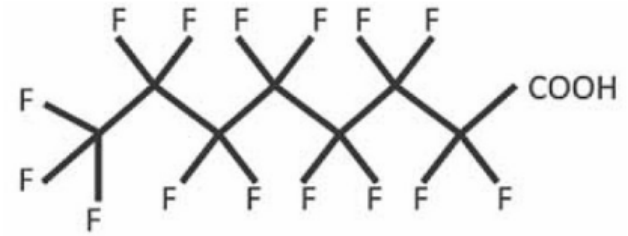
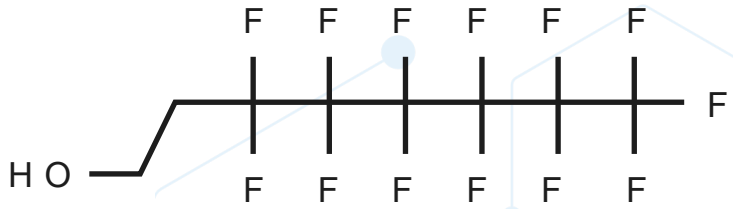
CLASSES OF PFAS



PERFLUOROALKYL

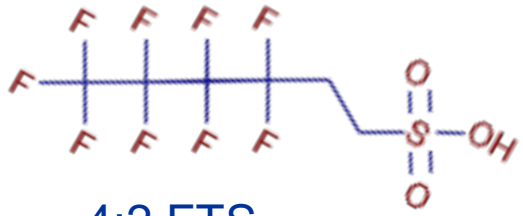
- All hydrogens on the carbons are replaced by fluorine
- Strongest chemical bond in nature
- Difficult to treat
- PFCAs and PFSAs



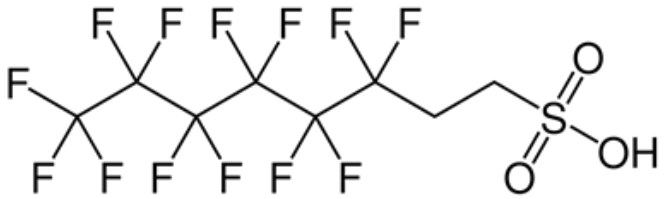
POLYFLUOROALKYL

- 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

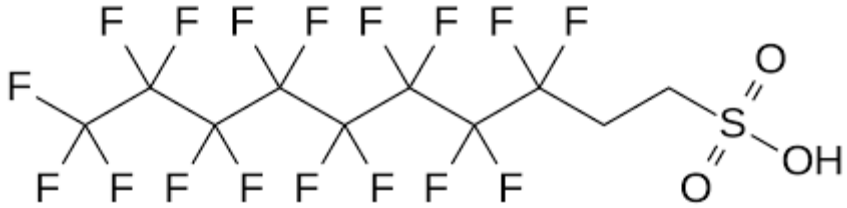
Polyfluorinated PFAS



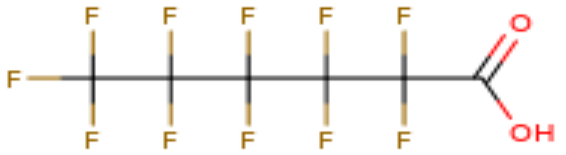
4:2 FTS



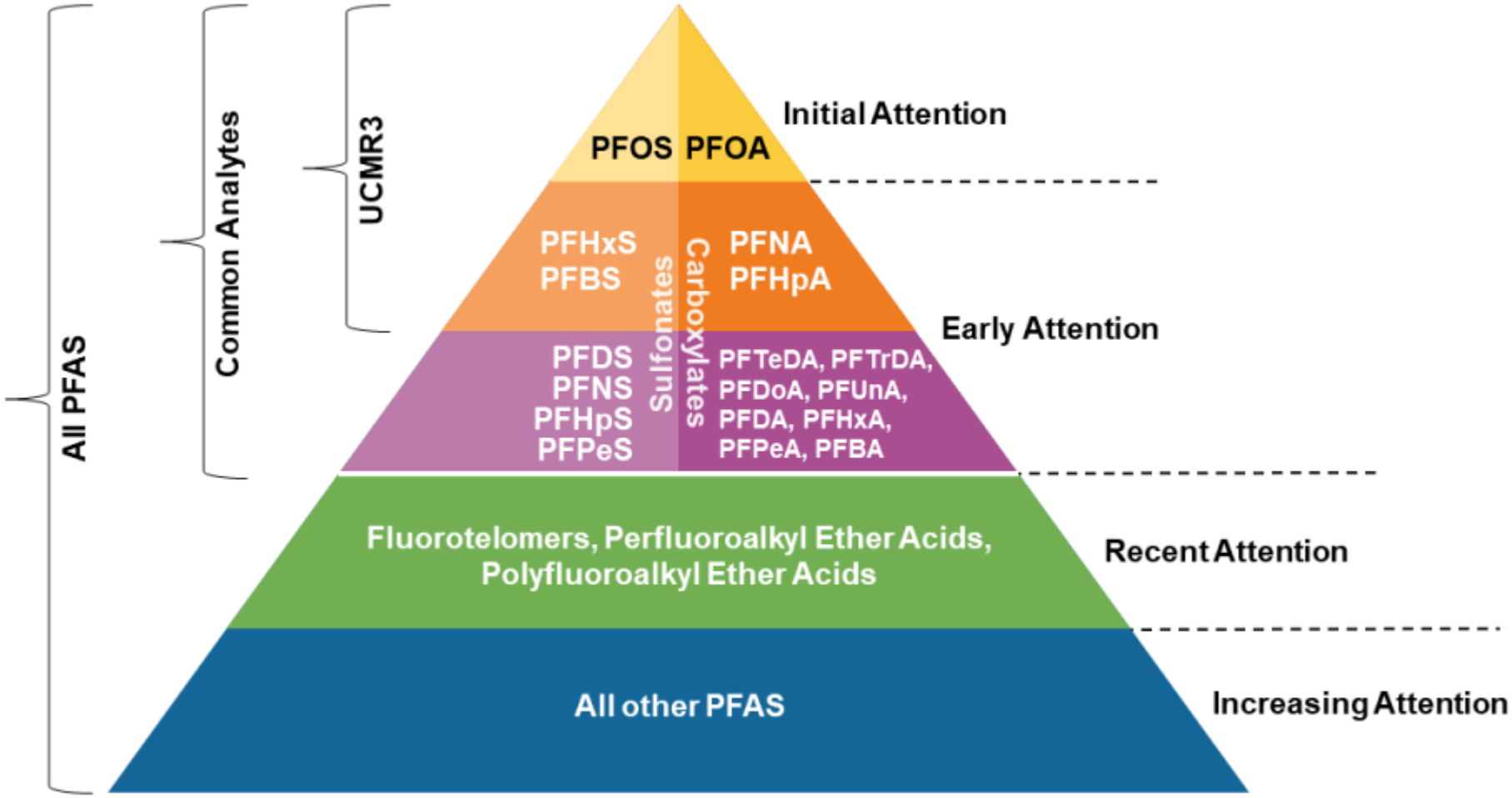
6:2 FTS (C8)



8:2 FTS

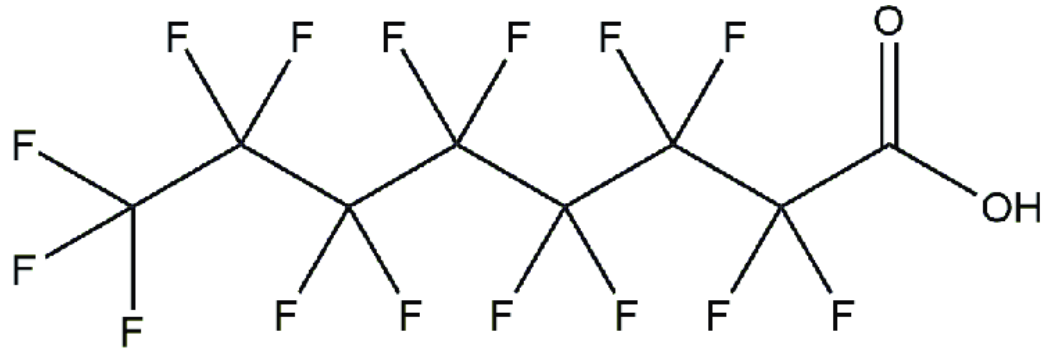


Which target compounds to focus on?

