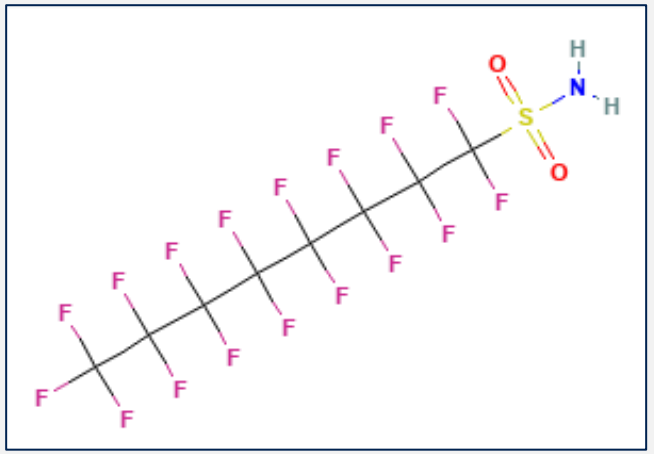


PFOS (PFSA)

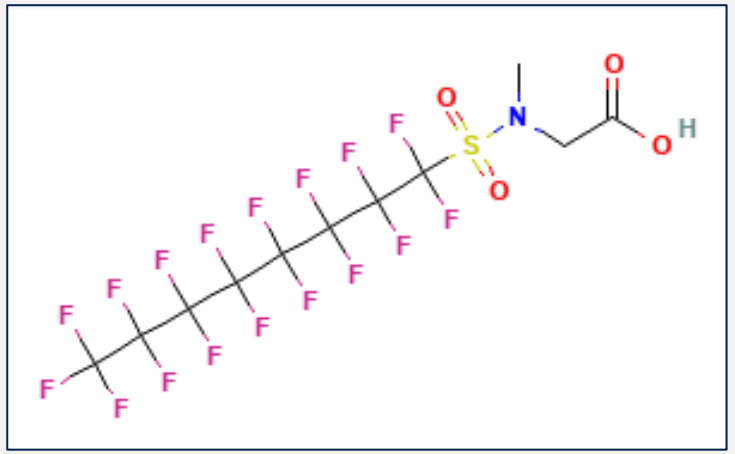
1633A EXP - Analytes



6:2 FTS (FTSA)

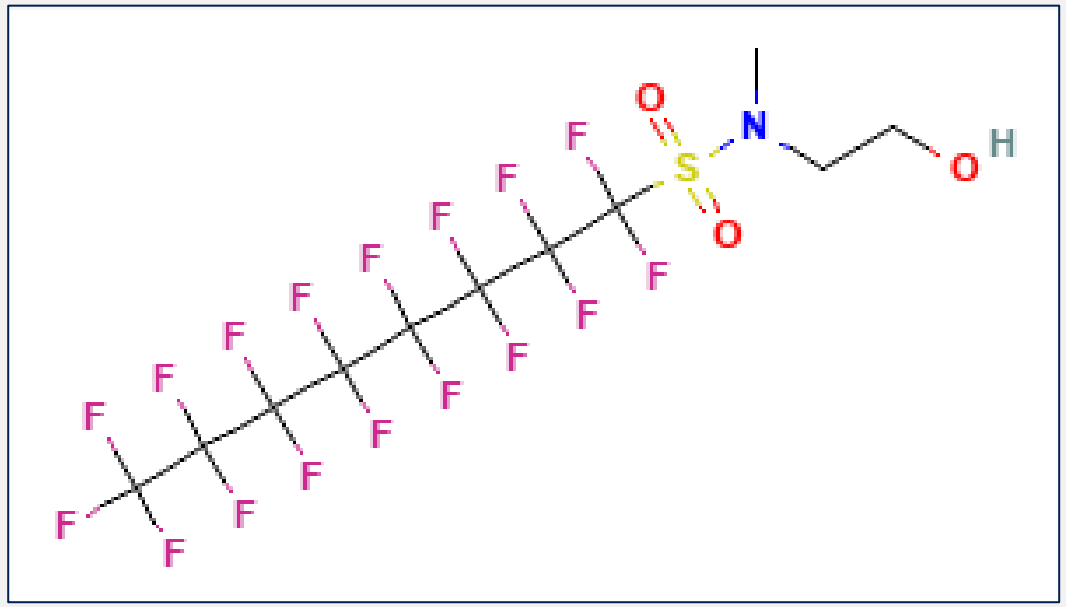


PFOSA (FASA)

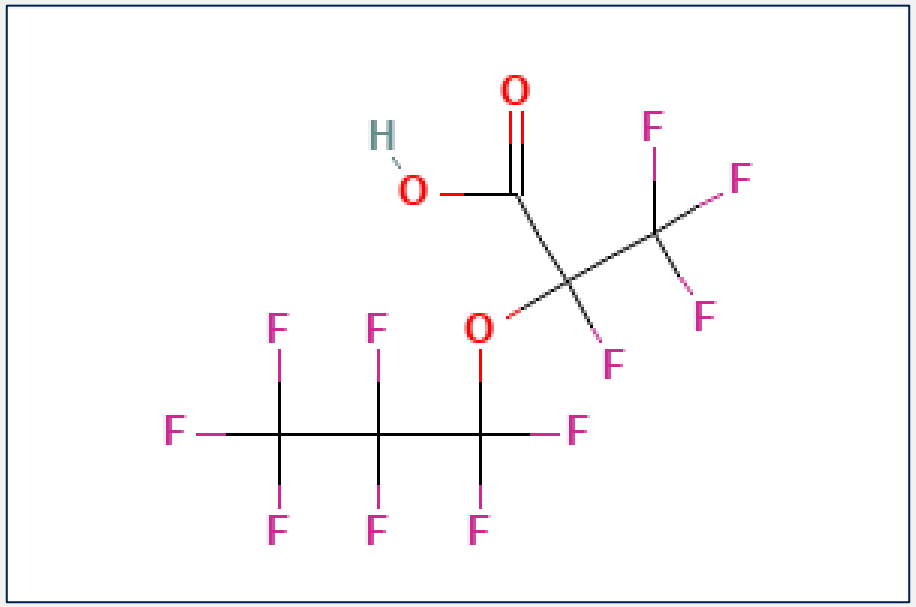


MeFOSAA (FOSAA)

