

PEOPLE ADVANCING SCIENCE

PFAS Methods Overview for Environmental Professionals

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Technical Specialist, PFAS



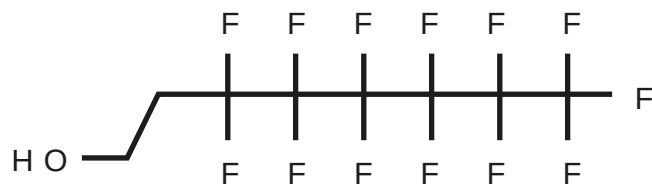
PFAS OVERVIEW

- ▶ **PFAS Chemistry**
- ▶ **Speciated PFAS Test Methods**
- ▶ **Organic Fluorine and Other Methods**



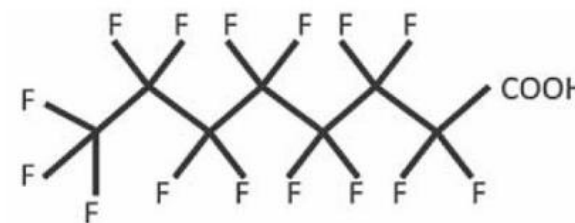
CLASSES OF PFAS

Per and Poly Fluorinated Alkyl Substances



POLYFLUOROALKYL

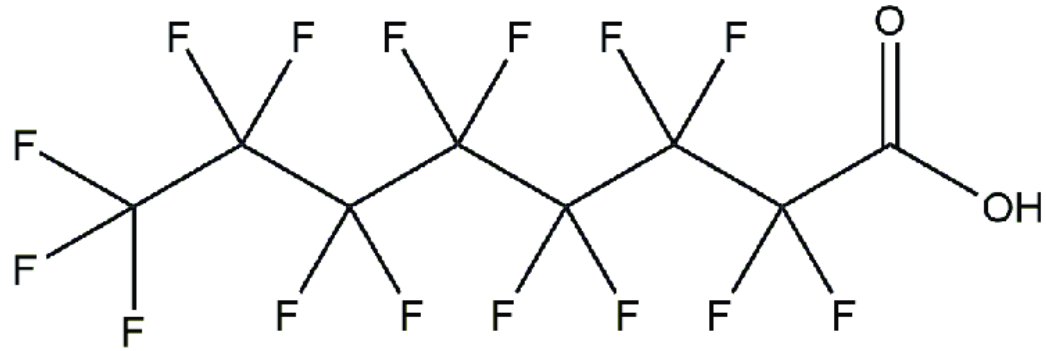
- ▶ Non-fluorine atom (usually H or O) attached to at least one, but not all, carbon atoms in the tail
- ▶ Creates a “weak link” susceptible to biotic or abiotic degradation
- ▶ More susceptible to treatment
- ▶ Fluorotelomers
- ▶ AKA precursors



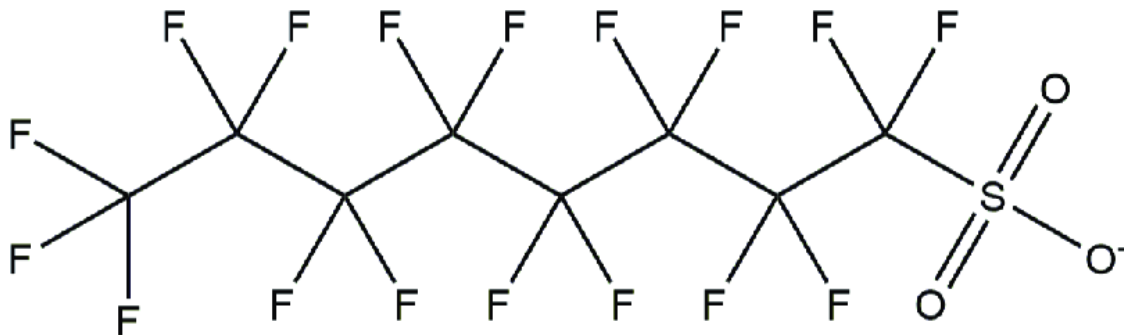
PERFLUOROALKYL

- ▶ All hydrogens on the carbons are replaced by fluorine
- ▶ Strongest chemical bond in nature
- ▶ Difficult to treat
- ▶ PFCAs and PFSAs

The Two Most Widely Study PFOA and PFOS



Perfluorooctanoic acid (PFOA)



Perfluorooctane sulfonate (PFOS)

-Let's Talk about Bonding C-F

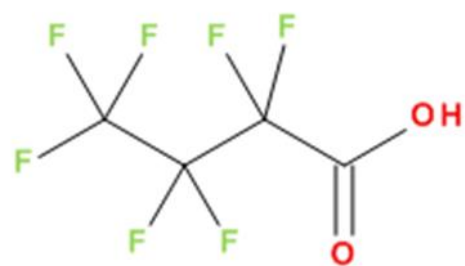
-Who made them?

-What are their uses?

-Why they are so good at what they are made for?

-Known Adverse Health effects.

Replacement PFAS



PFBA



PFBS



6:2 Fluorotelomer acrylate

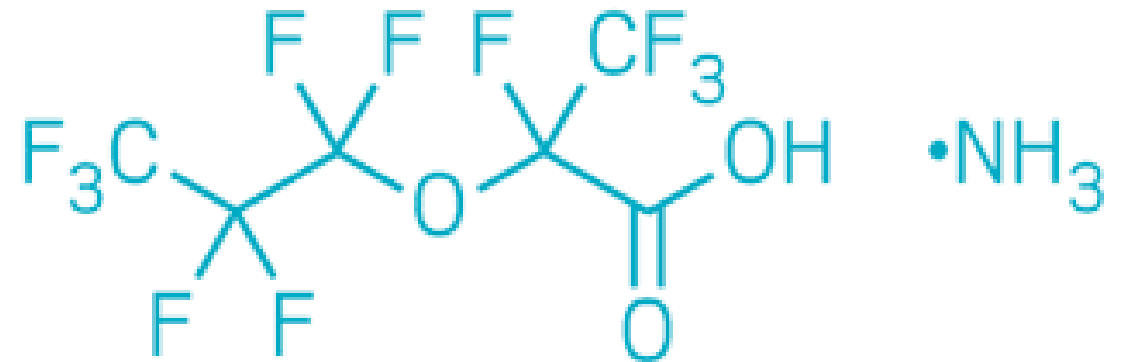
- Industry Claims they are safer
- Precursors are still longer chain C8
- PFBA-food packaging and film
- PFBS-surfactants/repellents, metal plating, pesticides, and flame retardants



AKA HFPO-DA (Dimer Acid)

Dupont 2007 as a replacement product for PFOA

GenX in the Lower Cape Fear River Basin



GenX

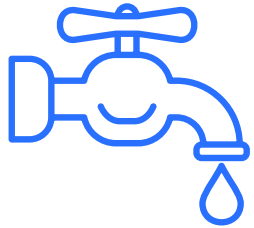
PFAS OVERVIEW

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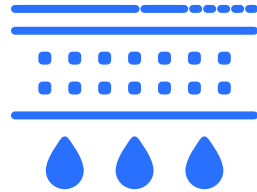


MATRICES

CHOOSING THE RIGHT TEST METHODS



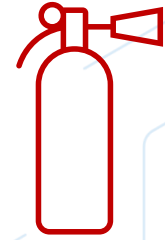
Drinking water



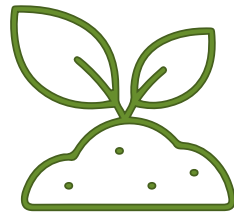
Groundwater, surface water, & leachate



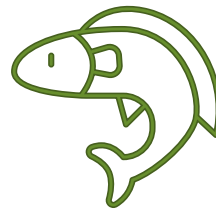
Wastewater, sludge & biosolids



AFFF – concentrate & diluted



Soil, sediment, solid waste & other solids



Biota – plant & animal tissue



Consumer & Industrial Products

METHOD	EPA 537.1	EPA 533
MATRIX	Drinking Water	Drinking Water
COMPOUNDS	18	25
HOLDING TIMES, DAYS	14/28	28/28
EXTRACTION	Solid Phase (SPE)	Solid Phase (SPE)
QUANTIFICATION	Internal Standard (IS)	Isotope Dilution (ID)
NOTES	Developed for UCMR 5 and additional PFAS. Does not replace 537.1.	



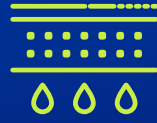
EPA Finalized National Primary Drinking Water Regulations for Six PFAS

Compound	Final MCLG	Final MCL (enforceable levels)
PFOA	Zero	4.0 parts per trillion (ppt) (also expressed as ng/L)
PFOS	Zero	4.0 ppt
PFHxS	10 ppt	10 ppt
PFNA	10 ppt	10 ppt
HFPO-DA (commonly known as GenX Chemicals)	10 ppt	10 ppt
Mixtures containing two or more of PFHxS, PFNA, HFPO-DA, and PFBS	1 (unitless) Hazard Index	1 (unitless) Hazard Index

- US EPA reports 25 compounds from EPA 533 and 4 that don't overlap from EPA 537.1
- Note: All 29 PFAS in EPA's UCMR 5 for its survey of the nation's public water systems are included in EPA Method 1633

ANALYTE	537.1	533
PFEESA		•
HFPOA-DA/Gen X	•	•
NFDHA		•
PFOS	•	•
PFUdA	•	•
N-MeFOSAA	•	
PFPeA		•
PFPeS		•
6:2 FTS		•
N-EtFOSAA	•	
PFHxA	•	•
PFDoA	•	•
PFOA	•	•
PFDA	•	•
PFHxS	•	•
PFBA		•
PFBS	•	•
PFHpA	•	•
PFHpS		•
PFNA	•	•
PFTeDA	•	
PFMOPrA		•
8:2 FTS		•
PFTTrDA	•	
9Cl-PF3PONS	•	•
4:2 FTS		•
11Cl-PF3OUdS	•	•
PFMOBA		•
ADONA	•	•

Method Comparison



NON-POTABLE
WATERS &
LEACHATE

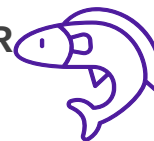


SOIL & OTHER
SOLIDS



BIOTA – PLANT &
ANIMAL TISSUE

METHOD	PFAS by Lab SOP/ DOD QSM B-15	EPA Draft Method 1633/ QSM B-24
MATRICES	Non-potable water, solids	Non-potable water, solids, biota
COMPOUNDS	Up to 40	40
HOLDING TIMES, DAYS	28/28	28/28*
EXTRACTION	Solid Phase (SPE)	Solid Phase (SPE)
QUANTIFICATION	Isotope Dilution (ID)	Isotope Dilution (ID)
NOTES	Labs required to modify 537 or other methods as 537/533 are prescriptive DW methods	Currently in multi-lab validation process



CWA Analytical Methods for Per- and Polyfluorinated Alkyl Substances (PFAS)

The EPA developed two new analytical methods to test for PFAS compounds in wastewater, as well as other environmental media.