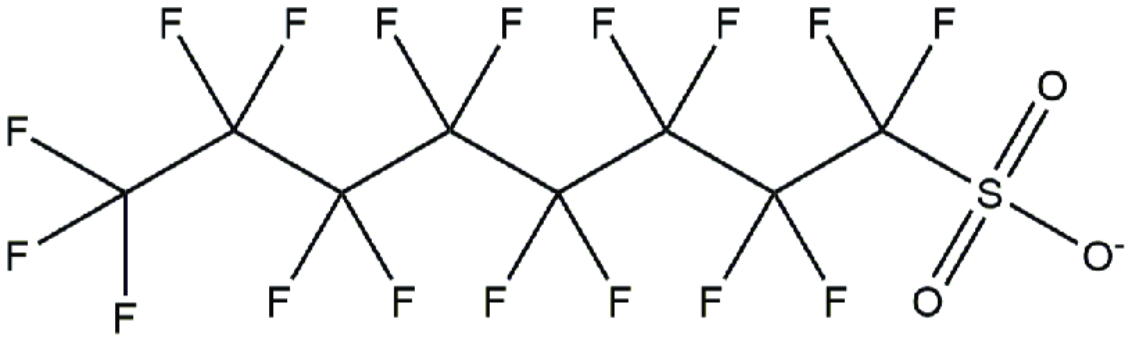


ITRC, 2022

The Two Most Widely Study PFOA and PFOS



Perfluorooctanoic acid (PFOA)



Perfluorooctane sulfonate (PFOS)

-Let's Talk about Bonding C-F

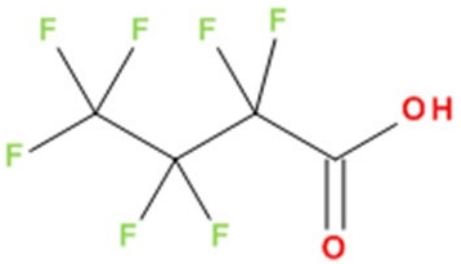
-Who made them?

-What are their uses?

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

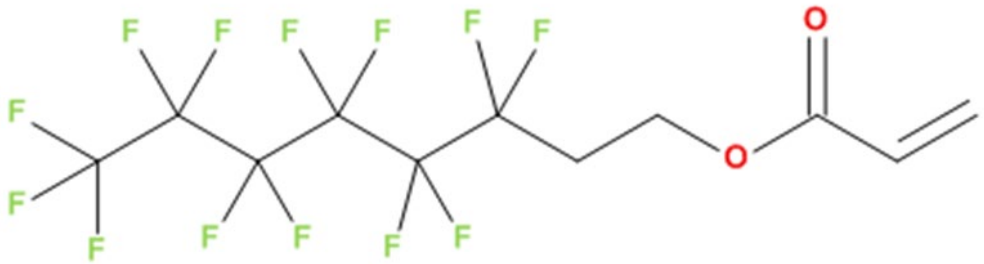
-Known Adverse Health effects.

Replacement PFAS



PFBA

PFBS



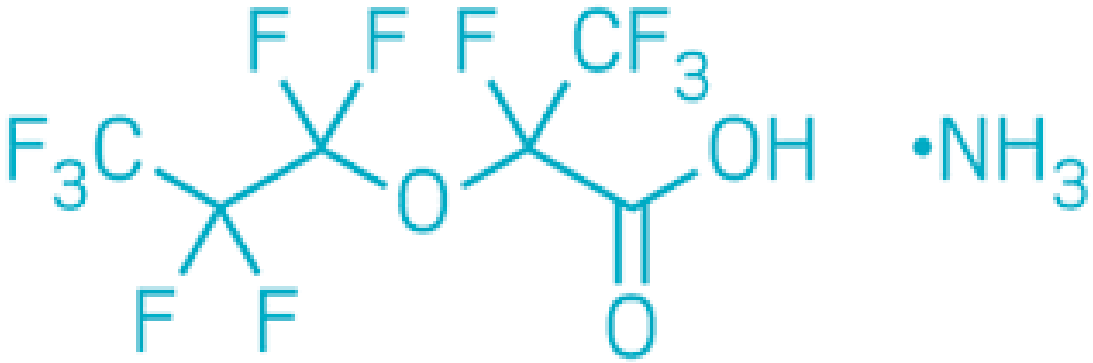
6:2 Fluorotelomer acrylate

- 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

GenX in the Lower Cape Fear River Basin

AKA HFPO-DA (Dimer Acid)

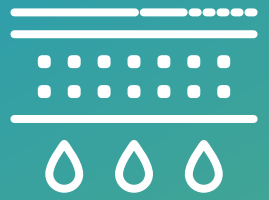
Dupont 2007 as a replacement product for PFOA



GenX

CHOOSING THE RIGHT TEST METHODS

Drinking water



Groundwater, surface water, & leachate

Wastewater, sludge & biosolids

AFFF – concentrate & diluted

Soil, sediment, solid waste & other solids

Air & emissions

Biota – plant & animal tissue

Selected industrial & consumer products

Proposed National Primary Drinking Water Regulation

- On March 14, 2023, US EPA issued the newest proposed National Primary Drinking Water Regulation
- Six PFAS included with enforceable limits/MCLs
  - PFOA
  - PFOS

  PFAS individually or in a mixture, partly due to co-occurrence:
  - PFHxS
  - HFPO-DA (GenX)
  - PFNA
  - PFBS

Source: USEPA

EPA 537.1

- First Published DW Method
- Reports 18 PFAS
- Used for Compliance
- FRB Required
- MS/MSD are part of QC
- Does not use Isotope Dilution

EPA 537.1 (18) DW only	
Acronym	**CAS Number**
PFHxA	307-24-4
PFHpA	375-85-9
PFOA	335-67-1
PFNA	375-95-1
PFDA	335-76-2
PFUnA	2058-94-8
PFDoA	307-55-1
PFTrDA	72629-94-8
PFTA	376-06-7
PFBS	375-73-5
PFHxS	355-46-4
PFOS	1763-23-1
NMeFOSAA	2355-31-9
NEtFOSAA	2991-50-6
HFPO-DA	13252-13-6
ADONA	919005-14-4
9Cl-PF3ONS	756426-58-1
11Cl-PF3OUdS	763051-92-9

EPA 533

Uses Isotope Dilution

Accounts for analyte losses

25 PFAS reported

Addition of source identifiers such as:

- »NFDHA (food packaging)
- »PFEESA (replacement)
- »PFMOPrA (manufacturing)
- »PFMOB (manufacturing)