1633A EXP - Analytes

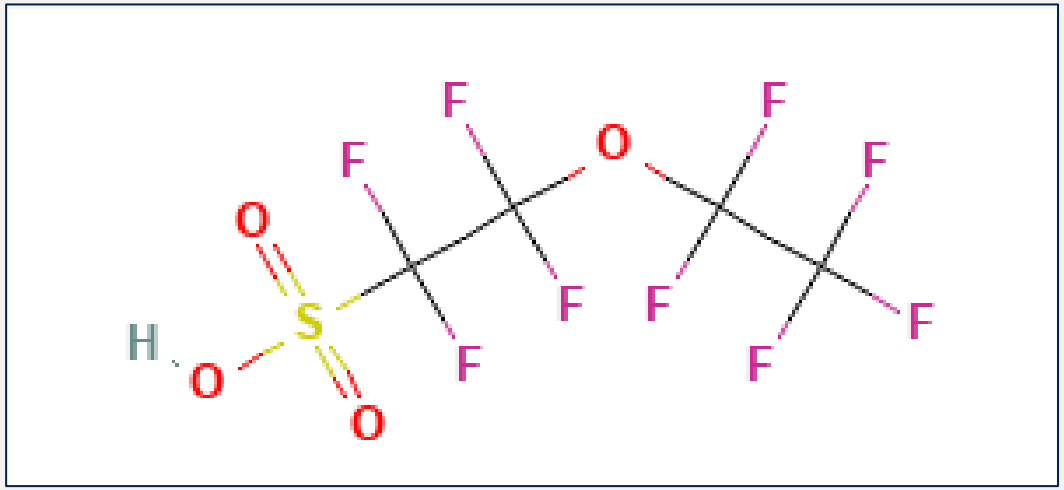


MeFOSE (FOSE)

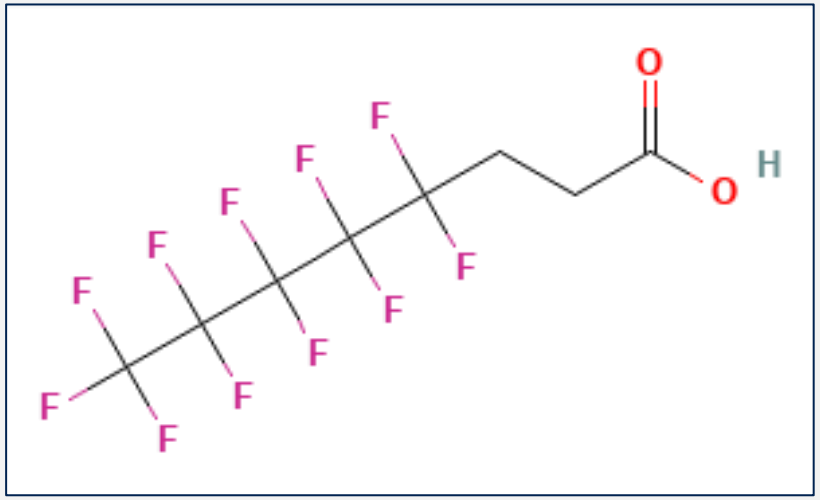


HFPO-DA (PFECA)

1633A EXP - Analytes

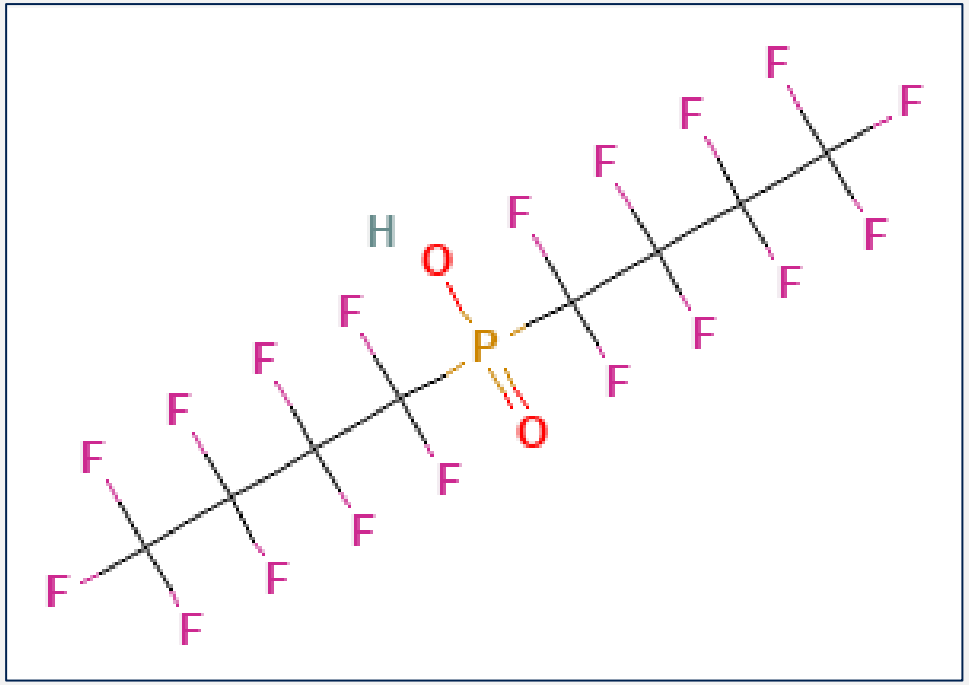


PFEESA (PFESA)