On this page:

- [Background](#)
- **NEW** [Method 1633 for 40 PFAS Compounds](#)
- **NEW** [Method 1621 for Adsorbable Organic Fluorine](#)
- **NEW** [Documents](#)
- [Related Information](#)



<https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas>

REGULATORY UPDATE

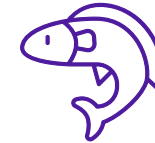
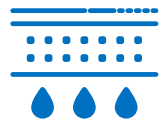
Federal - CWA NPDES – March 26, 2024

US EPA issues request for public comment for **Information Collection Rule (ICR): “U.S. Environmental Protection Agency POTW Influent PFAS Study Data Collection”** (EPA ICR No. 2799.01, OMB Control No. 2040–NEW).

Purpose:

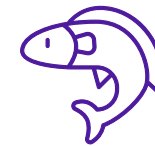
- EPA is conducting a POTW Influent PFAS Study to collect and analyze nationwide data on industrial discharges of PFAS to POTWs as well as PFAS in POTW influent, effluent, and sewage sludge.
- The data collection activities will produce a robust data set that will enable the EPA to characterize the type and quantity of PFAS in wastewater discharges as well as POTW influent, effluent, and sewage sludge.
- The data will primarily be used to identify and prioritize industrial point source categories where additional study or regulations may be warranted to control PFAS discharges.





EPA 1633

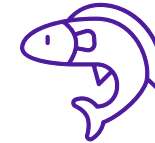
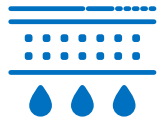
- Valid for 8 matrices - wastewater, surface water, groundwater, soils, biosolids, landfill leachate, biota, and sediment
- Joint EPA/DOD development
- Method is now final
- This method will eventually eliminate the use of “modified” methods/lab-specific SOPs
- There are several important differences between the “modified” method and 1633



EPA 1633 - Features

- Sample Volume Needed varies by matrix
- TSS limitations on aqueous matrices
- Prep restrictions
- Method modifications needed to water samples >100mg/L TSS
- Centrifuge/sub sample/multiple cartridges
- Moisture Content on solids-dry weight reporting
- Biosolid/Sludge limitations





EPA 1633 - Containers

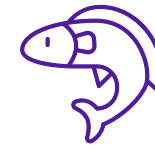
1633 Aqueous Containers



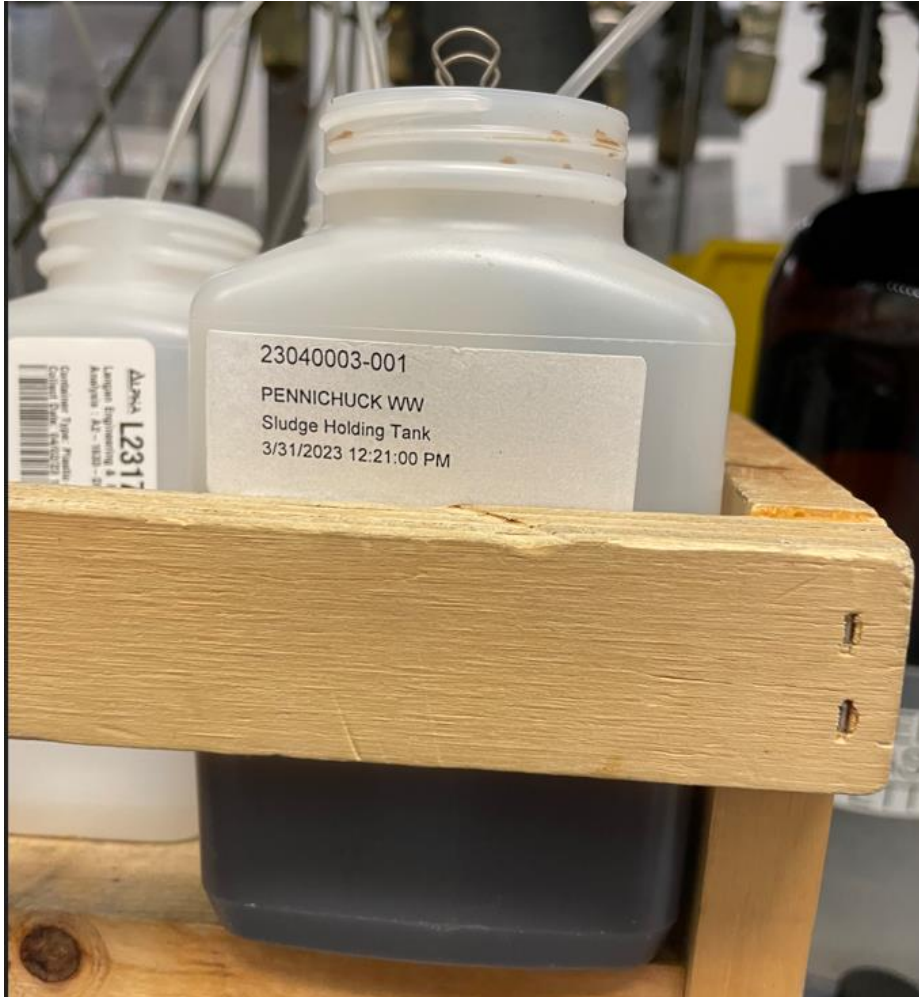
537M/PFAS by ID (Historical Containers)

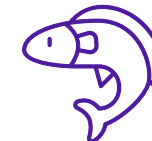
Solids Container





EPA 1633



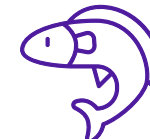
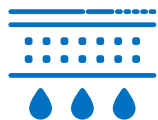


EPA 1633 - TSS Impacts – something to think about...



	Liquid	Solid
Analyte	ng/L	ug/kg
PFBA	53000	43
PFPeA	86000	96
PFHxA	130000	210
PFHpA	15000	34
PFOA	32000	79
PFNA	1700	3.8
PFDA	1300	3.1
PFUnA	<500	0.32
PFDaA	<500	0.53
PFTTrDA	<500	<0.17
PFTeDA	<500	0.26
PFBS	180000	430
PFPeS	<500	1.3
PFHxS	19000	49
PFHpS	<500	0.47
PFOS	5400	14
PFNS	<500	<0.17
PFDS	<500	<0.17
PFDoS	<500	<0.17
4:2FTS	<2000	<0.69
6:2FTS	4800	7.8
8:2FTS	<2000	2.6
PFOSA	<500	<0.17

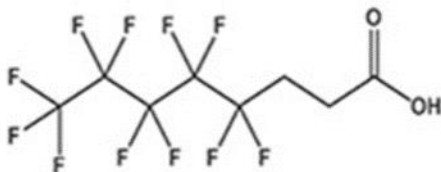
	Liquid	Solid
Analyte	ng/L	ug/kg
NMeFOSA	<500	<0.17
NEtFOSA	<500	<0.17
N-MeFOSAA	5900	14
N-EtFOSAA	3400	8
NMeFOSE	<5000	4.2
NEtFOSE	<5000	4.9
HFPO-DA	<2000	<0.69
ADONA	<2000	<0.69
9Cl-PF3ONS	<2000	<0.69
11Cl-PF3OUdS	<2000	<0.69
3:3 FTCA	<5000	<1.7
5:3 FTCA	220000	140
7:3 FTCA	32000	28
PFEESA	<1000	<0.35
PFMPA	<1000	<0.35
PFMBA	<1000	<0.35
NFDHA	<1000	<0.35



EPA 1633 – 40 PFAS Compounds

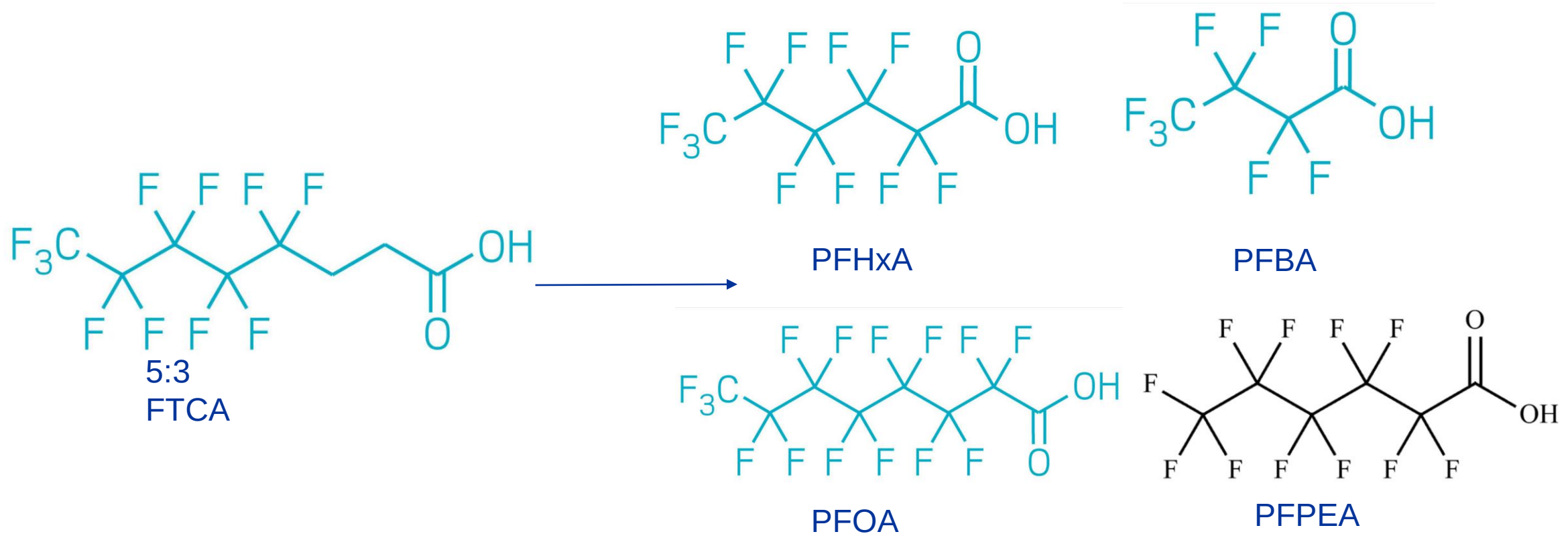
- Addition of Precursors will be insightful these can degrade to terminal PFAS like PFBA
- 5:3 fluorotelomer carboxylic acid (FTCA) is a common and often dominant constituent of PFAS found in landfills and is released from carpet in model anaerobic landfill reactors. This compound could prove to be an indicator of PFAS in the environment originating from landfills (Land et al. 2017, 2016).