Requires FRB

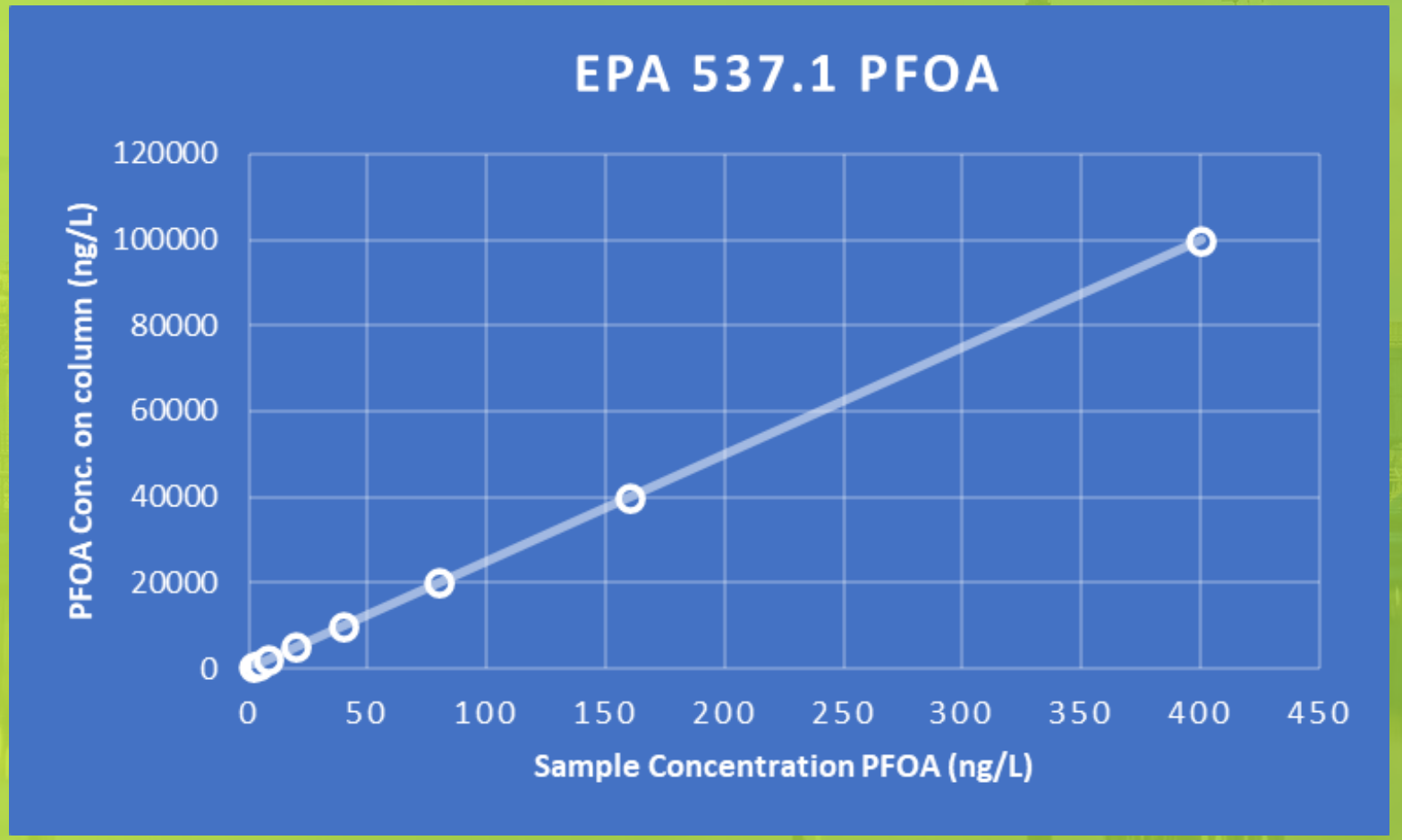
MS/MSD for QC

Analyte	Analyte
PFBA	PFOS
PFPeA	FTS 4:2
PFHxA	FTS 6:2
PFHpA	FTS 8:2
PFOA	PFMPA
PFNA	PFMBA
PFDA	HFPO-DA
PFUnA	NFDHA
PFDoA	ADONA
PFBS	PFEESA
PFPeS	9Cl-PF3ONS
PFHxS	11Cl-PF3OUdS
PFHpS	

USEPA reports 25 from EPA 533 and 4 that don't overlap from EPA 537.1

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		•
PFTrDA	•	
9Cl-PF3PONS	•	•
4:2 FTS		•
11Cl-PF3OUdS	•	•
PFMOBA		•
ADONA	•	•

TAKEAWAYS-MCLs of 4.0 ppt for PFOA/PFOS



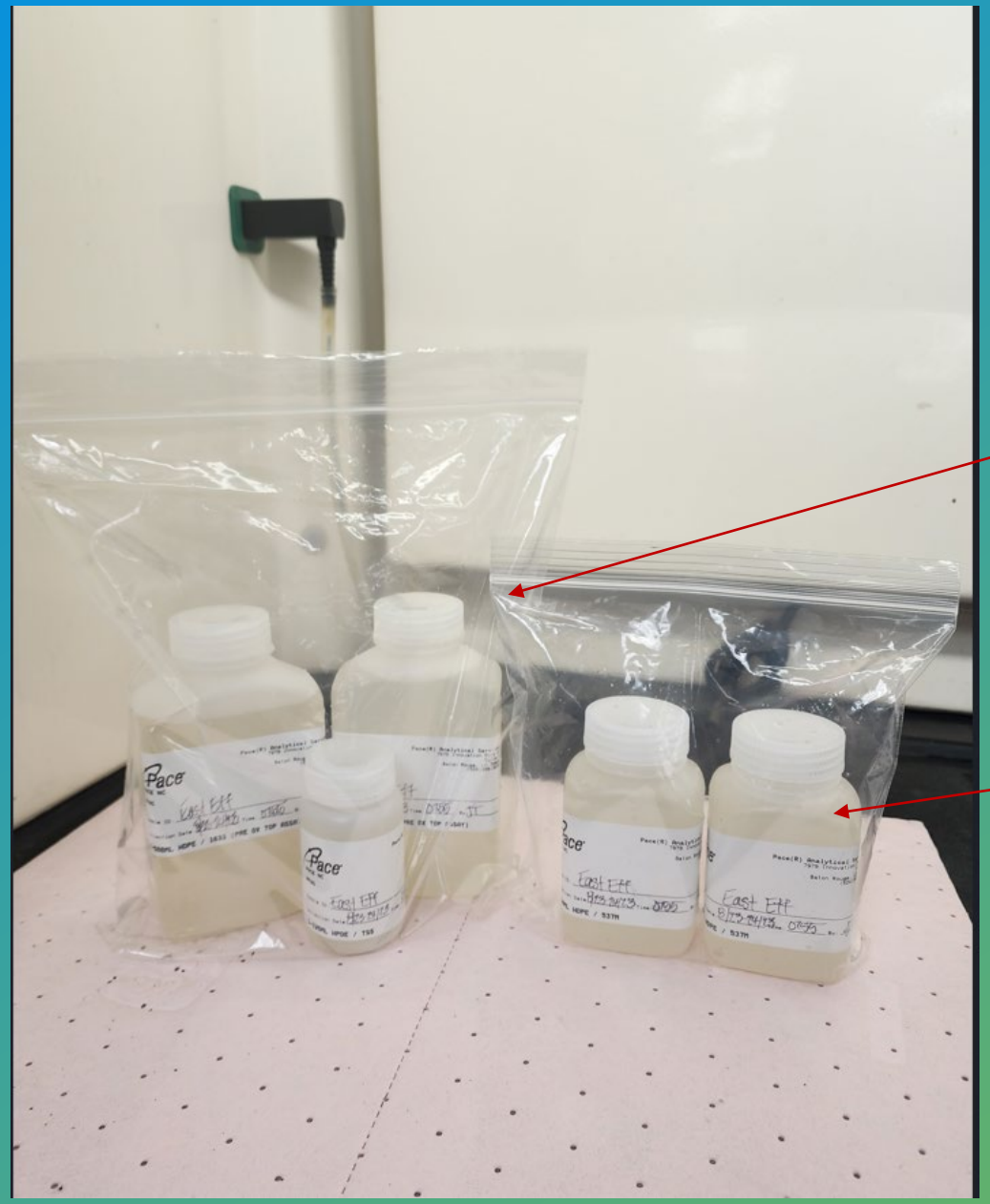
Draft Method EPA 1633

- EPA announced the method Sept 2021
- Eight matrices - wastewater, surface water, groundwater, soils, biosolids, tissue, leachate, and sediment
- Single lab validation, 2022 and on multi-lab validation
- We are on Draft 4
- EPA/DOD combined effort
- DM 1633 should phase out” 537Modified” methods
- DM 1633 will be finalized for aqueous matrices such as wastewater ahead of solids
- DM 1633 being added to NPDES permits and some municipal landfill groundwater monitoring programs

Image copied from: Cincinnati Enquirer

New Features / Protocols

- Protocol Standardization – EPA + DoD
- Multiple matrices addressed with one method – WW/GW/SW, landfill leachate, soils/sediments, biosolids, tissues
- Additional QA/QC (Bile salt resolution, new branched isomers, duplicate LCS)
- Prep restrictions
  - Method is only applicable to AQ <100mg/L TSS
  - Extract dilutions >10X require re-extraction
- SPE required for solid and tissue matrices – identical to AQ SPE procedure
- Sample storage: refrigerated OR frozen



1633 Aqueous Bottle

537M/PFAS by ID
(Historical Bottleware)

Aqueous: DM1633 vs. Legacy Method

Sample volume: 500 mL vs. 125 mL or 250 mL

- **Landfill leachates: 100 mL (RLs 5X higher)**

Pre-preparation: TSS required; subsample >100 mg/L

- **Draft 3: TSS flexibility; centrifugation allowed**
  - **QSM Table B-15: centrifugation allowed >1% solids**
  - **QSM Table B-24: silent on this matter (current version)**

Lower sorbent mass SPE (+ Glass wool) = slower sample loading

Dispersive carbon (dGCB) cleanup

Syringe filtration

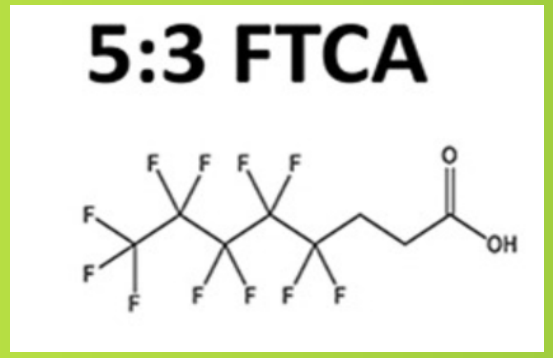
DM1633

- Sample mass: 5 g (dry mass) vs. various masses (1 - 5 g)
  - Biosolids: 0.5 g (dry mass; RLs 10X higher)
- Three-fold solvent extraction (Methanolic NH4OH) – shake/centrifuge/decant; dGCB cleanup
- Solvent exchange/volume reduction – methanolic to aqueous
  - % Solids / sample water content
- SPE – identical to aqueous SPE protocol (~50 mL volume)
- Method modification?

