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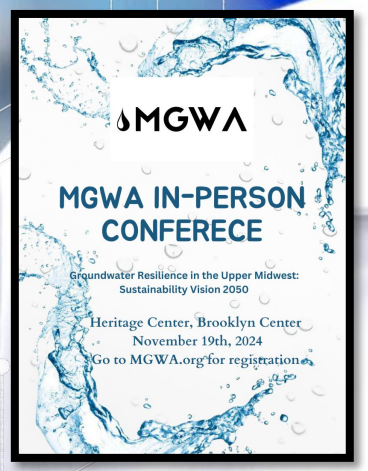
PEOPLE ADVANCING SCIENCE

EPA PFAS Test Methods Are Now Final, What That Means for Ground Water Professionals



ICE BREAKER (2X)

How many of you are familiar with ASTM D8421?

How many have used ASTM D8421?

Corporate PFAS Team

Paul R. Jackson
Program Manager, Environmental
Compliance & Emerging Contaminants
813-731-1595
Paul.Jackson@pacelabs.com

Lindsay Boone
Program Manager, Environmental
Compliance & Emerging Contaminants
910-262-5098
Lindsay.Boone@pacelabs.com

Jim Occhialini
V.P., Technical Sales
508-380-8618
jocchialini@alphalab.com

Nick Nigro
Product Manager, PFAS
608-692-7645
Nick.Nigro@pacelabs.com

Stephen Somerville
Technical Director, PFAS
804-516-5887
Stephen.Somerville@pacelabs.com

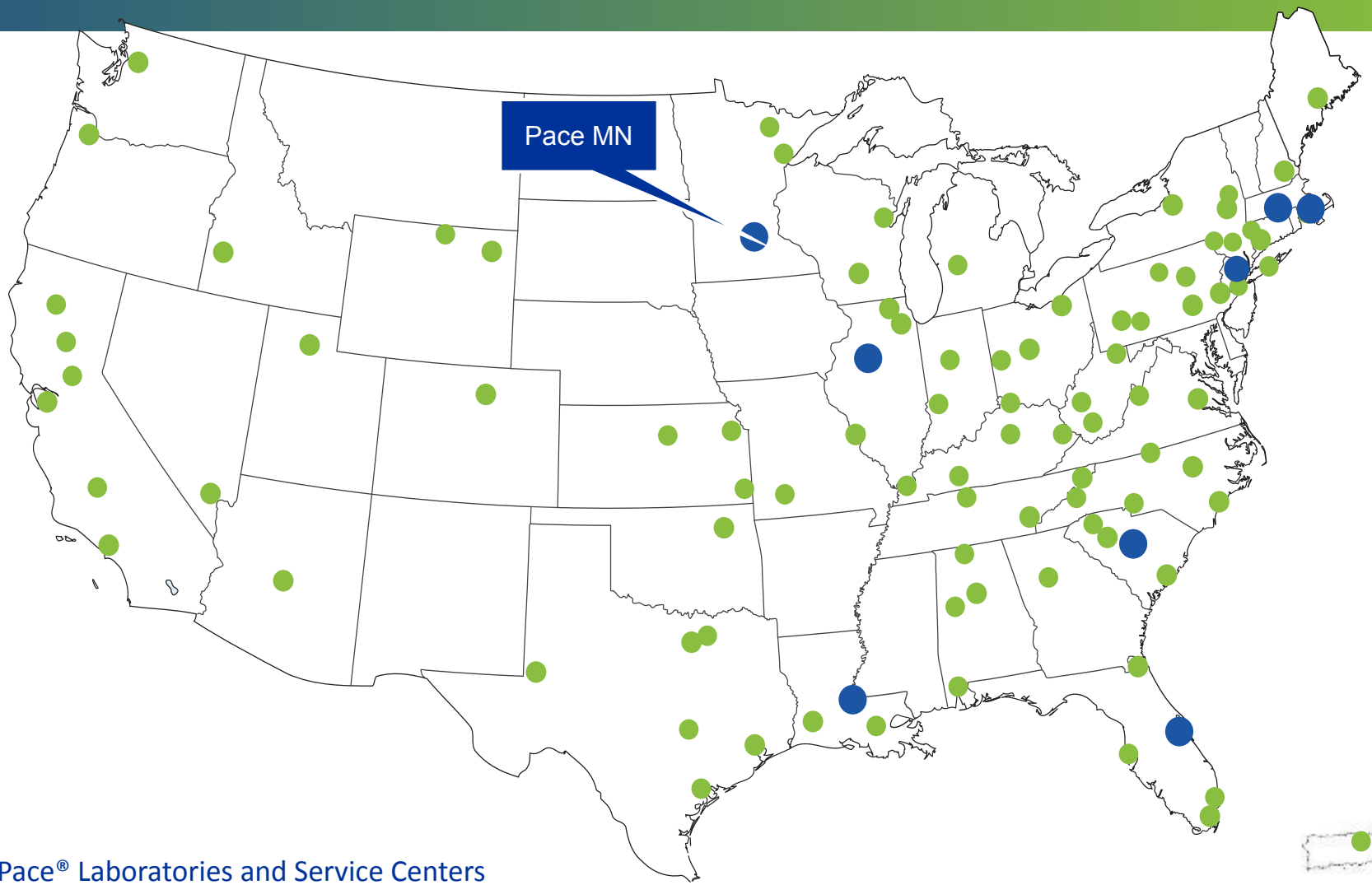
Mike McFadden
Senior Account Manager/
Federal Program Manager
919-868-5215
Mike.McFadden@pacelabs.com