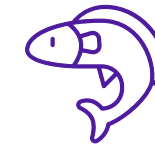
5:3 FTCA



Analyte	Analyte
PFBA	8:2 FTS
PFPeA	PFOSA
PFHxA	N-MeFOSAA
PFHpA	N-EtFOSAA
PFOA	HFPO-DA
PFNA	PFMOPrA
PFDA	ADONA
PFUnDA	9Cl-PF3ONS
PFDODA	11Cl-PF3OUdS
PFTTrDA	3:3 FTCA
PFTeDA	5:3 FTCA
PFBS	7:3 FTCA
PFPeS	N-EtFOSA
PFHxS	N-EtFOSE
PFHpS	NFDHA
PFOS	N-MeFOSA
PFNS	N-MeFOSE
PFDS	PFDoS
4:2 FTS	PFEESA
6:2 FTS	PFMOBA

5:3 FTCA has several potential degradation pathways





EPA 1633 – Lower Detection Limits

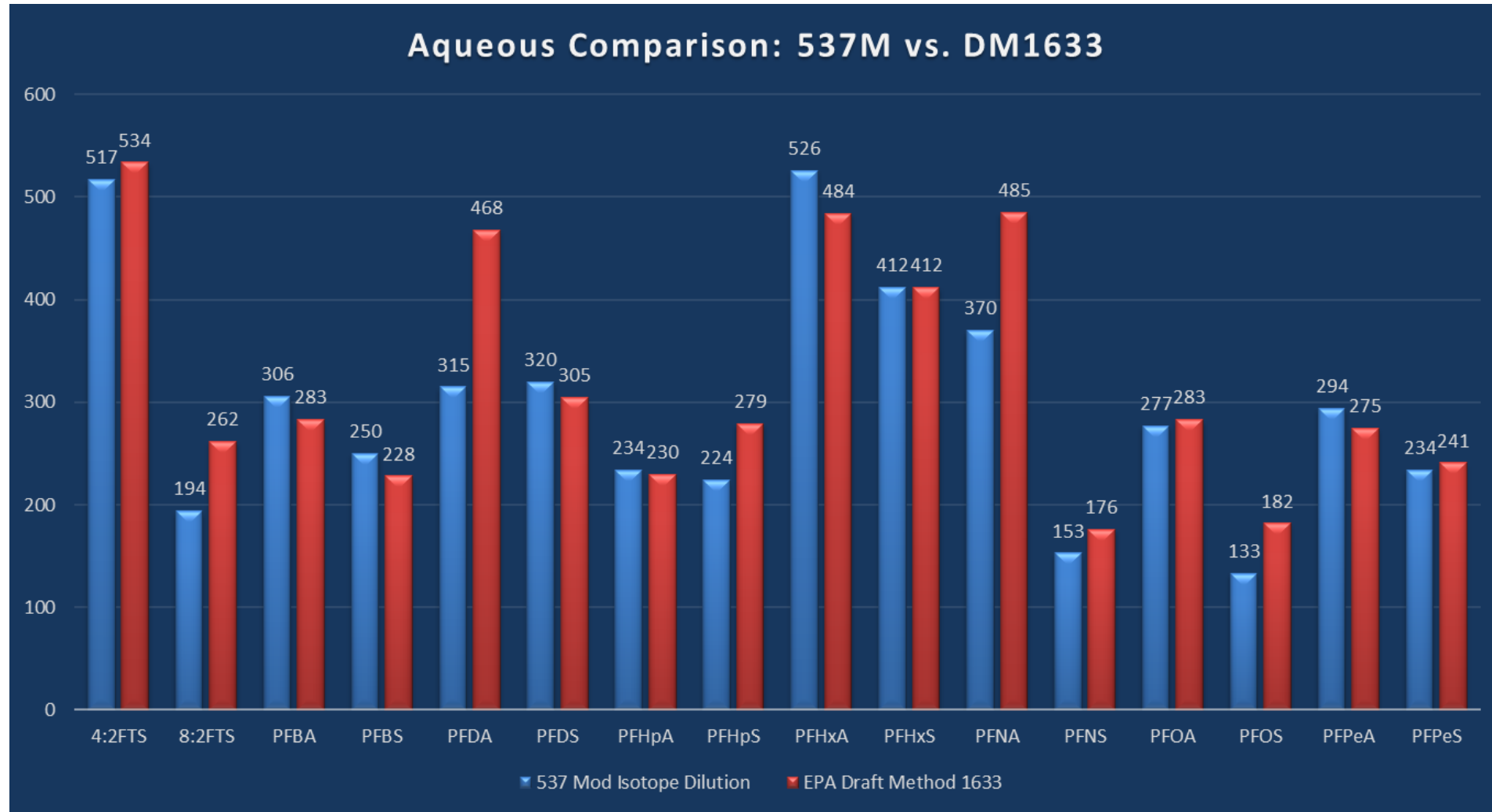
Acronym	Water, ng/L		Solids, µg/kg	
	LOQ	DL	LOQ	DL
PFBA	4	0.55	0.8	0.14
PFPeA	2	0.29	0.4	0.06
PFHxA	1	0.12	0.2	0.08
PFHpA	1	0.16	0.2	0.03
PFOA	1	0.16	0.2	0.04
PFNA	1	0.17	0.2	0.04
PFDA	1	0.18	0.2	0.04
PFUnA	1	0.18	0.2	0.03
PFDoA	1	0.17	0.2	0.04
PFTTrDA	1	0.20	0.2	0.03
PFTeDA	1	0.17	0.2	0.03
PFBS	1	0.10	0.2	0.03
PFPeS	1	0.12	0.2	0.03
PFHxS	1	0.17	0.2	0.03
PFHpS	1	0.11	0.2	0.02
PFOS	1	0.26	0.2	0.05
PFNS	1	0.22	0.2	0.04
PFDS	1	0.15	0.2	0.03
PFDoS	1	0.34	0.2	0.03
PFOSA	1	0.15	0.2	0.05

Acronym	Water, ng/L		Solids, µg/kg	
	LOQ	DL	LOQ	DL
NEtFOSA	1	0.14	0.2	0.06
NMeFOSA	1	0.15	0.2	0.03
NEtFOSE	10	2.36	2.0	0.44
NMeFOSE	10	1.52	2.0	0.40
NEtFOSAA	1	0.28	0.2	0.03
NMeFOSAA	1	0.19	0.2	0.05
4:2 FTS	4	0.63	0.8	0.15
6:2 FTS	4	0.95	0.8	0.14
8:2 FTS	4	0.54	0.8	0.13
PFMPA	2	0.32	0.4	0.04
PFMBA	2	0.30	0.4	0.04
HFPO-DA	4	0.89	0.8	0.10
NFDHA	2	0.49	0.4	0.06
ADONA	4	0.57	0.8	0.10
PFEESA	2	0.48	0.4	0.05
9CI-PF3ONS	4	0.73	0.8	0.08
11CI-PF3OUdS	4	0.94	0.8	0.11
3:3FTCA	5	1.48	1.0	0.21
5:3FTCA	25	1.88	5.0	1.11
7:3FTCA	25	2.56	5.0	1.00