40 PFAS Compounds in Draft 1633

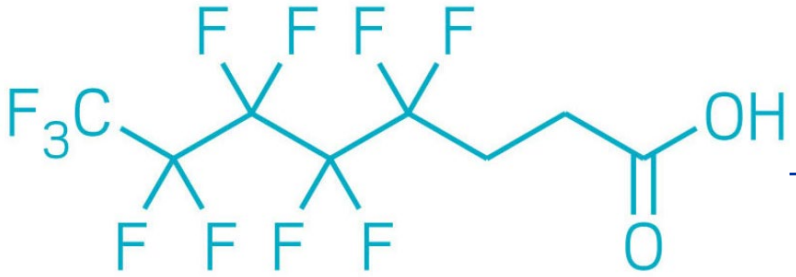
Analyte	Analyte
PFBA	8:2 FTS
PFPeA	PFOSA
PFHxA	N-MeFOSAA
PFHpA	N-EtFOSAA
PFOA	HFPO-DA
PFNA	PFMOPrA
PFDA	ADONA
PFUnDA	9Cl-PF3ONS
PFDoDA	11Cl-PF3OUdS
PFTrDA	**3:3 FTCA**
PFTeDA	**5:3 FTCA**
PFBS	**7:3 FTCA**
PFPeS	N-EtFOSA
PFHxS	N-EtFOSE
PFHpS	NFDHA
PFOS	N-MeFOSA
PFNS	N-MeFOSE
PFDS	PFDoS
4:2 FTS	PFEESA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

- 1633 will help unify PFAS lists
- All 29 PFAS from UCMR 5 are included in this method
- Can aid drinking water plants in source identification of PFAS present in their raw and finished product

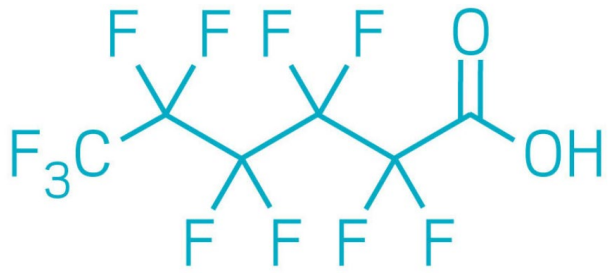


5:3 fluorotelomer carboxylic acid (FTCA) is a common and often dominant constituent of PFAS found in landfills and is released from carpet in model anaerobic landfill reactors. This compound could prove to be an indicator of PFAS in the environment originating from landfills (Lang et al. 2017[63], 2016[64]).

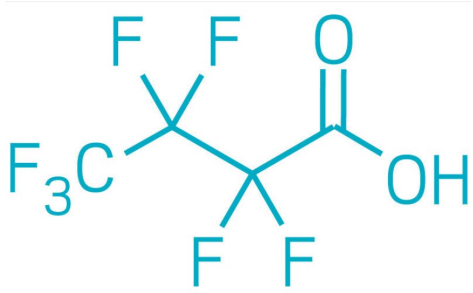
5:3 FTCA has several potential degradation pathways



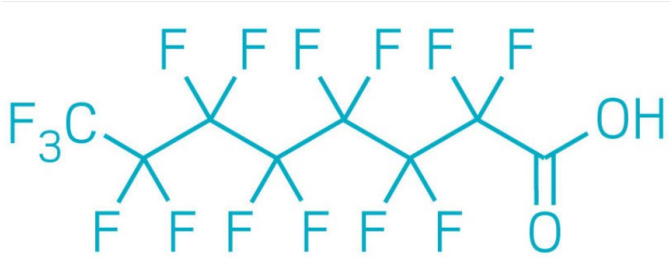
5:3
FTCA



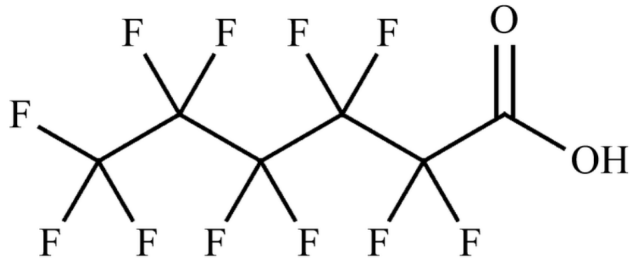
PFHxA



PFBA



PFOA

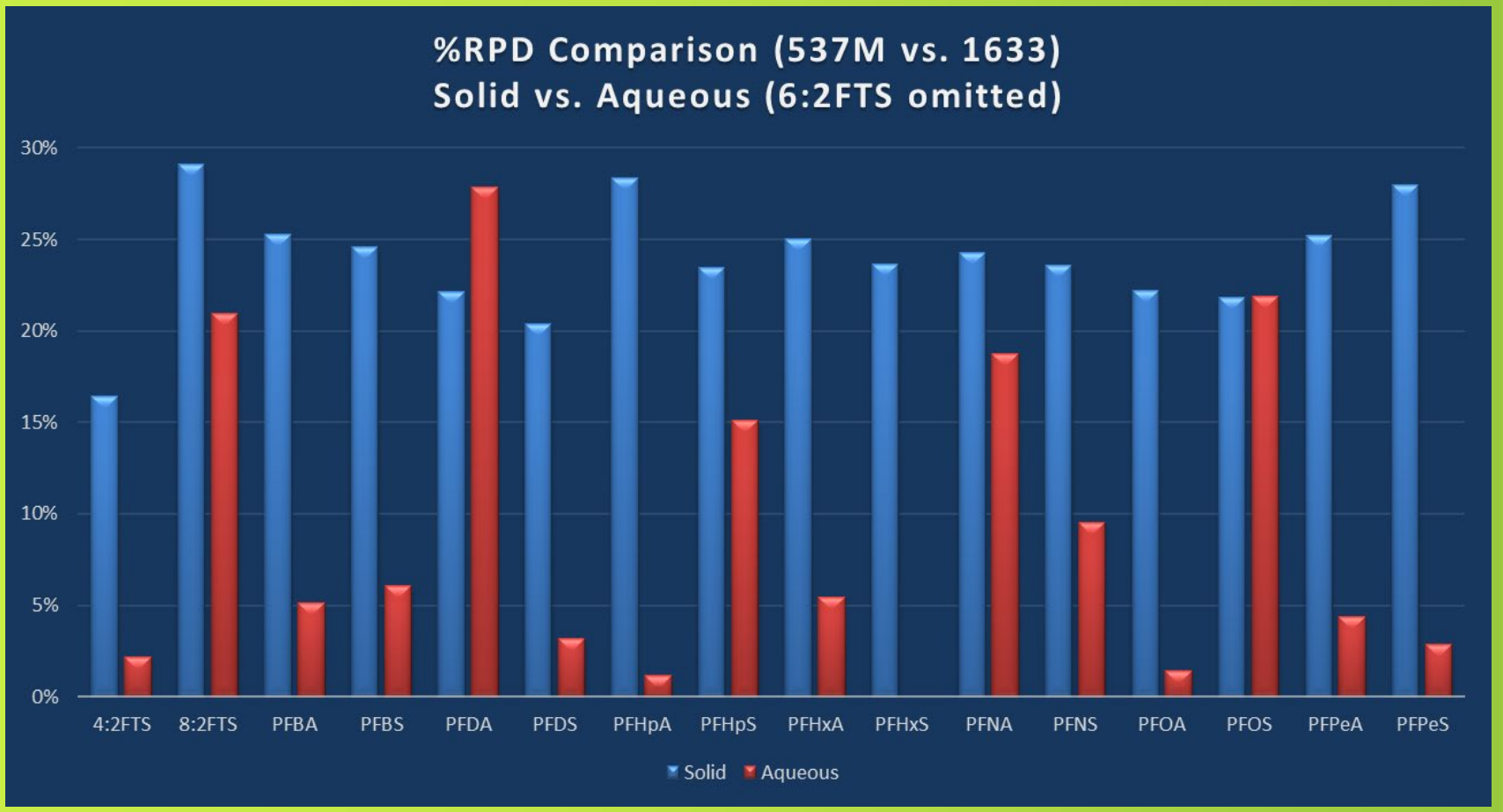


PFPEA

TSS Impacts-Something to think about…

Analyte	Liquid ng/L	Solid 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
PFDoA	<500	0.53
PFTrDA	<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