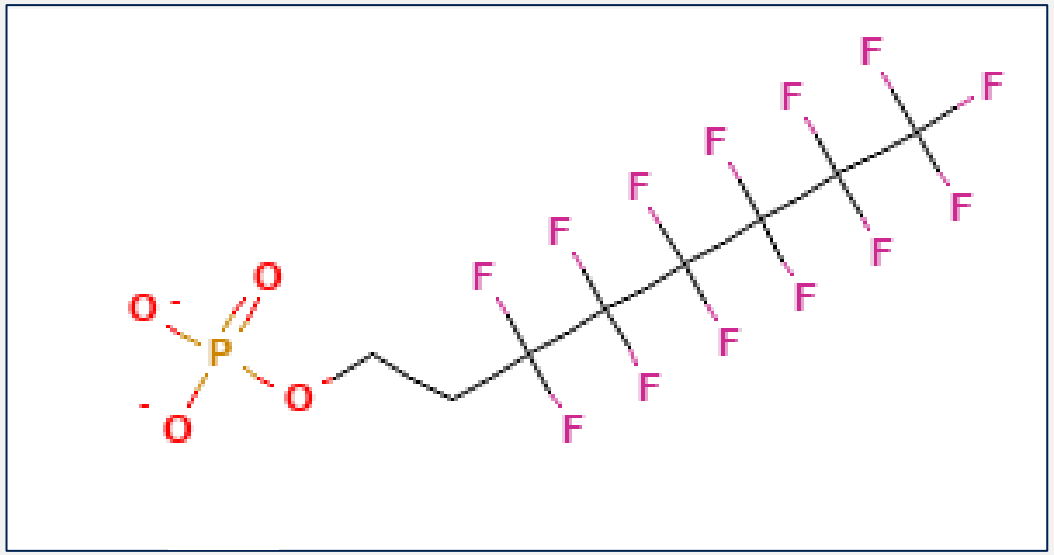


5:3 FTCA (FTCA)

1633A EXP - Analytes

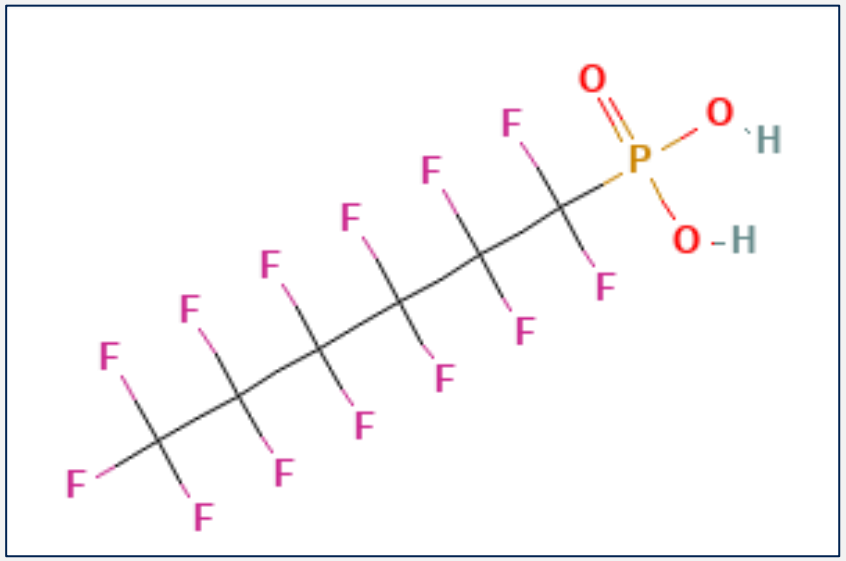


4:4PFPiA (PFPiA)

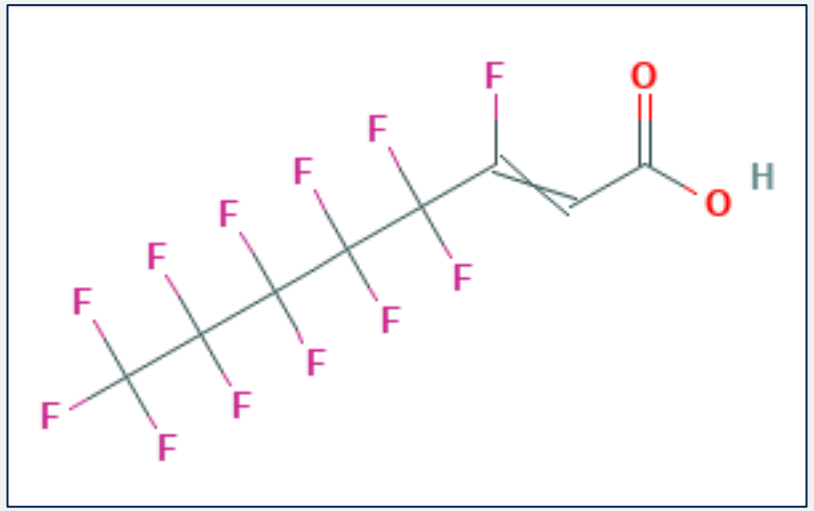


6:2 diPAP (diPAP)

1633A EXP - Analytes

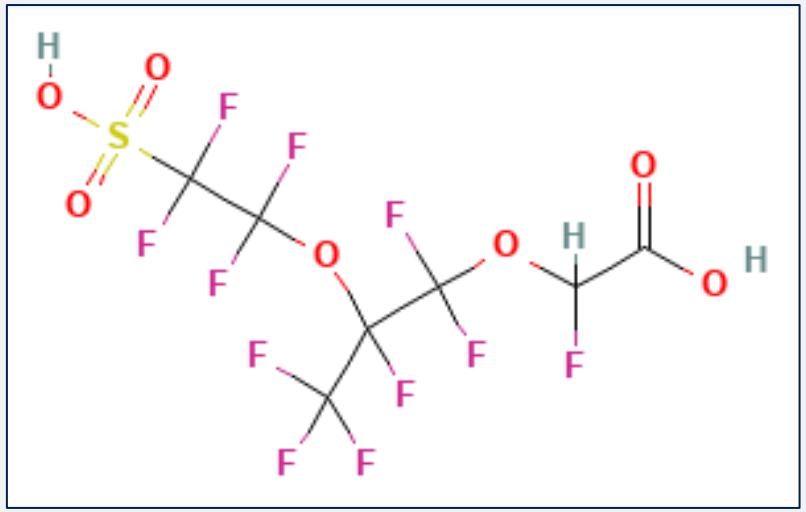


PFHxPA (PFPA)