Note: Detection limits for Leachate are 5× and Biosolids are 10×

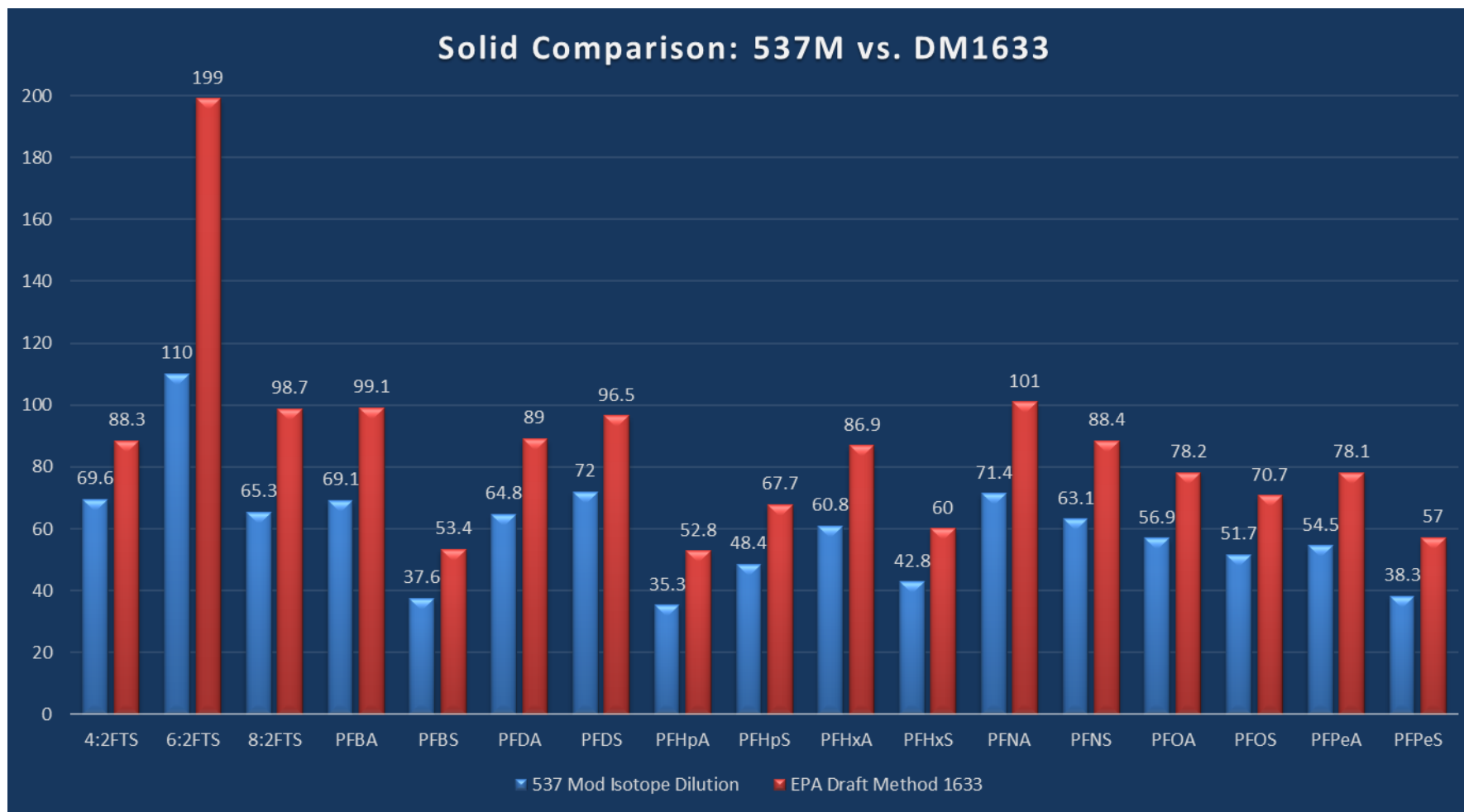
EPA Method 1633 vs PFAS by ID/537M Comparison - Water

- Water also showed high 1633 bias, but not as consistent (75%)

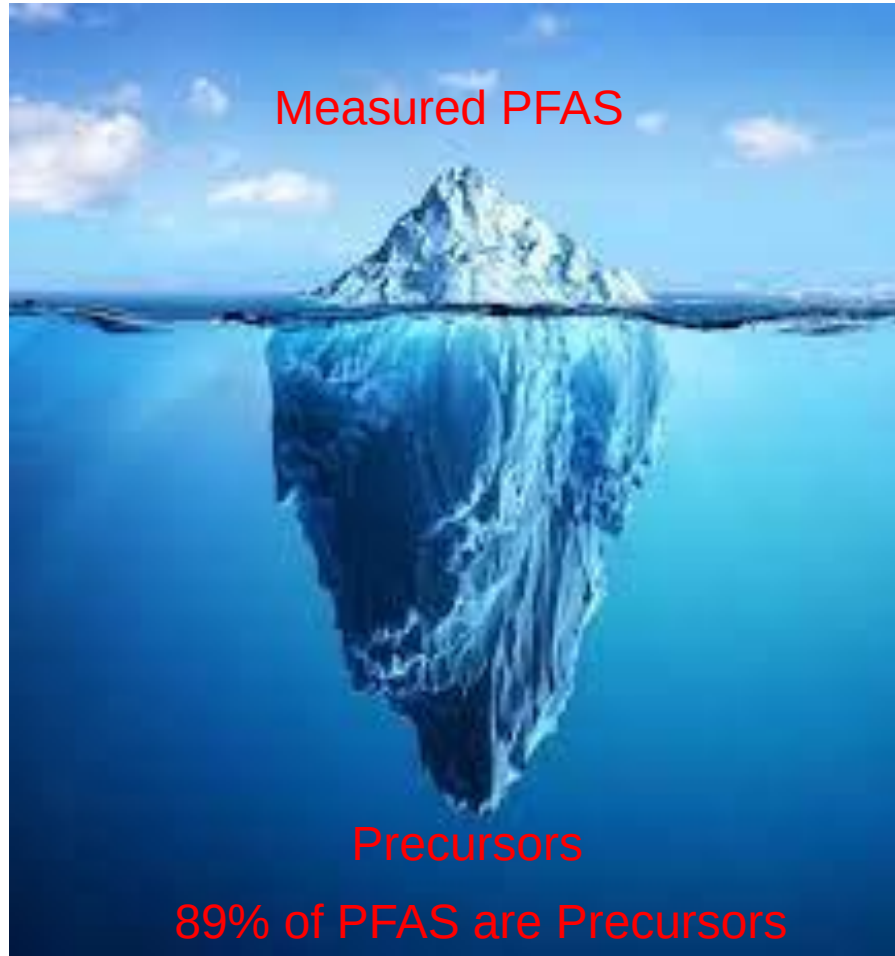


EPA Method 1633 vs PFAS by ID/537M Comparison - Soil

- Soil showed consistently high 1633 bias (100% of the time)
- Greater extraction efficiency with 1633 method

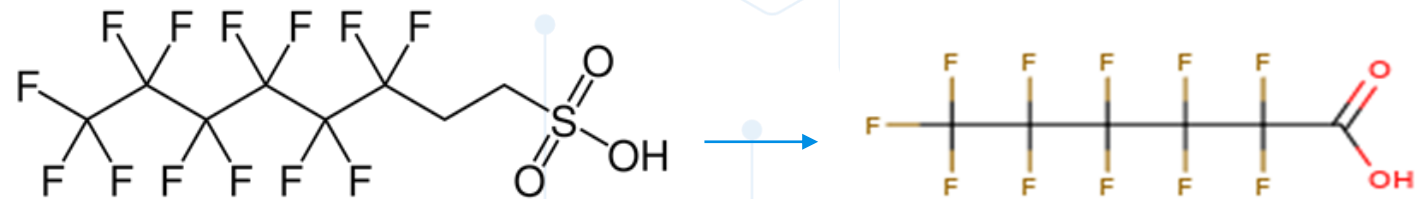


TOP (Total Oxidizable Precursor Assay)



Heat/Oxidation →

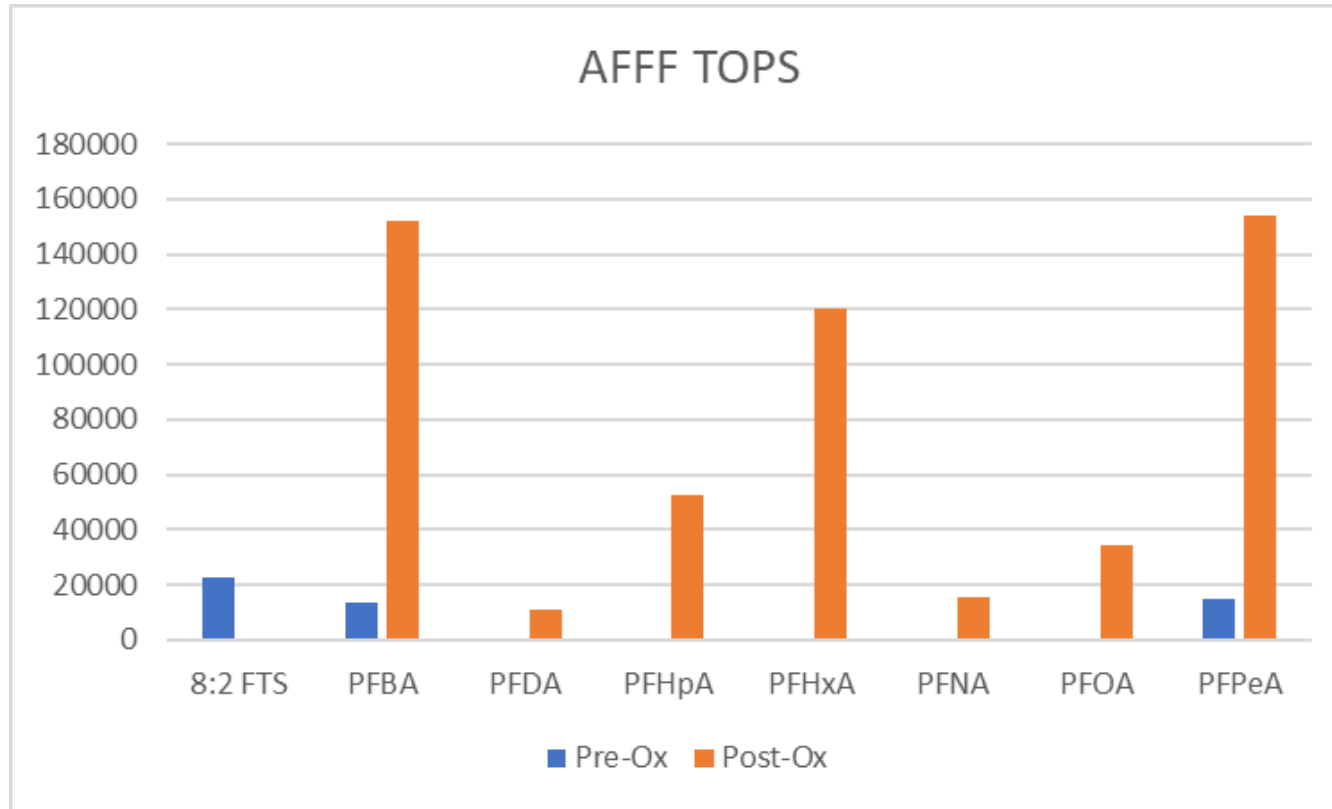
Under TOPS conversion occurs of known and unknown precursors to terminal PFAS (PFCA). Degradation of any precursor would be to an equal or shorter chain length.