Pace® PFAS LABS

3700+
Employees

~ 120
Locations

500+
Certifications



AGENDA

- “PFAS” Definition
- Method Overview
- Solids in My Sample, Oh My!
- “Final” Methods?
- Q&A

HOPEFUL TAKE-AWAYS

- ✔ **ASTM D8421/ 8327 is a powerful tool**
- ✔ **Turbid/ High TSS GW samples is an important consideration**

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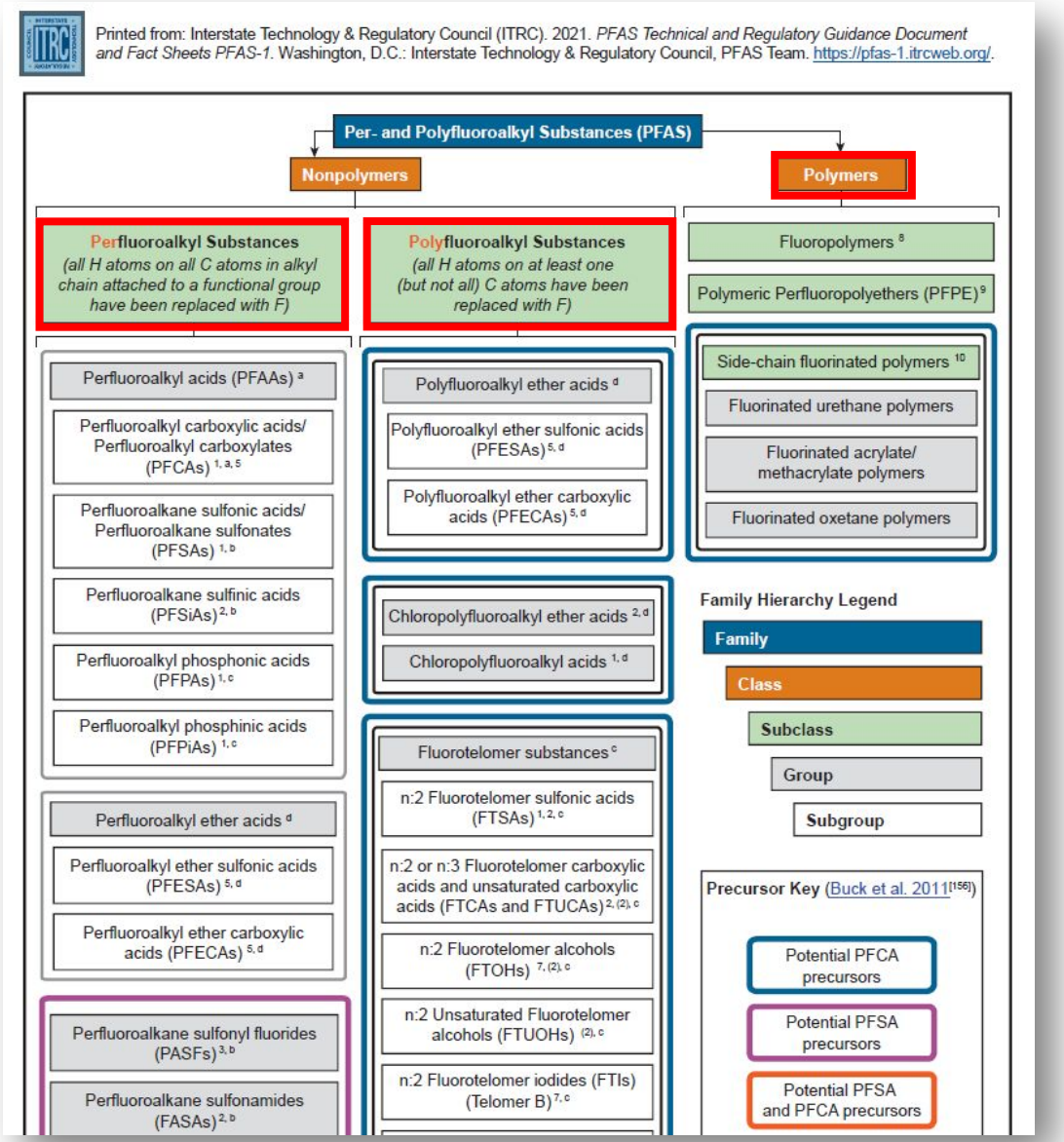
ITRC PFAS Family Tree



- Perfluoroalkyl are *mostly* "terminal" PFAS compounds (most widely studied and regulated)
- Polyfluoroalkyl are entirely "precursors."
- FUN FACT: approximately **89%** of all 4,729 PFAS compounds (in 2018 OECD database) are precursors.
- What about polymers?
  - PTFE (Teflon®)
  - SCFP – e.g., fluorinated acrylate-, methacrylate- and urethane-based polymers (e.g., Scotchgard™) – PRECURSORS
- ITRC family tree is a great resource! See Section 2.2.2 from PFAS Technical and Regulatory Guidance Document.

PFAS Definition – Overview

SOURCE	DEFINITION	HOW MANY?
Buck et al. (2011)	A subset of fluorinated substances is the highly fluorinated aliphatic substances that contain 1 or more C atoms on which all the H substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety CnF2n+1–. These compounds are hereafter referred to as ‘‘perfluoroalkyl and polyfluoroalkyl substances’’ and denoted by the acronym PFASs.	268 (excludes fluoropolymers)
Buck et al. (2021)	Bottom-up evaluation, using 2011 definition (241 commercially relevant) and adding 15 compounds that did not meet or were excluded from the 2011 definition (but commercially relevant): HFEs, HFOs, refrigerants, or containing an aromatic ring.	256 (commercially relevant)
OECD 2018	Database of compounds that contain a −CnF2n− (n ≥ 3) or −CnF2nOCmF2m− (n and m ≥ 1) moiety.	4,729
OECD 2021 and ECHA 2023 (proposed)	New Definition: PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) is a PFAS.	>7 million (PubChem, based on OECD definition)
EPA CompTox	51 “PFAS-related” lists in CompTox database, all with specific definitions and varying levels of curation.	Up to 14,735
EPA	EPA OPPT Working Definition: a structure that contains the unit R-CF2-CF(R')(R''), where R, R', and R'' do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included). This definition identifies chemicals with at least two adjacent carbon atoms, where one is fully fluorinated and the other is at least partially fluorinated. **Most recently (2023), EPA appears to have eliminated its definition, citing that it will look at the definition on a case-by-case basis, depending on the context and regulatory program that is being considered.**	Program-dependent (2023)