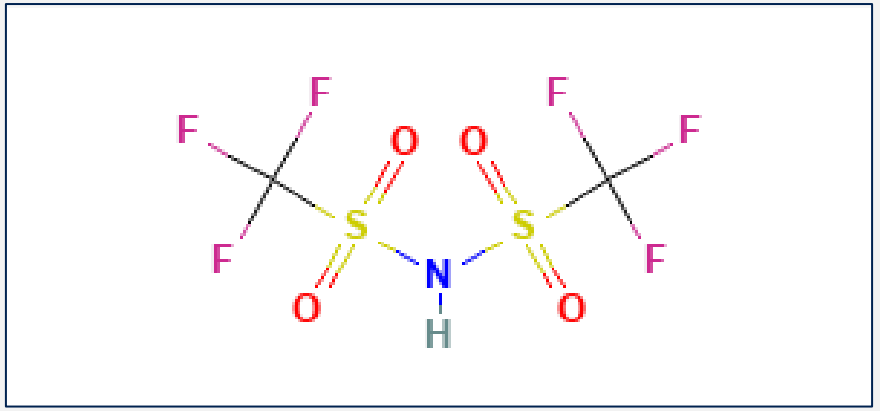


5:3 FTCA (FTUCA)

1633A EXP - Analytes



Diprotic



TFSI (PFSI)

Ultra-Short PFAS

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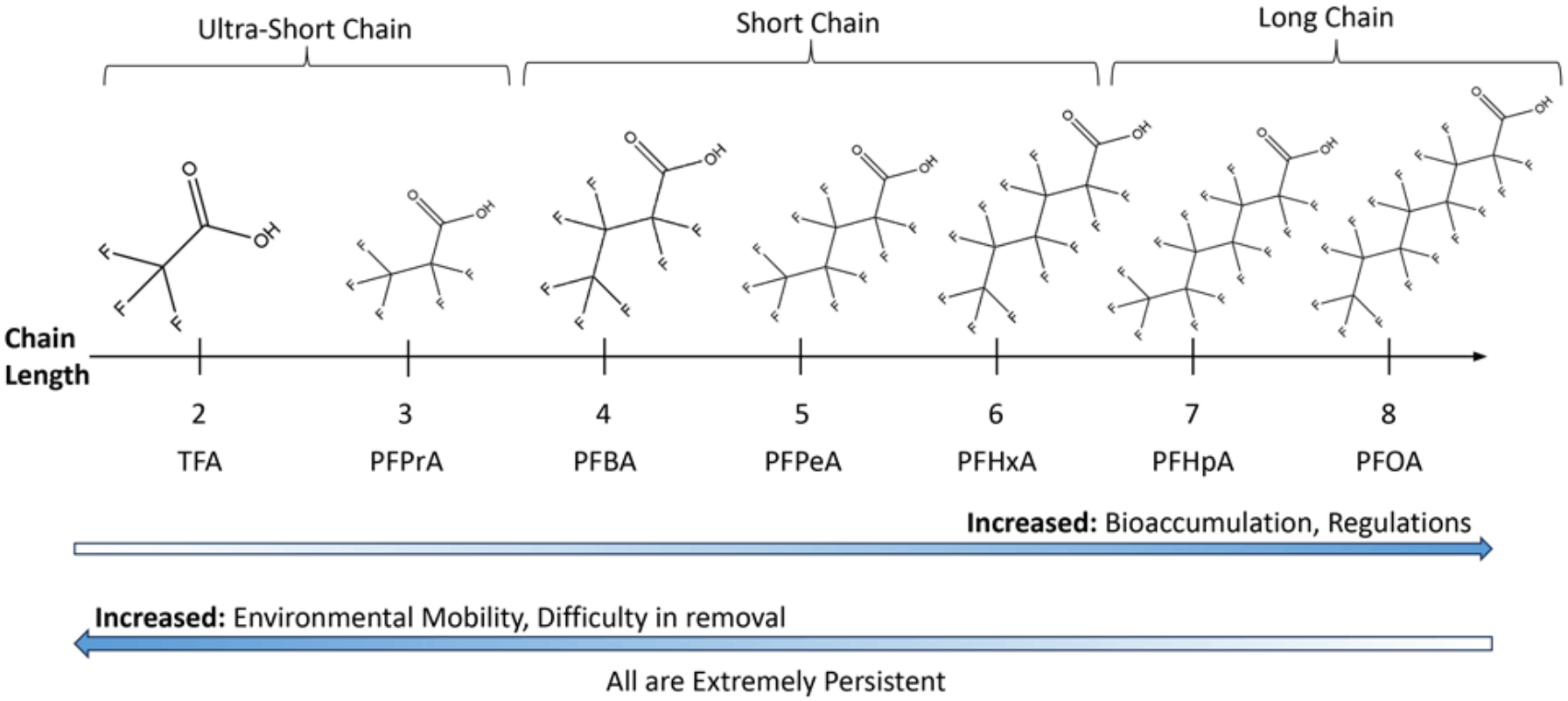
PFAS classification by Chain Length

Table 2-3. Short-chain and long-chain PFCAs and PFSAs

Number of Carbons	4	5	6	7	8	9	10	11	12
PFCAs	Short-chain PFCAs				Long-chain PFCAs				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFSAs	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
	Short-chain PFSAs		Long-chain PFSAs						

Ultra-Short, Short, and Long Chain PFAS



Key Environmental Concerns

- Extreme Mobility
- Persistence
- Removal Challenges
- Widespread Distribution
- Bioaccumulation?