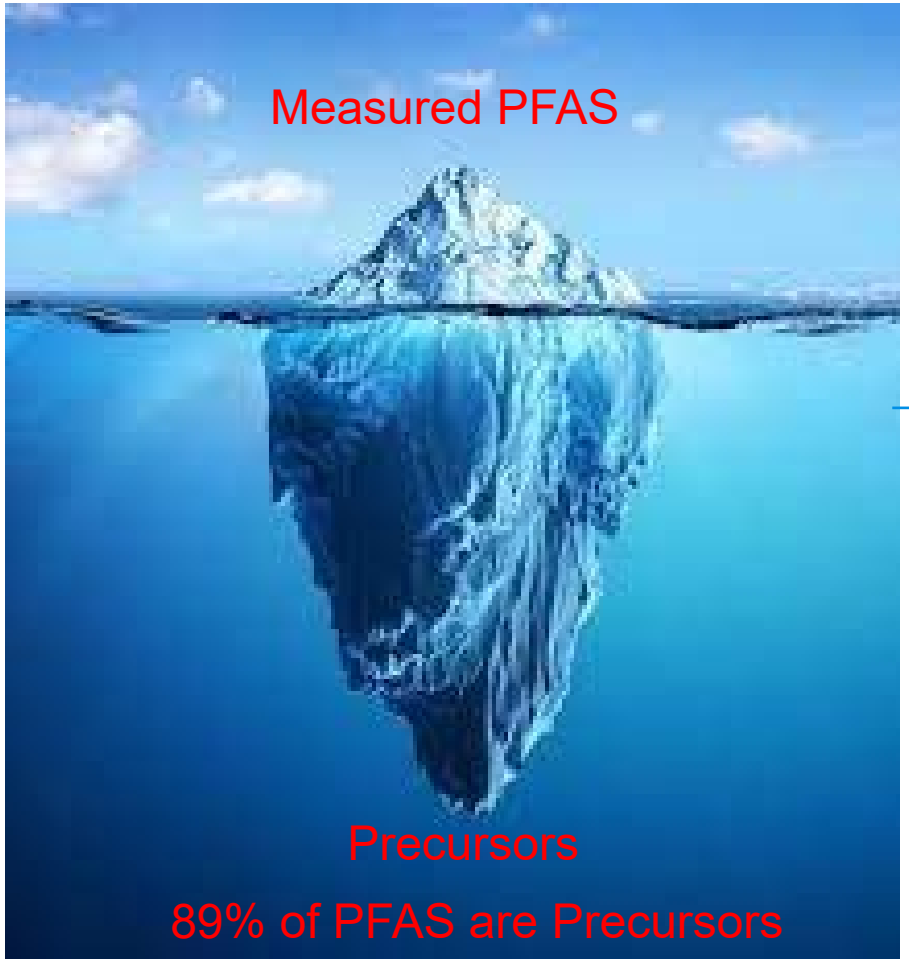
Analyte	Liquid ng/L	Solid ug/kg
NMeFOSA	<500	<0.17
NEtFOSA	<500	<0.17
N-MeFOSAA	5900	14
N-EtFOSAA	3400	8
NMeFOSE	<5000	4.2
NEtFOSE	<5000	4.9
HFPO-DA	<2000	<0.69
ADONA	<2000	<0.69
9Cl-PF3ONS	<2000	<0.69
11Cl-PF3OUdS	<2000	<0.69
3:3 FTCA	<5000	<1.7
5:3 FTCA	220000	140
7:3 FTCA	32000	28
PFEESA	<1000	<0.35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



	Solid	Aqueous
4:2FTS	16%	2%
8:2FTS	29%	21%
PFBA	25%	5%
PFBS	25%	6%
PFDA	22%	28%
PFDS	20%	3%
PFHpA	28%	1%
PFHpS	23%	15%
PFHxA	25%	5%
PFHxS	24%	0%
PFNA	24%	19%
PFNS	24%	10%
PFOA	22%	1%
PFOS	22%	22%
PFPeA	25%	4%
PFPeS	28%	3%

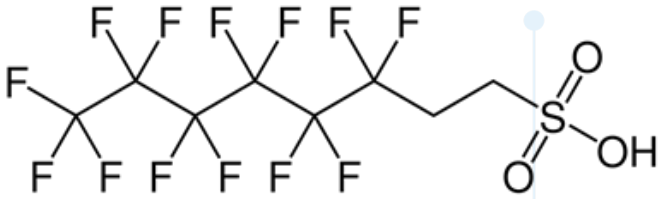
We like: <30%RPD for Solids
<20%RPD for Aqueous

TOP (Total Oxidizable Precursor Assay)

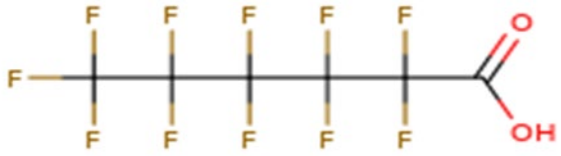


Heat/Oxidation

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.