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TEST METHODS

Non-potable water & Landfill Leachate

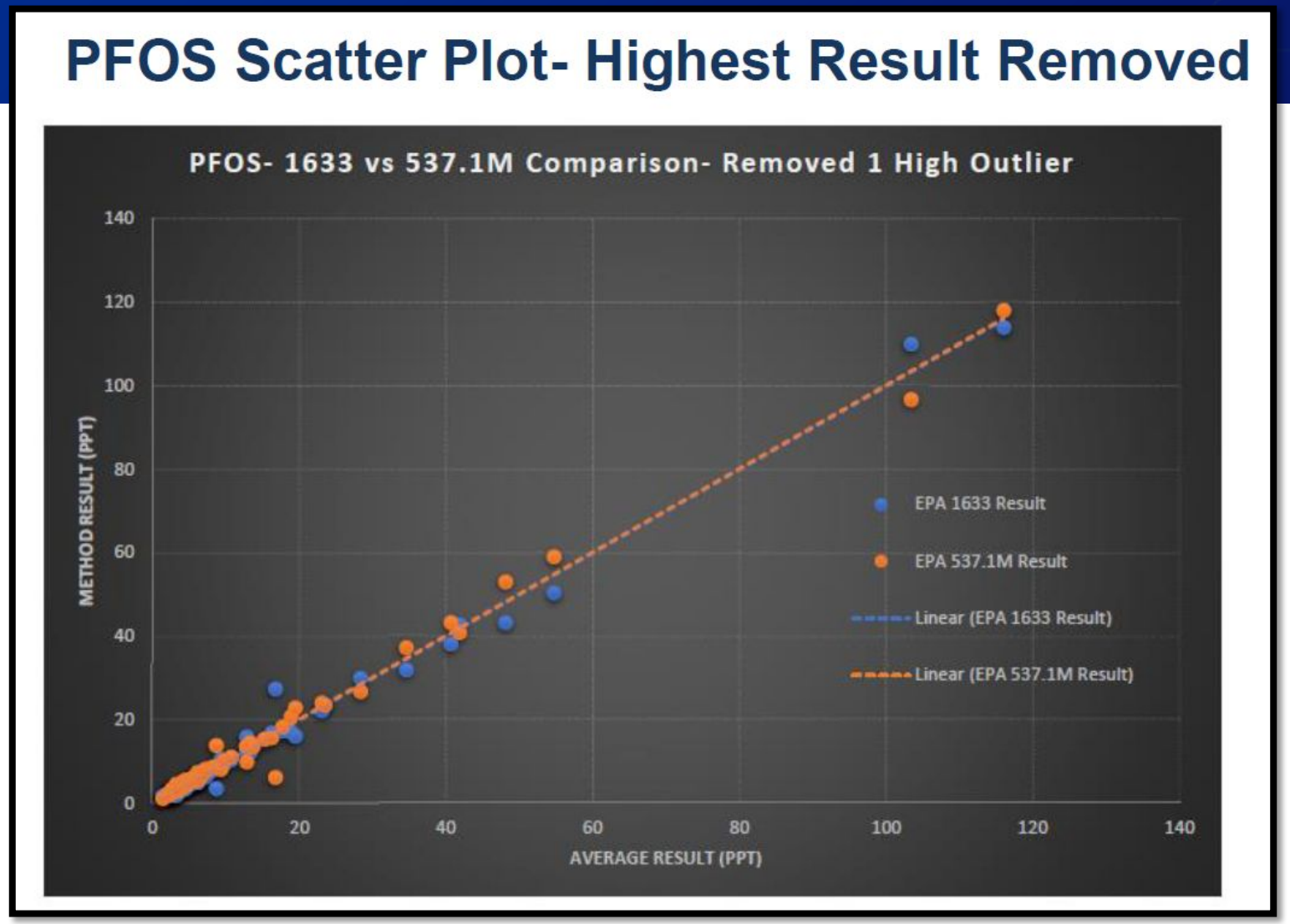
Soil, Sediment, Biosolids, Tissue

METHOD	537M	1633
MATRIX	Non-DW	Non-DW
COMPOUNDS	Lab-dependent (>40)	40 +
HOLDING TIMES, DAYS	28/ 28	28/ 28 AQ* 90/ 28 SOLIDS
EXTRACTION	SPE	SPE
QUANTIFICATION	Isotope Dilution	Isotope Dilution
NOTES	Rapidly on decline, but still accepted depending on regulatory venue and project DQOs	Became “Final” in January 2024

Did You Know?

- 1633 is a “performance-based” method?
- No material concerns with comparability