Current Methods for Ultra-Shorts

- No published methods
- Laboratory developed method
  - Direct injection (co-solvation)
  - LC/MS/MS
  - Isotope dilution
- So why not add to EPA 1633A?

Ultra-Short PFAS

- Direct Aqueous Injection (DAI)
- 10 Target analytes
  - PFCA, PFSA, PFECA, and PFSI
- LC/MS/MS
- Isotope Dilution
- Reporting Limits between 5 and 60 ppt
- SPE method and soil/sediment method in development
  - Investigate tissue and consumer products methods

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Total Oxidizable Precursors (TOP)

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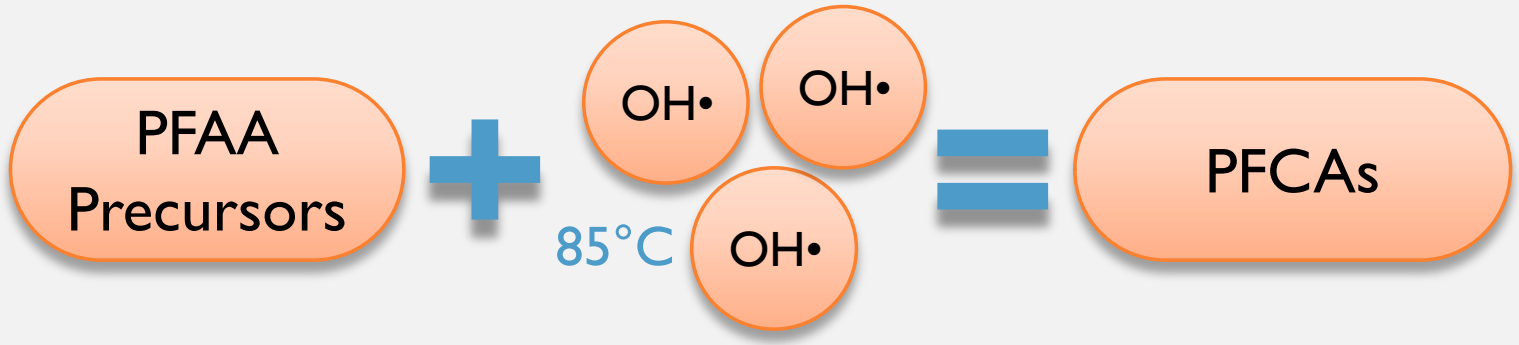
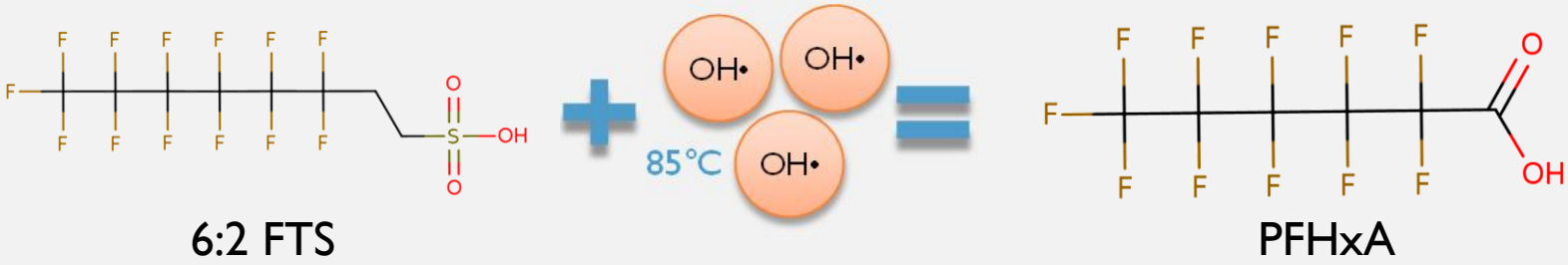
Total Oxidizable Precursor (TOP) Assay

- Cons
  - Matrix interference
  - Forms non-measurable transformation products
  - Not robust
  - Over & Under oxidation
- Pros
  - Quantify precursor PFAS with Chain length





6:2 FTS

PFHxA

Under-oxidation = 6:2 FTS untransformed
Over-oxidation = PFHxA, PFPeA, PFBA, PFPrA, PFEtA, TFA