6:2 FTS

PFHxA

TOPS Table Pre-Ox and Post-Ox



	Pre-Ox	Post-Ox
8:2 FTS	22300	0
PFBA	13700	152000
PFDA	0	10900
PFHpA	0	52600
PFHxA	0	120000
PFNA	0	15500
PFOA	0	34500
PFPeA	14900	154000
Total	50900	539500

TOP Assay Biosolids

- EPA is supposed to be working on a method 2025
- Pace is revamping TOP Assay Q3 2024 based on Houtz method
- 1633 Pre and Post
- Adding positive and negative controls
- Currently competition on oxidizing reagent
- Inhibits full oxidation
- Appropriate methods 1633, Mod537, D8421

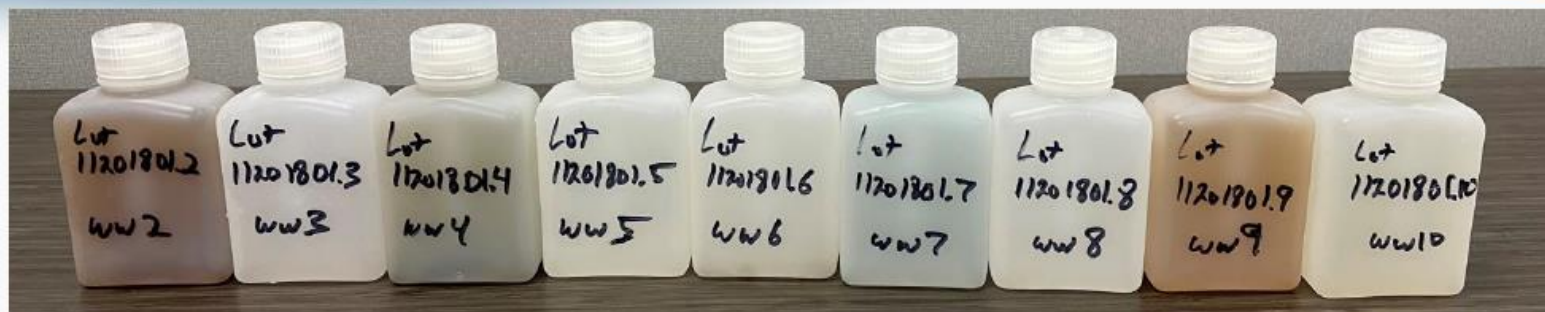


PFAST[®]

EPA 8327/ASTM D8421/D8535

- LOQ ~10 ppt
- Pricing is a plus
- Faster on average TAT
- Currently 10 PFAS Compounds-
which include your heavy hitters
 - PFOA, PFOS, PFBS, and
Gen X
- List to expand to 40 plus PFAS
2023
- Useful for pilot studies, bench scale
remediation technologies,
destruction technologies
- SW-846 8327 and ASTM D8421
needs vary by regulatory agency

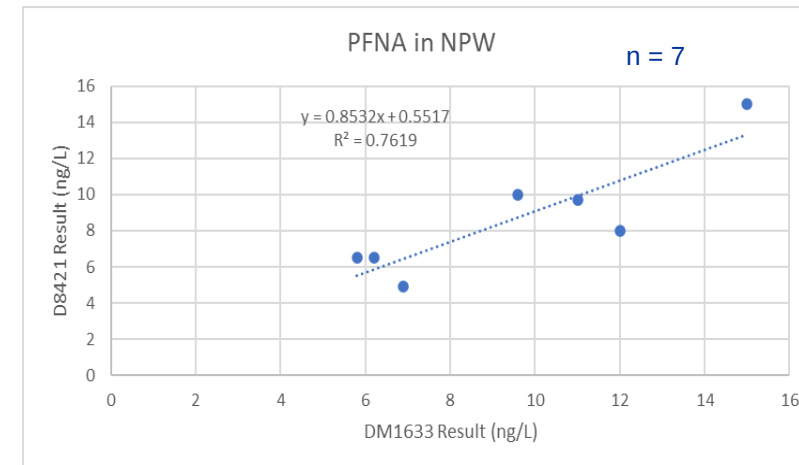
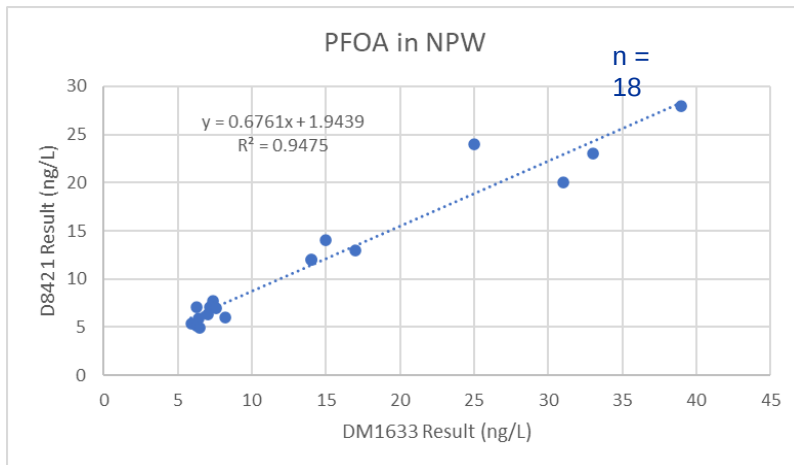
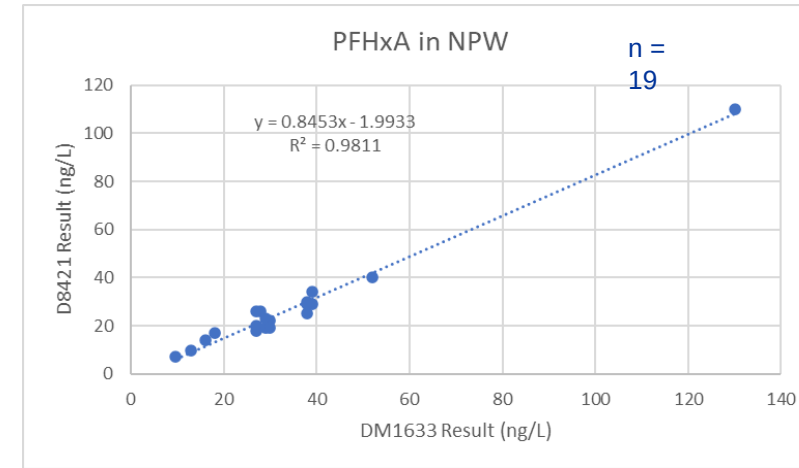
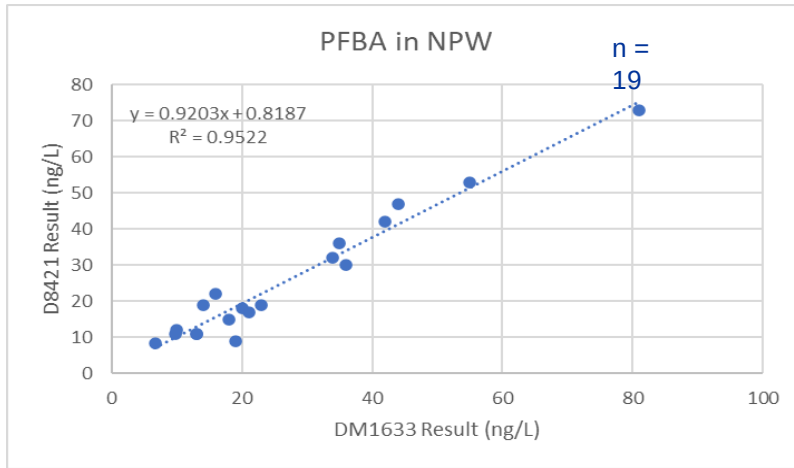
Eleven Matrices



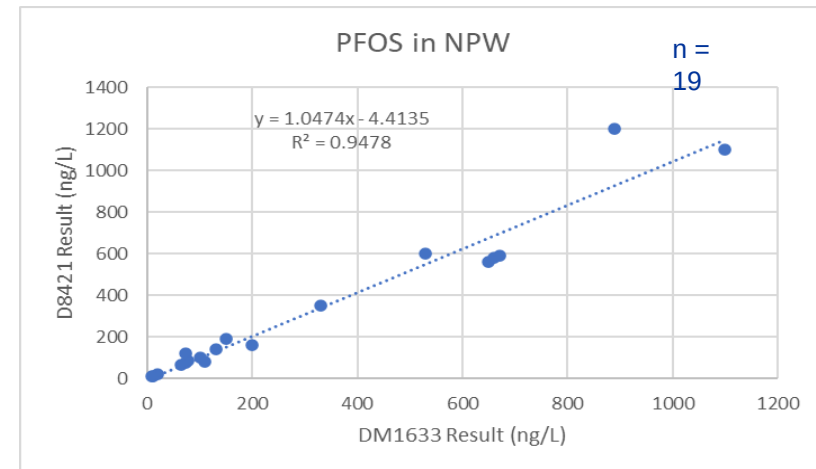
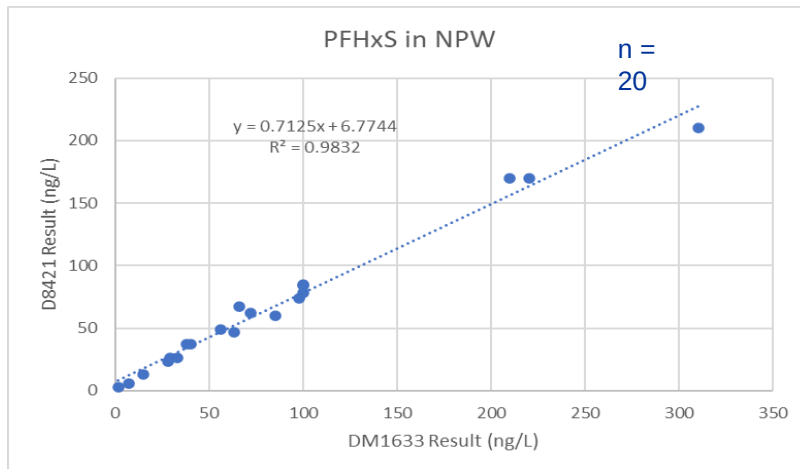
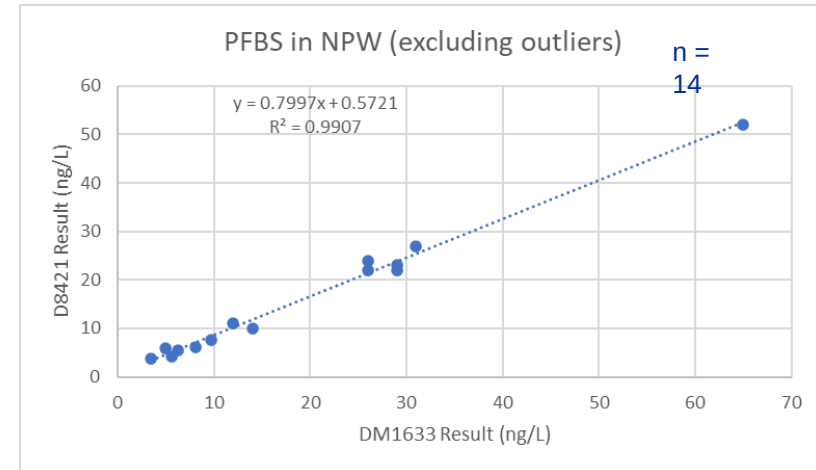
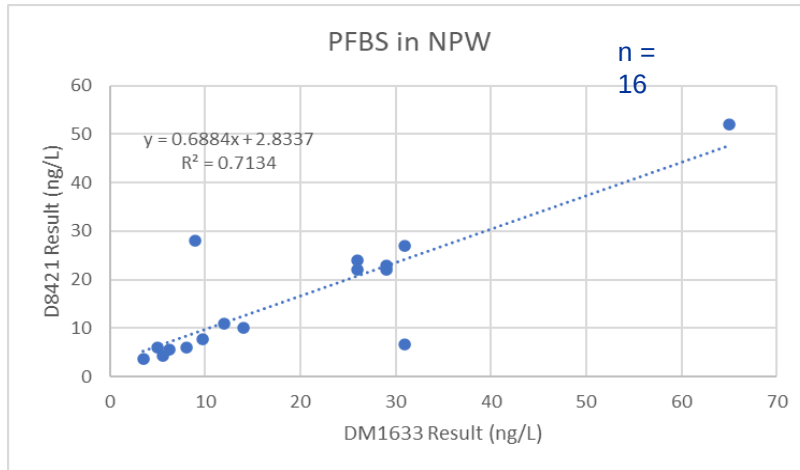
Nine sources supplied by OW/OST/EAD