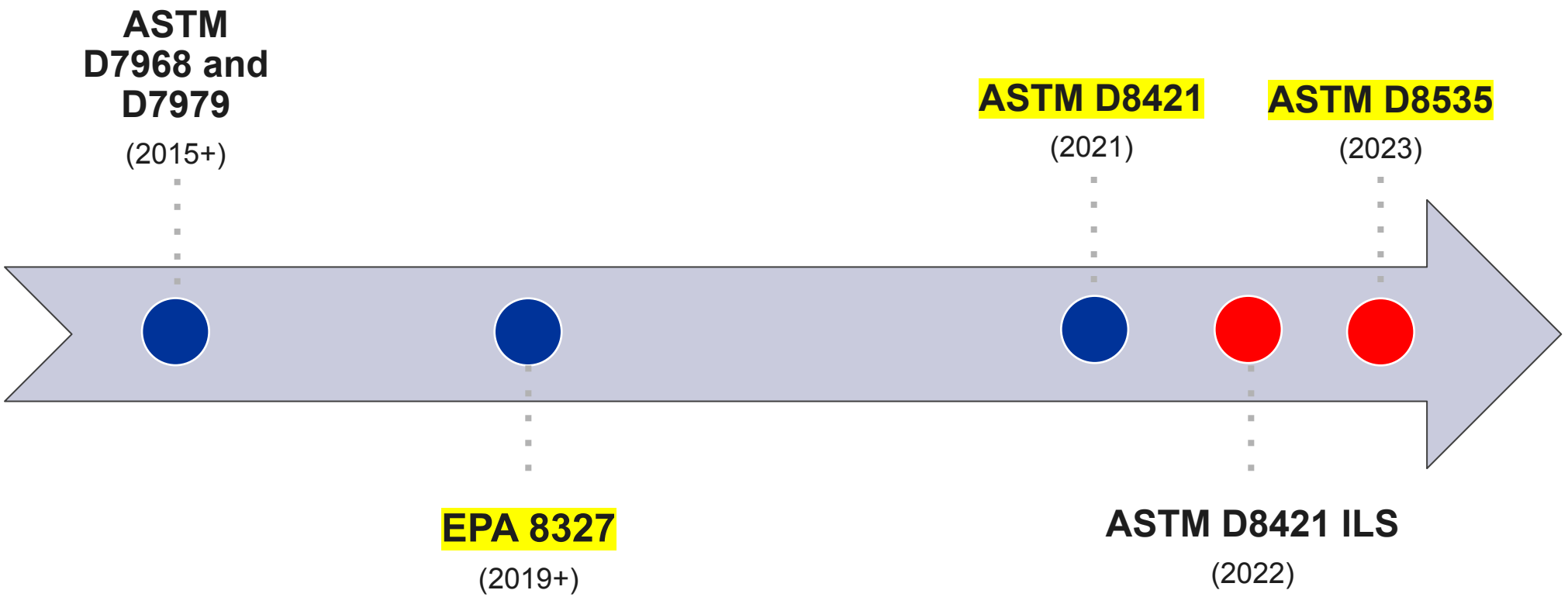
537M vs. 1633 Comparison



EPA 1633 Development Timeline

- August 2021: First Draft Published
  - October 2021: MLV process begins (Pace Baton Rouge)
- June 2022: Second Draft Published
- December 2022: Third Draft Published
  - "Final" control limits for WW matrix (only)
- July 2023: Fourth Draft Published
  - "Final" control limits for all AQ (WW, +GW, +SW)
- January 2024: "*Final*" Method, with data for all 8 applicable matrices
  - WW (3rd Draft); GW/SW (4th Draft); leachate, soil, sediment, biosolid, tissue (Final Method)