Analytical Data

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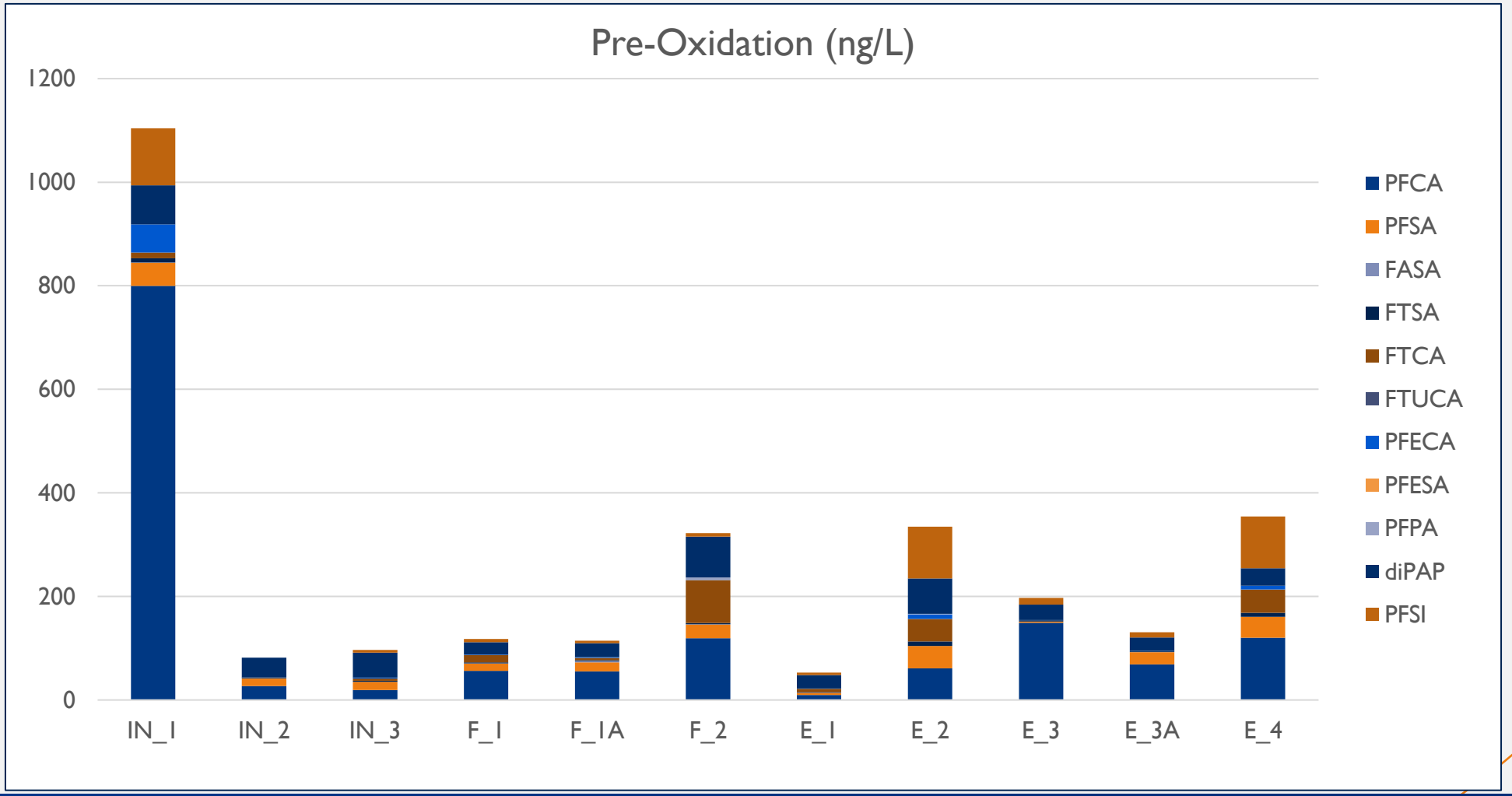
QC Samples

- 1633A EXP – MB, LLLCS, LCS, and LCSD
  - MB – 6:2 diPAP
  - LCS/LCSD
    - Two high recoveries – MeFBSA and 6:2 diPAP
    - Five high RSD, < 44%
  - LLLCS
    - Two high recoveries – MeFBSA and 6:2 diPAP
    - 11 high RPD for new target analytes