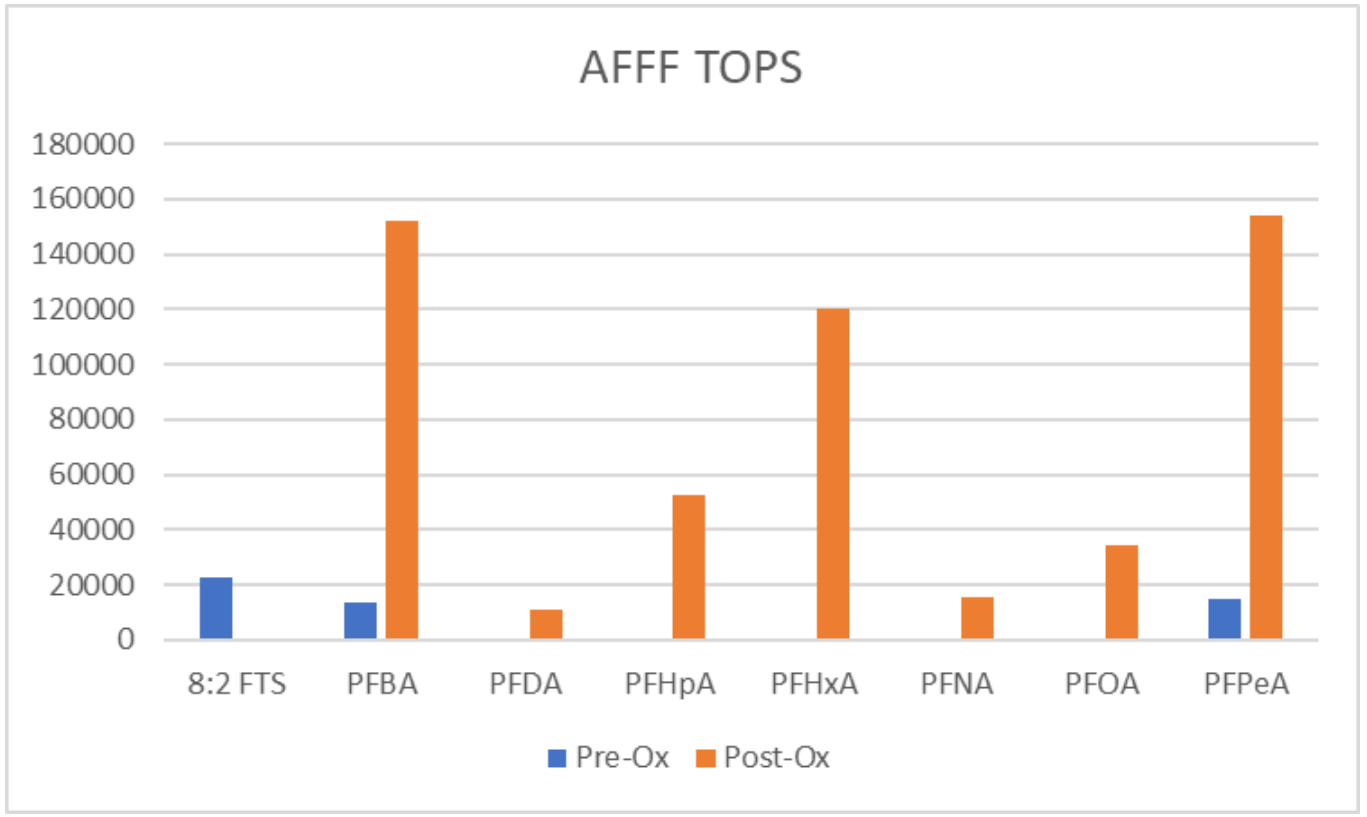
6:2 FTS



PFHxA

https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/

TOPS Table Pre-Ox and Post-Ox

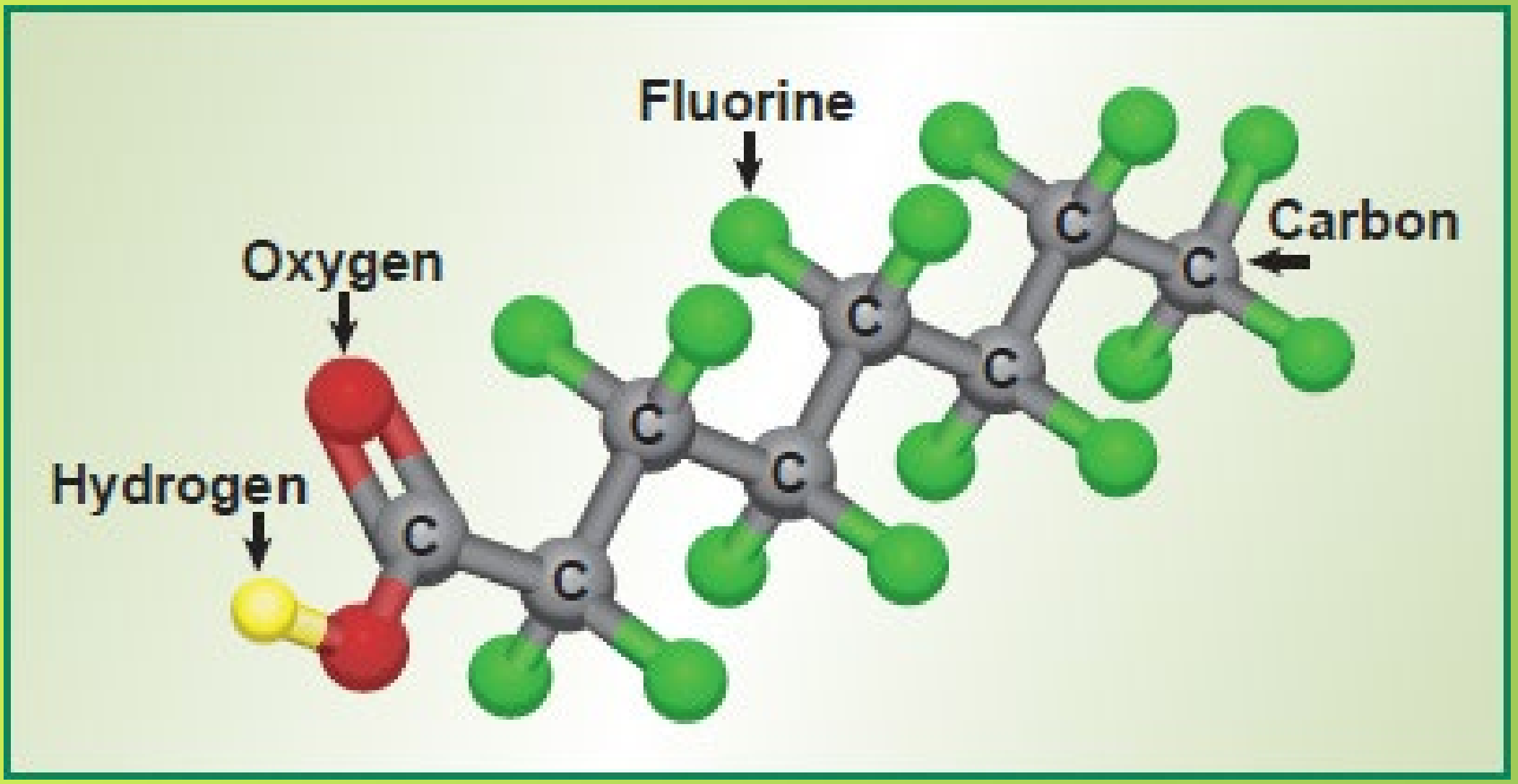


	Pre-Ox (ppt)	Post-Ox (ppt)
8:2 FTS	22300	0
PFBA	13700	152000
PFDA	0	10900
PFHpA	0	52600
PFHxA	0	120000
PFNA	0	15500
PFOA	0	34500
PFPeA	14900	154000
Total	50900	539500

P*FAST*®
EPA 8327/ASTM D8421

- LOQ ~10 ppt
- Pricing is a plus
- Faster on average TAT
- Smaller sample volume
- List includes 40 plus PFAS
- All PFAS from 1633 and UCMR5 included
- Useful for pilot studies, bench scale remediation technologies, destruction technologies
- SW-846 8327 and ASTM D8421 needs vary by regulatory agency

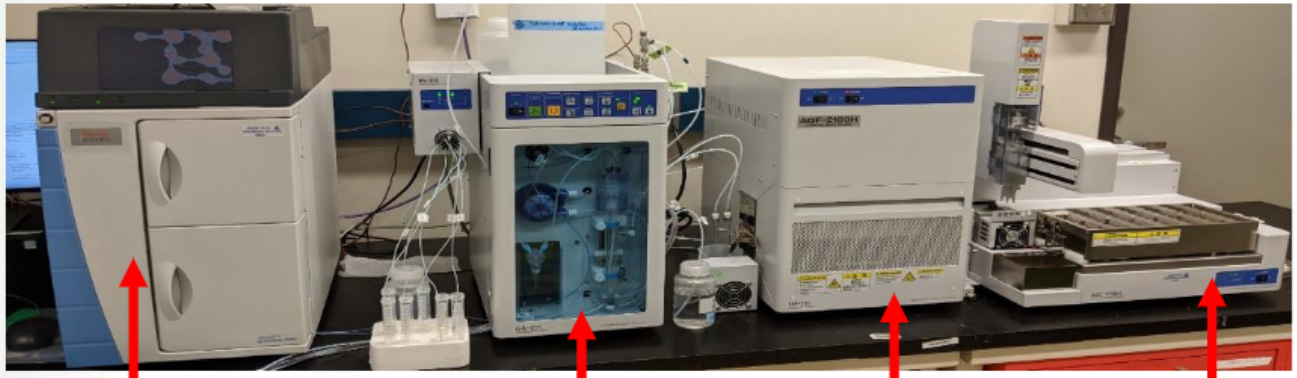
What is Organofluorine?