- Landfill Leachate
- Metal Finisher
- POTW Effluent 1
- Hospital
- POTW Influent
- Bus Washing Station
- Powerplant
- Pulp and Paper
- POTW Effluent 2
- Ground Water
- Surface Water

D8421 vs. DM1633: Carboxylic Acids

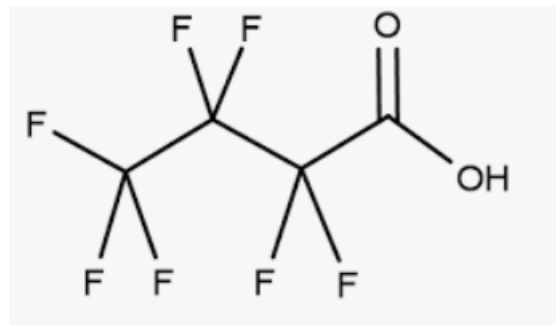


D8421 vs. DM1633: Sulfonic Acids



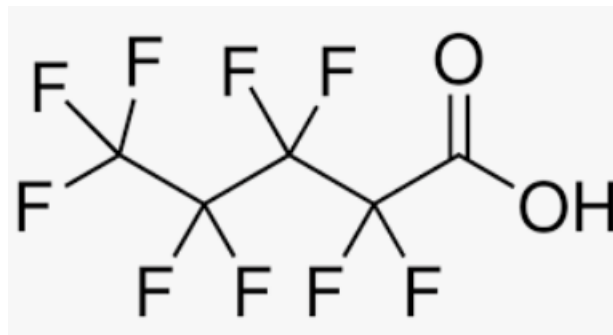
Pace 537M vs. D8421: Leachate

Sample Name	Method	Anlayte	Result	DL	RL	Units	RPD
1	D8421-ID	PFBA	24	8.0	48	ng/L	4
1	PFAS by ID SOP	PFBA	26	6.0	40	ng/L	
2	D8421-ID	PFBA	28	7.9	47	ng/L	14
2	PFAS by ID SOP	PFBA	37	3.0	20	ng/L	
3	PFAS by ID SOP	PFBA	29	0.56	3.7	ng/L	3
3	D8421-ID	PFBA	31	7.8	47	ng/L	
4	D8421-ID	PFBA	27	7.9	47	ng/L	2
4	PFAS by ID SOP	PFBA	28	0.50	3.4	ng/L	
5	PFAS by ID SOP	PFBA	34	6.0	40	ng/L	16
5	D8421-ID	PFBA	47	7.9	47	ng/L	



Pace 537M vs. D8421: Leachate

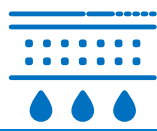
Sample Name	Method	Anlayte	Result	DL	RL	Units	RPD
1	PFAS by ID SOP	PFPeA	87	5.4	40	ng/L	2
1	D8421-ID	PFPeA	83	14	48	ng/L	
2	D8421-ID	PFPeA	93	13	47	ng/L	4
2	PFAS by ID SOP	PFPeA	100	2.7	20	ng/L	
3	D8421-ID	PFPeA	96	13	47	ng/L	5
3	PFAS by ID SOP	PFPeA	86	0.50	3.7	ng/L	
4	D8421-ID	PFPeA	81	13	47	ng/L	2
4	PFAS by ID SOP	PFPeA	78	0.46	3.4	ng/L	
5	PFAS by ID SOP	PFPeA	110	5.4	40	ng/L	19
5	D8421-ID	PFPeA	160	13	47	ng/L	



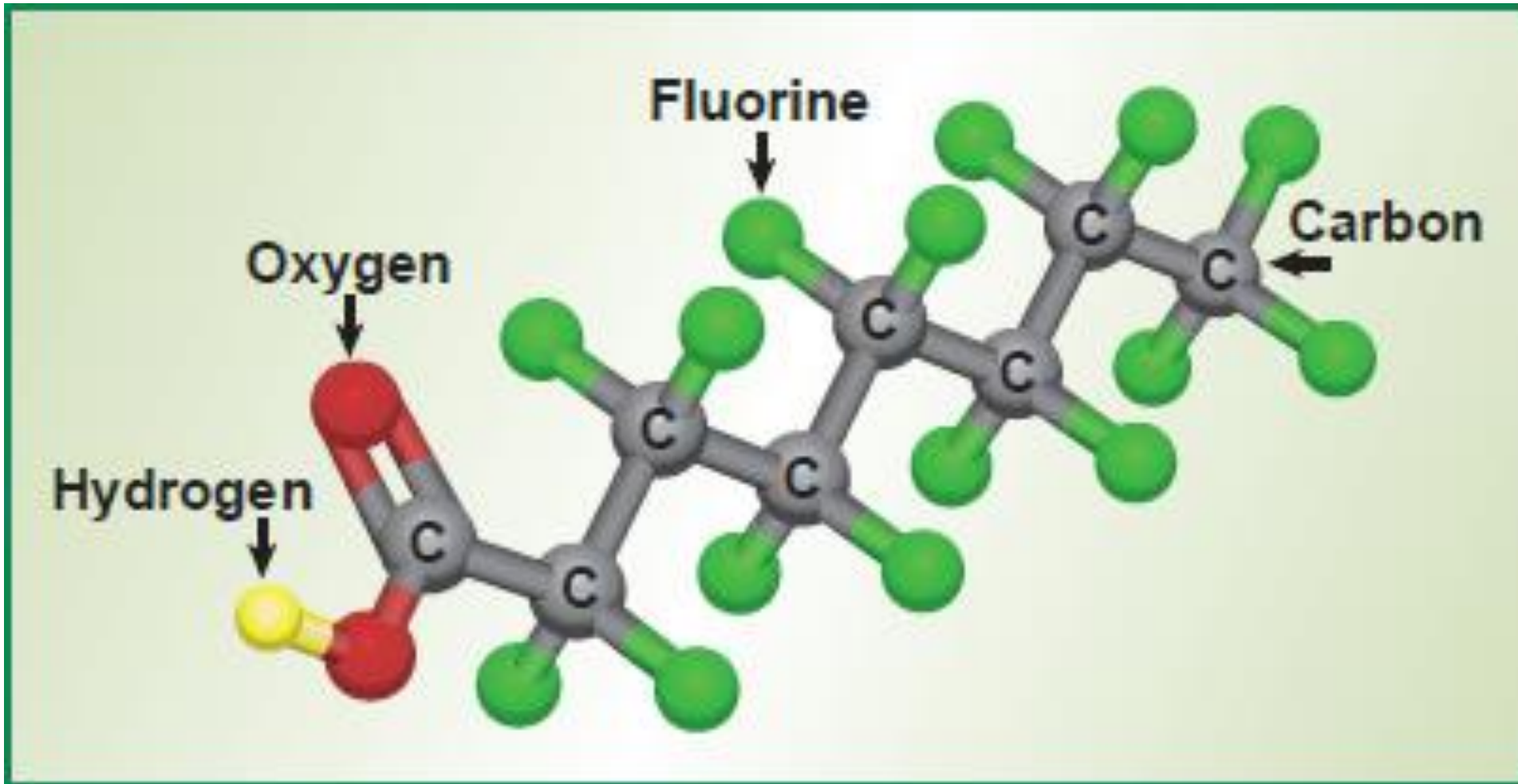
PFAS OVERVIEW

- ▶ **PFAS Chemistry**
- ▶ **Speciated PFAS Test Methods**
- ▶ **Organic Fluorine and Other Methods**





What is Organic Fluorine?