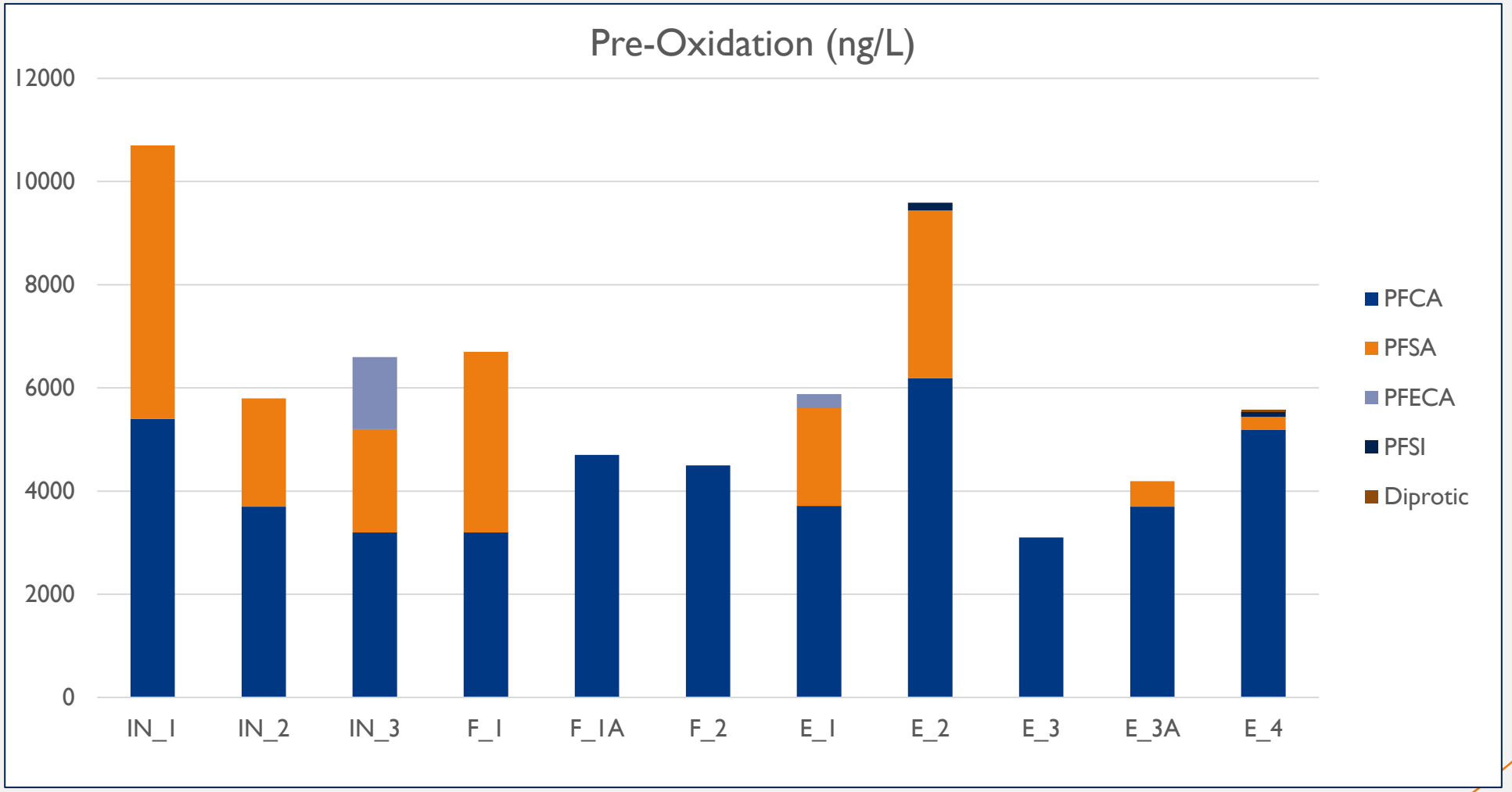
QC Samples

- Ultrashorts– MB, LCS, and LCSD
  - Typical RL between 10 – 60 ppt
  - MB – no detections above the reporting limits
  - LCS/LCSD
    - Average recoveries pass criteria
    - Range from 75% to 112%, most in the 90s
    - RSD < 20% for all samples, only two above 10%