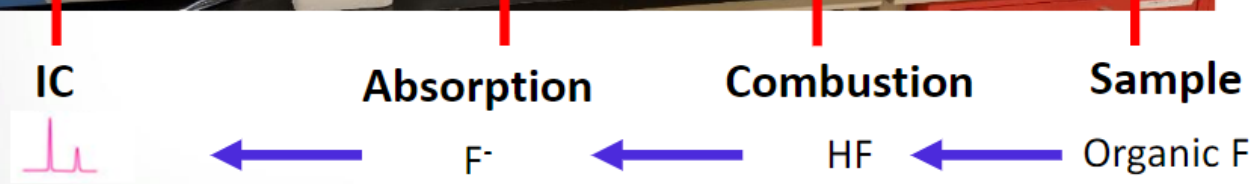


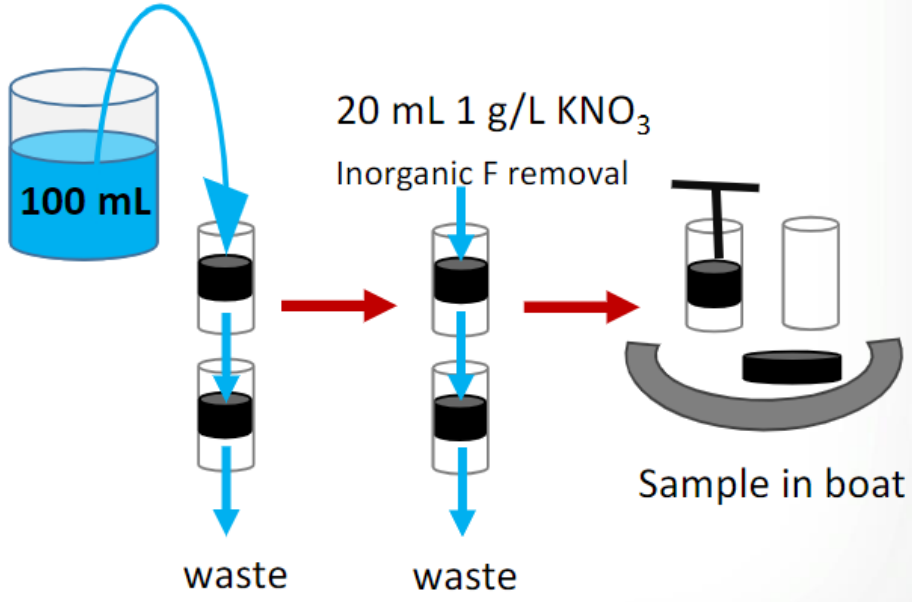
Approach – AOF/CIC

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

Method Considerations

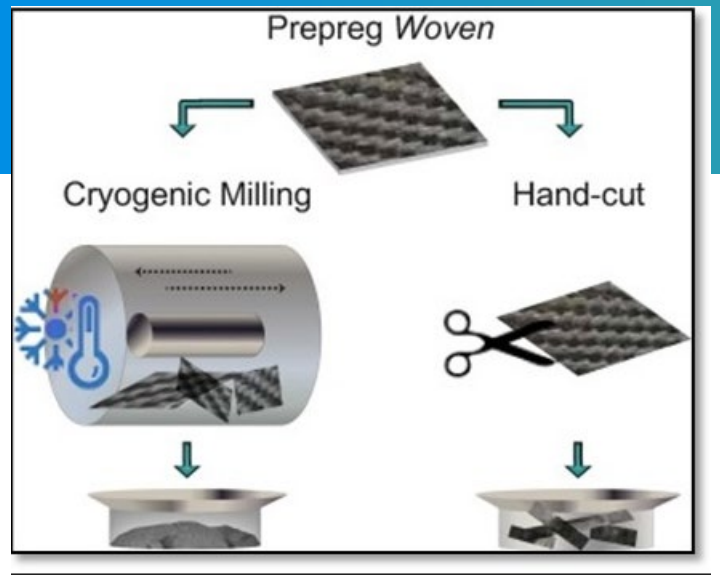
- There are other “organofluorine” compounds (e.g., refrigerants, pesticides, and pharmaceuticals).
- Extraction efficacy (AOF/EOF) will be challenging to monitor; can’t use internal standards or surrogates for unknown samples……but…..QC is even “more” important.
- **1 ppb PFOA ≠ 1 ppb organofluorine**
  - PFOA (as F) = PFOA * 0.69 (i.e., 69% fluorine by mass; remainder is carbon, hydrogen, and oxygen).
- Therefore, multiply ∑PFAS * 0.65 (on average) to convert to “as F” basis to compare to TOF/AOF/EOF result.
- Method sensitivity is a critical element of the DQO process, to be discussed with the lab.

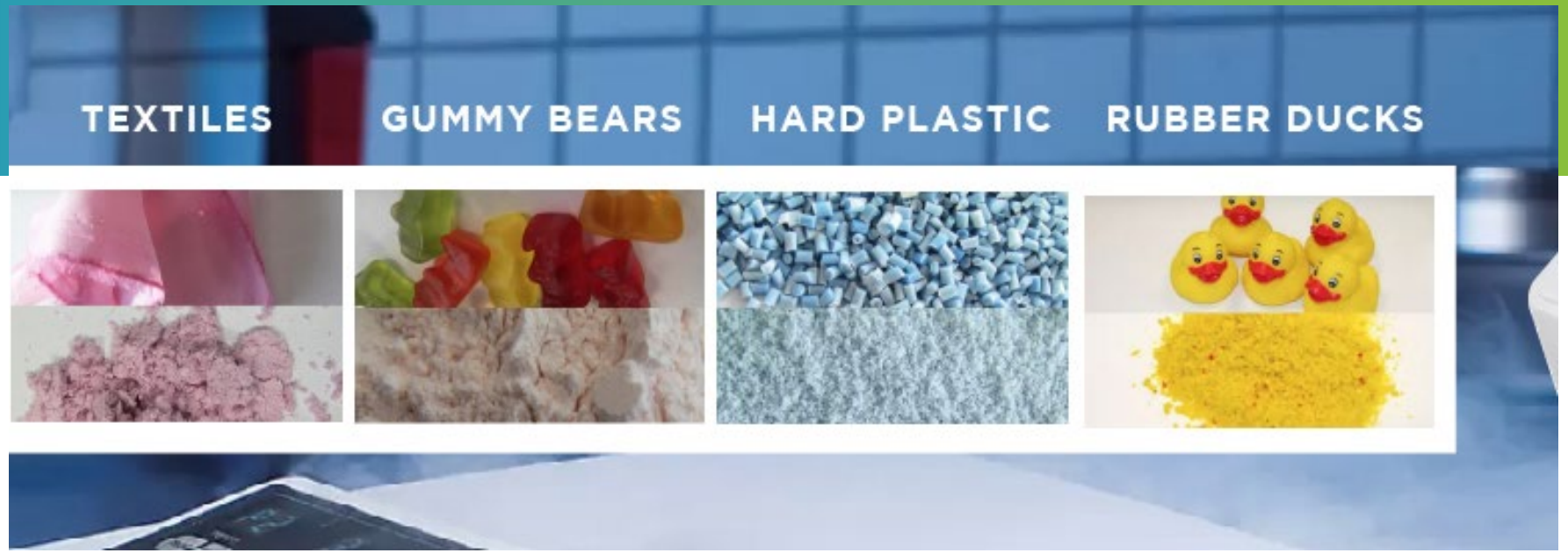
AOF Results for Industrial Discharge

Sample ID	AOF (ug/L)	SUM PFAS (ng/L)	SUM PFAS (ug/L)	SUM PFAS as F (ug/L)	SUM PFAS as % of AOF	AOF FACTOR
Discharge A	970	450	0.45	0.288	0.03%	3368
Discharge B	47	204	0.204	0.13056	0.28%	360
Discharge C	6.3	99	0.099	0.06336	1.01%	99
Discharge D	14	368	0.368	0.23552	1.68%	59

- Sum of PFAS is from 1633 data
- Sum of PFAS as F is 1633 total X 0.64 The 0.64 is the average percent of all 40 PFAS where the weight comes from Organic Fluorine.
- As you can see from Discharge A our results is 970 ppb for AOF but our Sum of PFAS as F is 0.288 ppb. This shows we are only accounting for 0.03% of Organic Fluorine when looking at the 1633 results.
- AOF considers all Precursors and PFAS we can't measure along with other compounds herbicides , pesticides , pharmaceutical, etc. that contain Organic Fluorine.

Uptake in Consumer Product Testing





States potentially banning the intentional addition of PFAS to products.