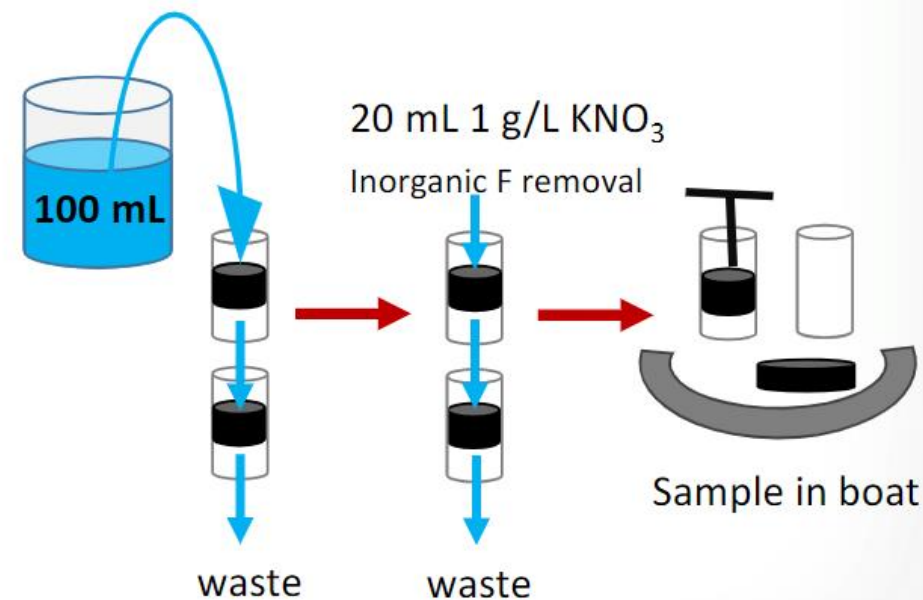
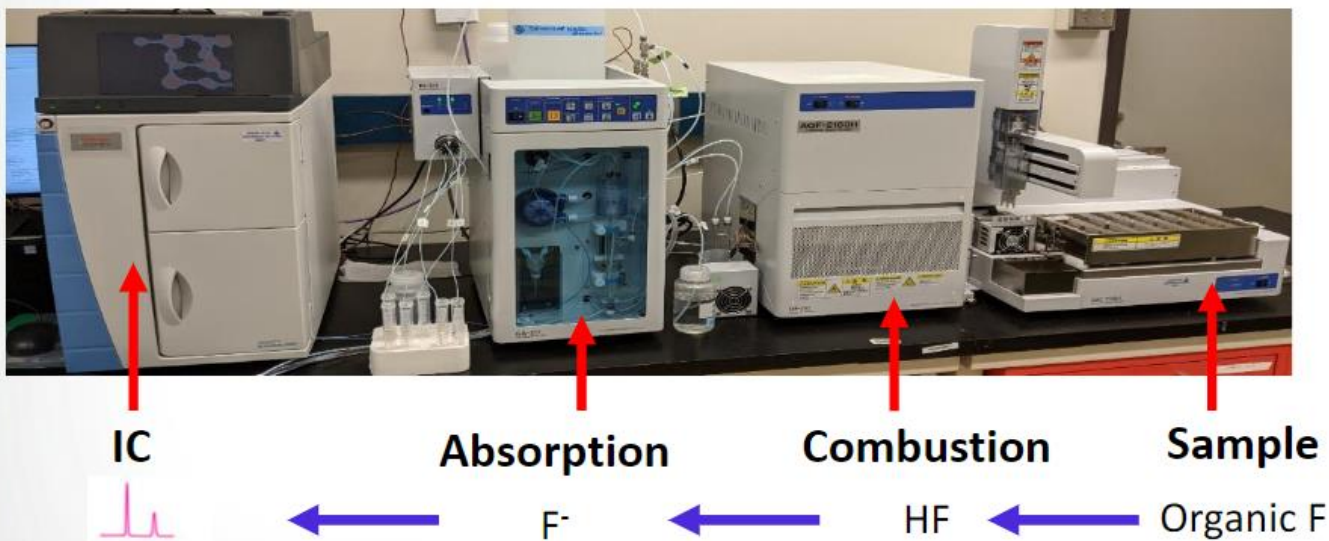


Adsorbable Organic Fluorine (AOF) EPA 1621

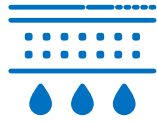
- SCREENING METHOD
- *Method 1621* Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)
 - “Estimates the concentration of AOF”
 - ”...numerical results generated not expected to be as accurate or precise as those from targeted methods for PFAS.”
- **Screening data** can support an intermediate or preliminary decision but should eventually be supported by definitive data before a project is complete.
- **Definitive data** should be suitable for final decision-making (of the appropriate level of sensitivity, precision and accuracy, as well as legally defensible).

How:

- Screening method adsorbs contaminants onto granular activated carbon, removal of inorganic fluoride with nitrate solution, followed by combustion of the carbon
- Organofluorine compounds are converted to fluoride in the combustion process and measured by ion chromatography



Method Detection Limit: 1.4 - 2.2 µg/L

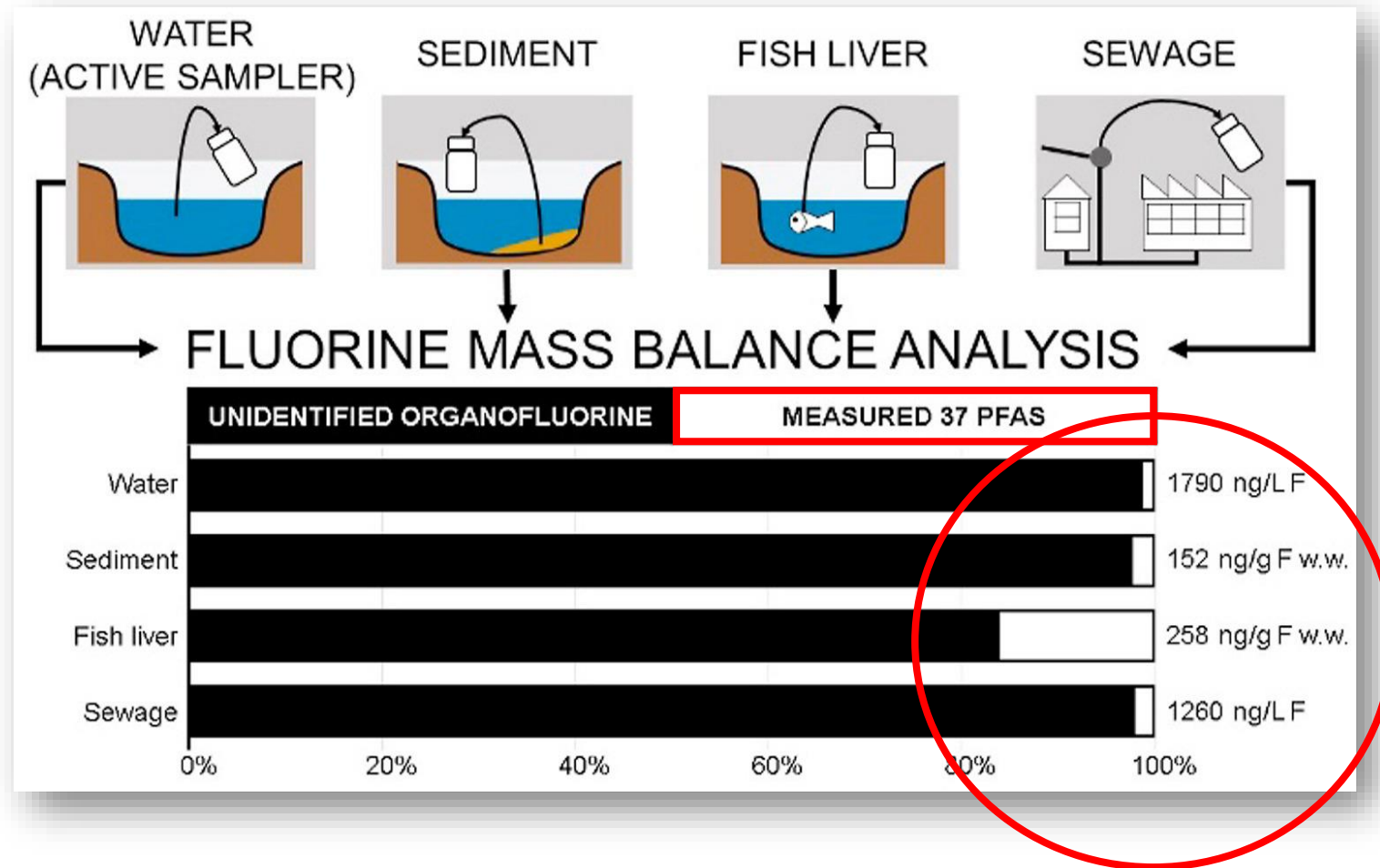


Industrial Discharge Results EPA 1621 and EPA 1633 (as Fluorine)

Sample ID	AOF in ppb	Total 1633 as F in ppb	Sum of PFAS 1633 as %AOF
Discharge A	970	0.288	0.03
Discharge B	47	0.131	0.28
Discharge C	6.3	0.063	1.01
Discharge D	14	0.235	1.68

AOF considers all PFAS we can't measure using targeted methods, most of which are considered precursors, along with other organic fluorine containing compounds that *may* be present including *some* herbicides, pesticides, and pharmaceuticals.