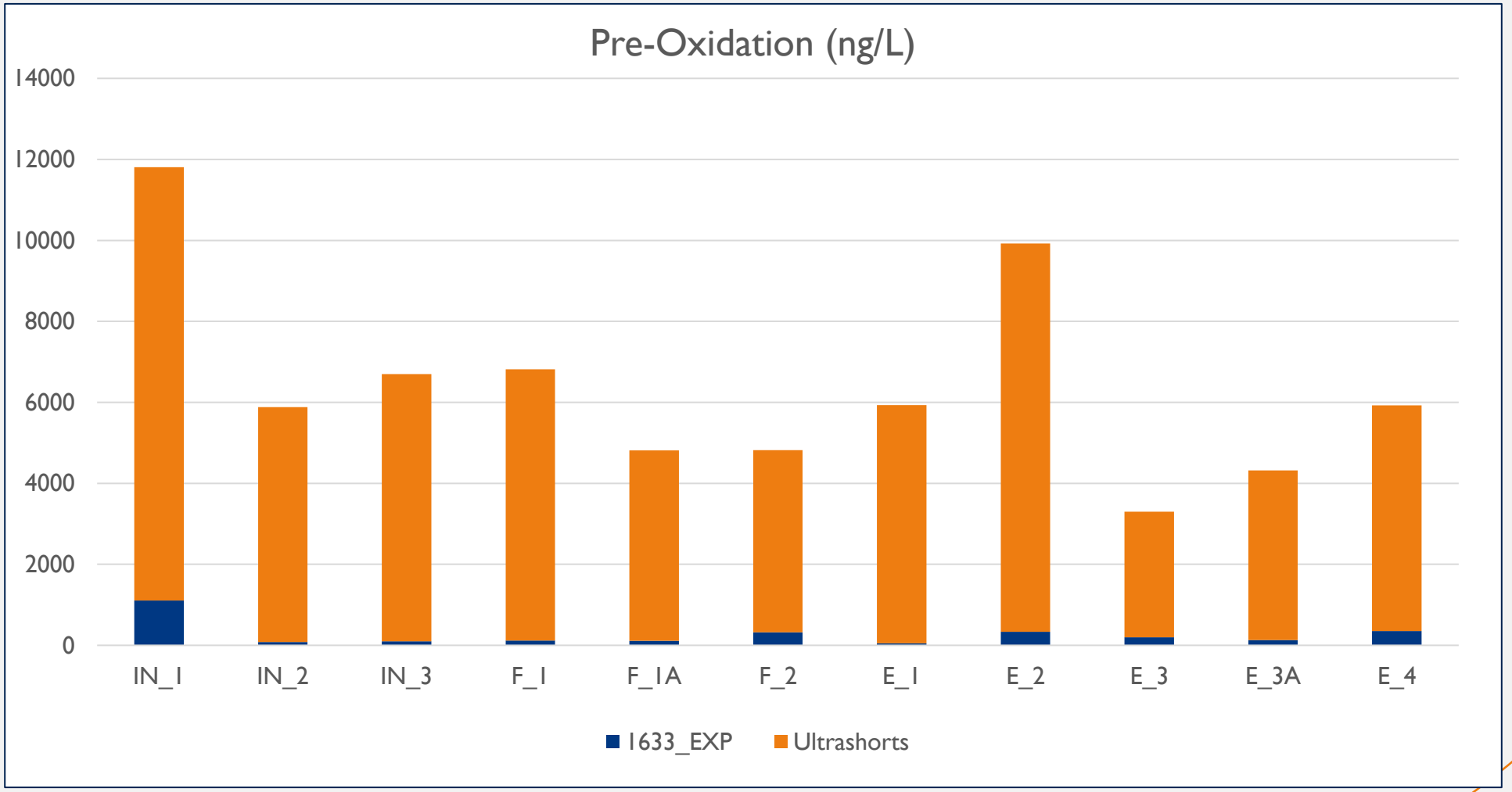
1633A EXP – Sample Results



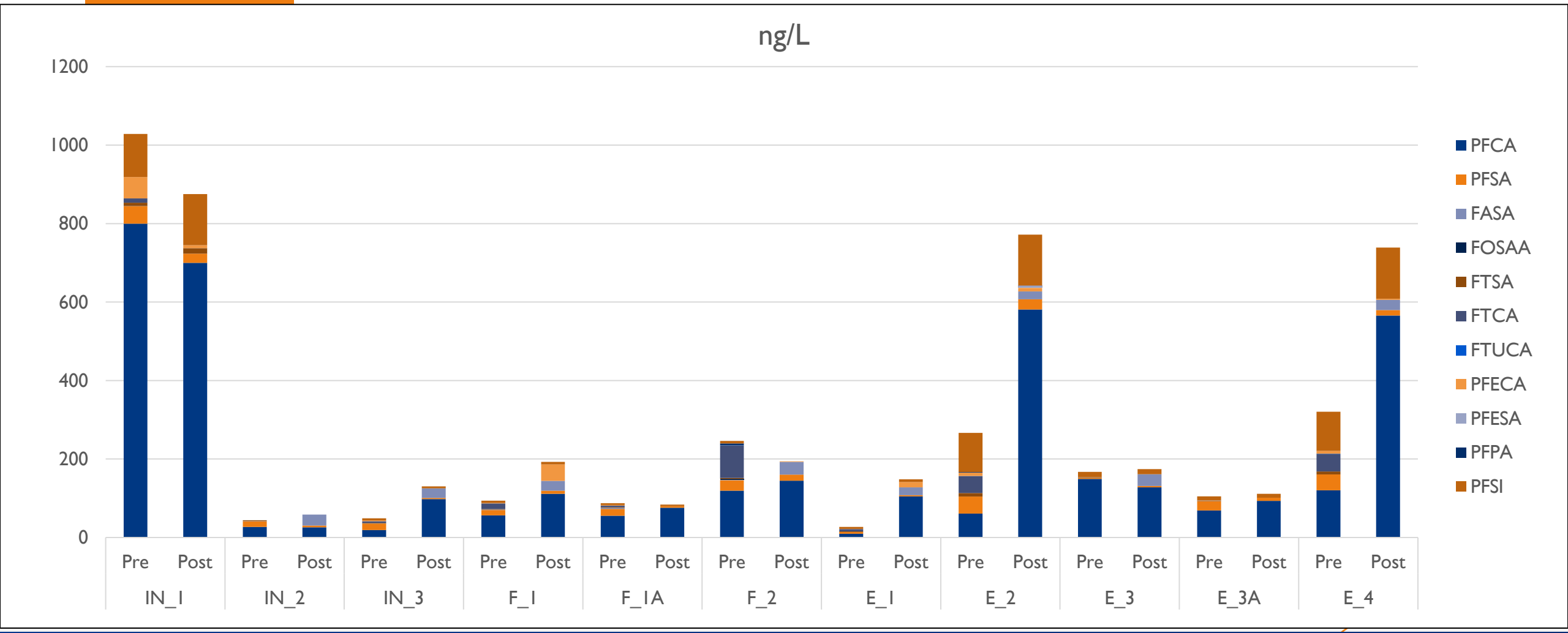
Ultrashorts – Sample Results



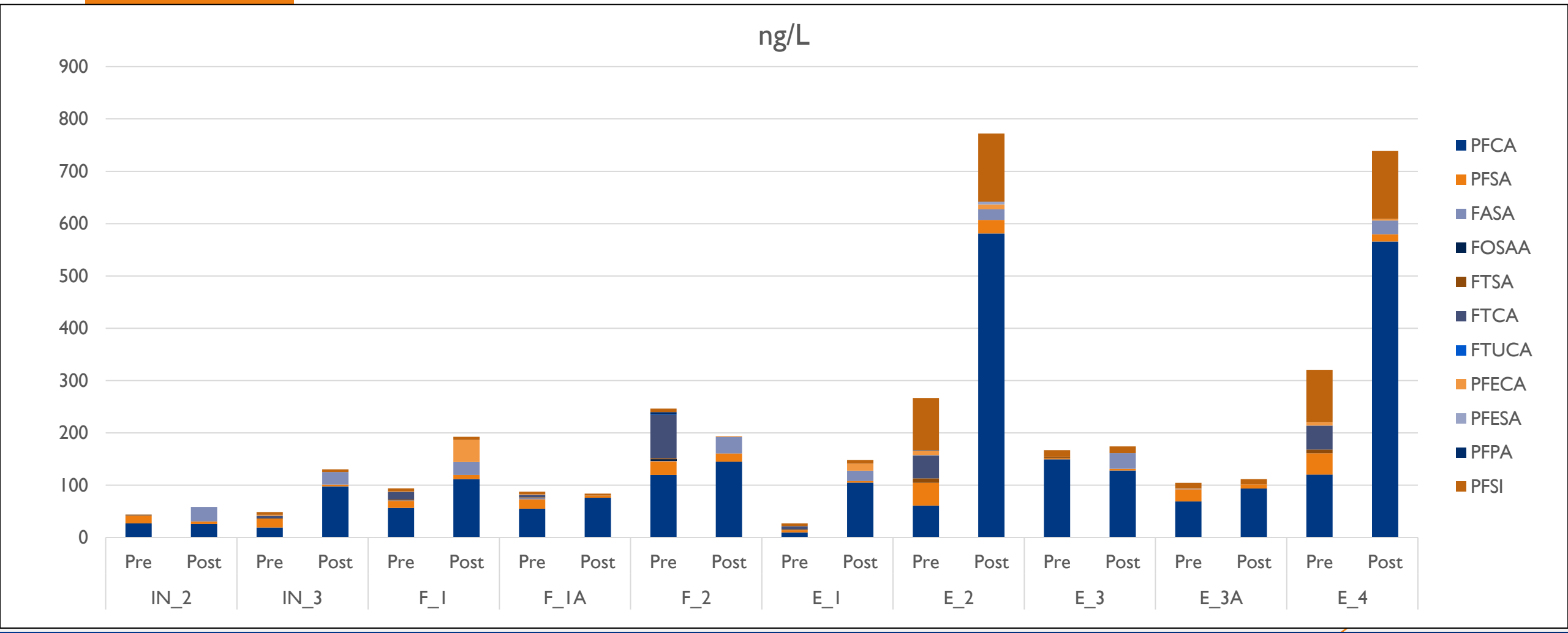
1633A EXP vs Ultrashorts – Sample Results



1633A EXP – TOP Sample Results



1633A EXP – TOP Sample Results



Ultrashorts – TOP Sample Results