- Maine
- California
- Minnesota

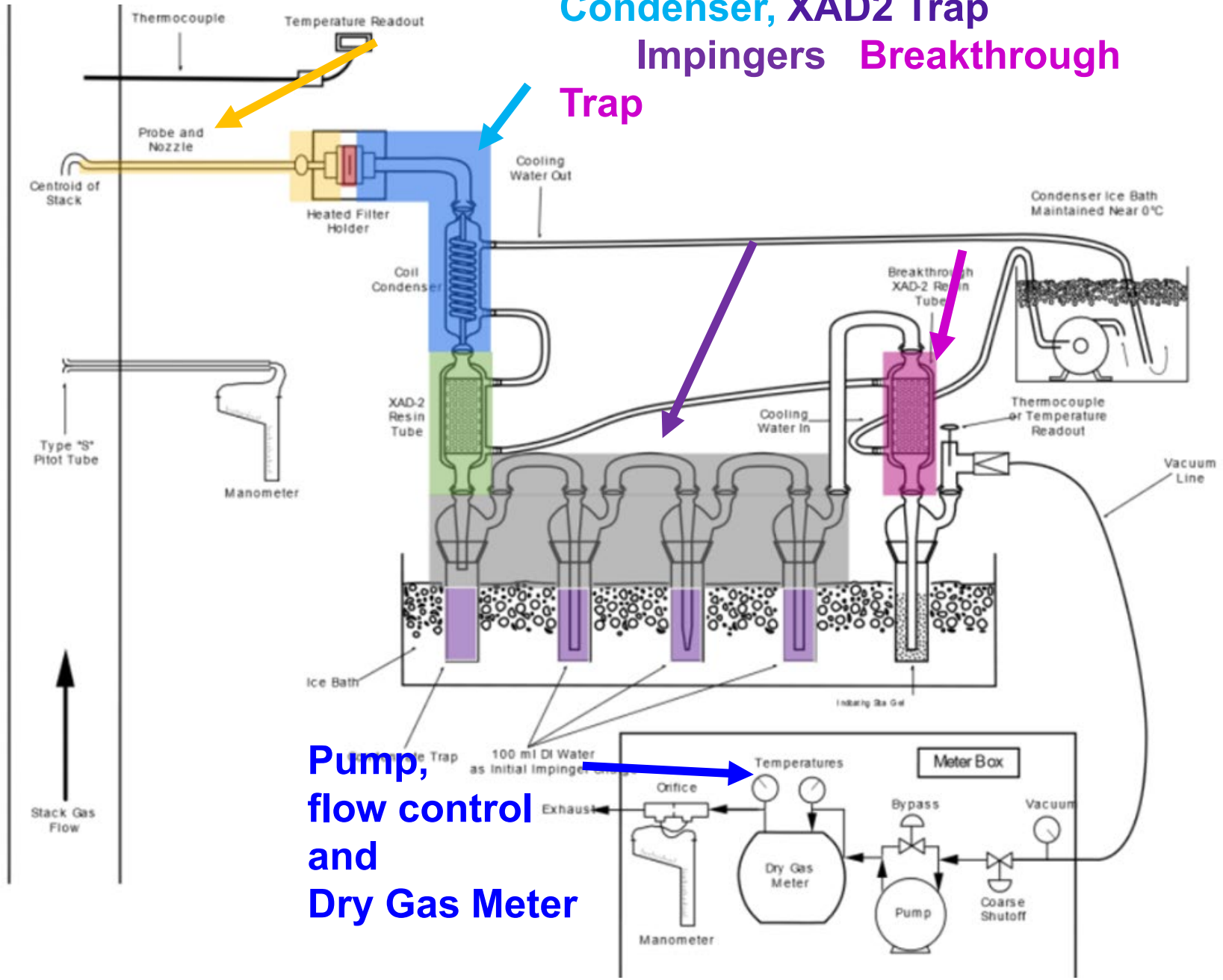
The MPCA is implementing Amara's Law, which is a new pollution prevention law that restricts the use of per- and polyfluoroalkyl substances (PFAS) in products sold and distributed in Minnesota. The timeline of Amara's Law includes:

- January 2025: Ban on intentionally added PFAS in 11 product categories.
- January 2026: Manufacturers must report to MPCA on any use of intentionally added PFAS in their products.
- January 2032: Ban on intentionally added PFAS for all products, unless the MPCA determines they are a currently unavoidable use.

OTM 45 from EPA

- Probe inserted into the stack
- Pump draws stack gas sample through the apparatus or “train”
- Dry Gas Meter measures volume of dry stack gas sample drawn through train
- PFAS particles (or on particles) collected in the heated probe and filter
- PFAS in gaseous phase collected in ice-cooled XAD2 Trap and Impinger Water (bubbles through the water)
- Breakthrough Trap
- Sample fractions recovered from each colored section in diagram (in field)
- Sample fractions sent to the Lab for extraction and Analysis

Sampling Probe and Filter
Condenser, XAD2 Trap
Impingers Breakthrough Trap



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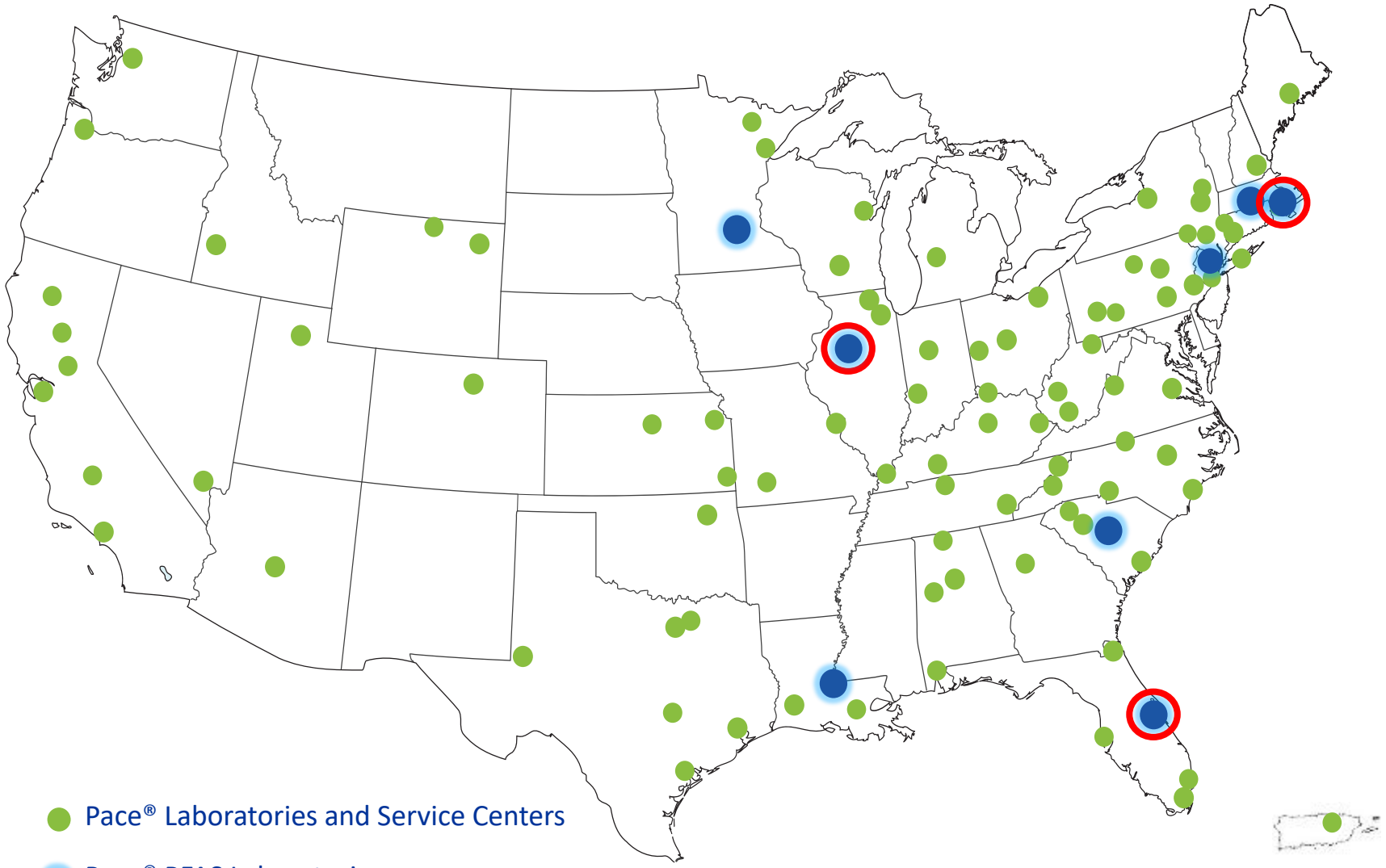
3700+
Employees

~ 120
Locations

500+
Certifications



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THANK YOU

Additional resources:

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

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