Example Fluorine Mass Balance



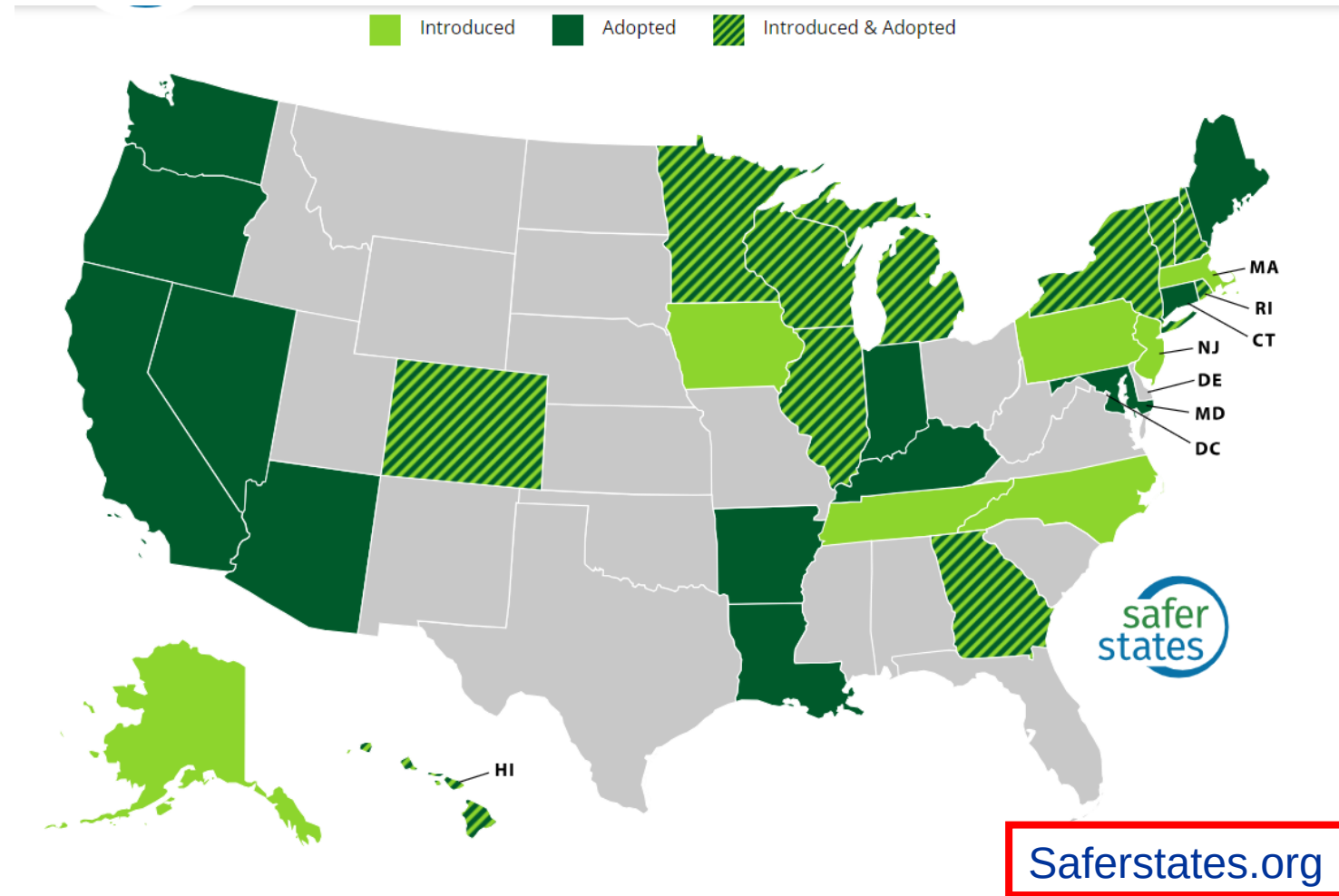
[Aro et al., 2021a](#)

Fluorine mass balance analysis of selected environmental samples from Norway

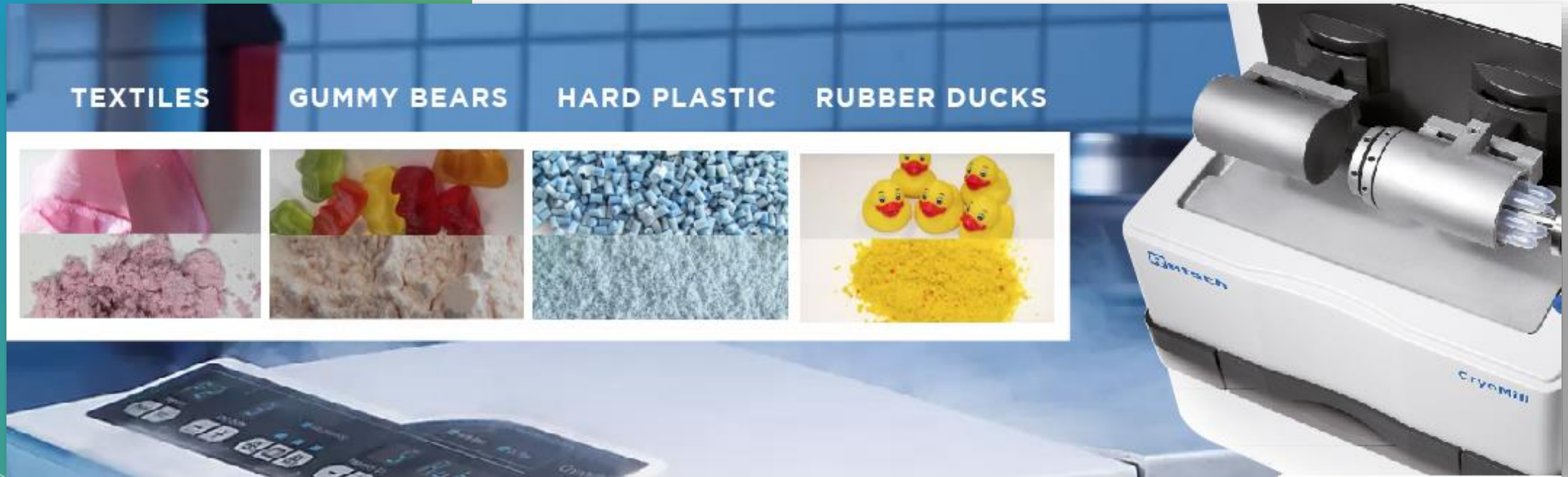
Chemosphere, 283 (2021), Article 131200

WHY Test?

Comply with a current or pending future regulation.



Cryomill Prep for PFAS in Consumer Products



Pace® PFAS LABS

3700+

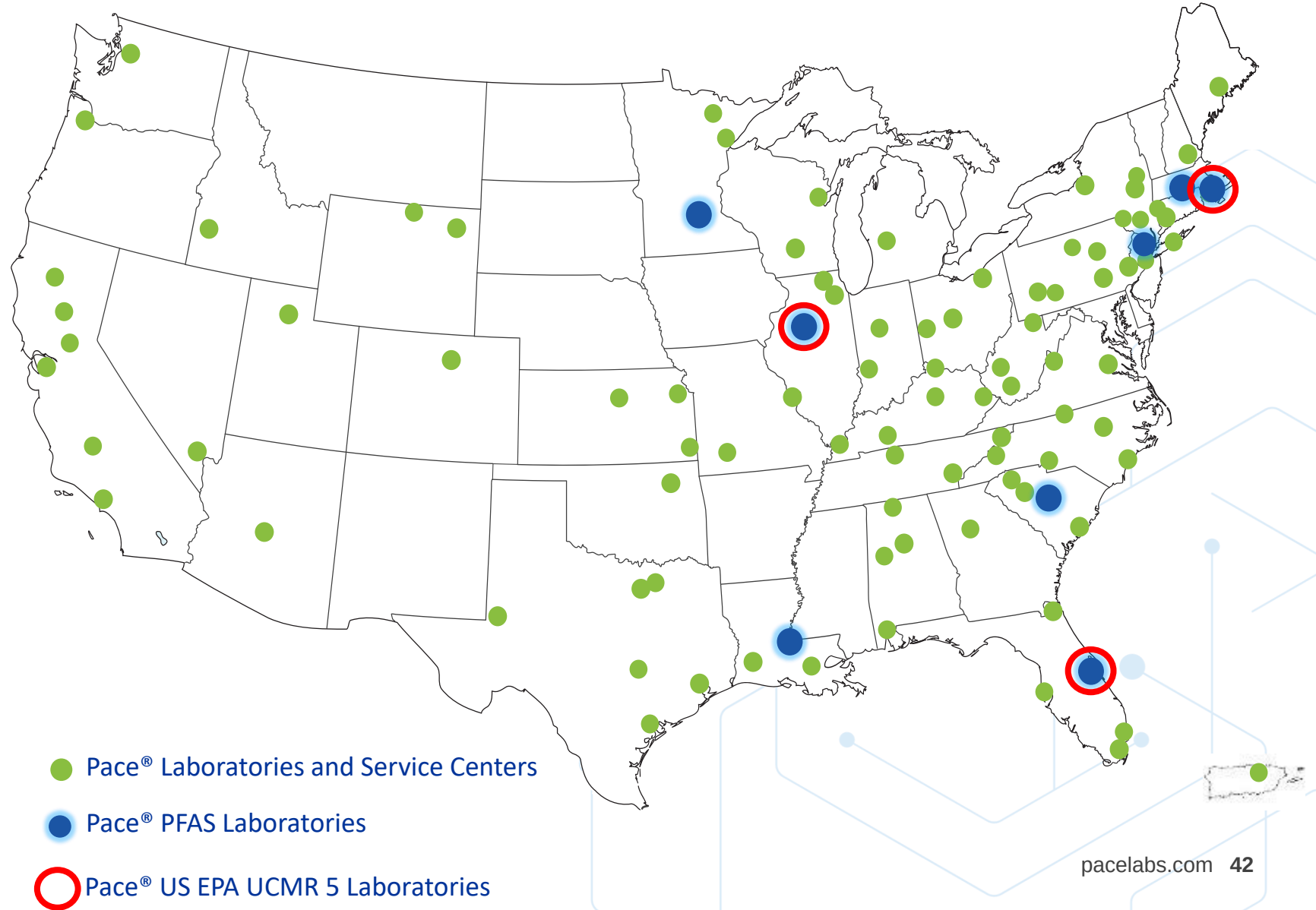
Employees

~ 120

Locations

500+

Certifications



TURNAROUND TIMES

Method	Routine TAT in Business Days
EPA 537.1/533	10-15
EPA Draft Method 1633 - NPW	15-20
EPA Draft Method 1633 - Solids	15-20
EPA Draft Method 1633 - Biota (includes prep)	30
PFAS by ID/537M/QSM B-15 (NPW and Solids)	15
PFAS by ID/537M/QSM B-15 - Biota (includes prep)	30
TOP Assay	15-20
Cryomill/Consumer-Industrial Products	20
EPA Draft Method 1621	15
EPA 8327/ASTM D8421 & D8535	10

Rush TAT consistently available for:

- **1633**
- **8327/D8421/D8535**
- **537M**
- **537.1 & 533**

CORPORATE PFAS TEAM



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PEOPLE ADVANCING SCIENCE

QUESTIONS?

THANK YOU

Additional resources:

- PFAS.com
- PACELABS.COM | Search: PFAS

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