8327 and D8421/D8535 Timeline



Method Comparison Summary

Method	Matrix	Compounds	Calibration/ Quantification	Notes
ASTM D7968	Soil/ Solids	31	External Standard	New method (D8535) published to replace D7968
ASTM D7979	NPW	31	External Standard	New method (D8421) published to replace D7979
EPA 8327	**NPW (Solids*)**	**24**	**External Standard**	**Developed using D7979** • **Same fundamental procedure as D7979 and D8421**
ASTM D8421 ASTM D8535	**NPW Solids**	**44**	**External Standard (optional Isotope Dilution)**	**Replaces D7979/ D7968** • **Increase compounds to 44** • **Multi-lab validated (discussed in deep-dive)**

TEST METHODS

Non-potable water & Leachate

Soil, landfills & other solids

METHOD	ASTM D8421/D8535 and EPA 8327
MATRIX	Non-potable water and solids
COMPOUNDS	44 (Pace)
HOLDING TIMES, DAYS	28
EXTRACTION	Direct Injection (co-solvation, filter)
QUANTIFICATION	Isotope Dilution* (Pace)
NOTES	ASTM D8421 completed an ILS; while published reporting limits are a little higher, lab working on reducing reporting limits

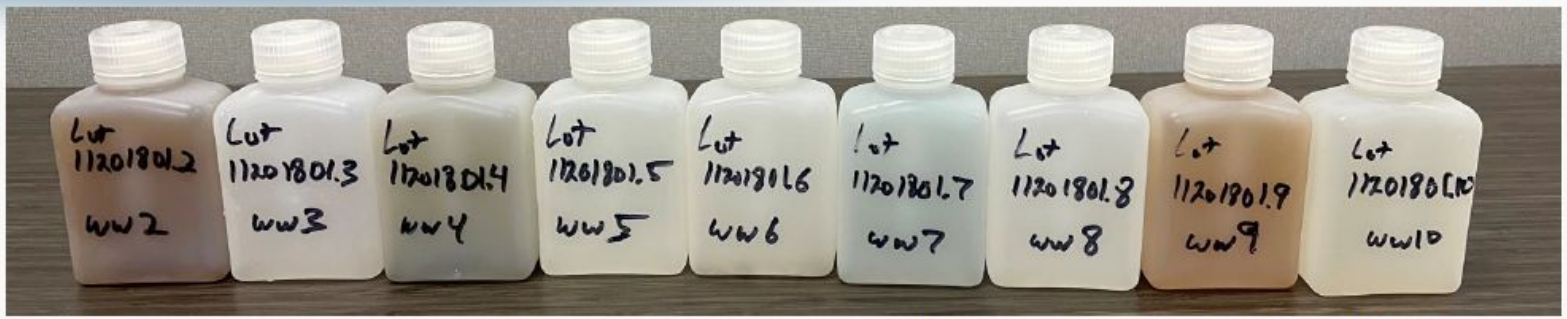
Advantages

- 5 mL sample size (AQ) *triplicate
- Faster TAT
- Lower cost
- **Will likely be added to 40CFR Part 136**

ASTM D8421 Inter-Laboratory Study (ILS)

- Voluntary program – commercial, state, and EPA labs
- Scope
  - ✔ 44 target compounds (DM1633 + 4)
  - ✔ 24 surrogate compounds
- 11 different aqueous challenge matrices (see next slide)
  - ✔ 20-800 ng/L spikes
- Resulted in 8 sets (8 labs) of data for evaluation

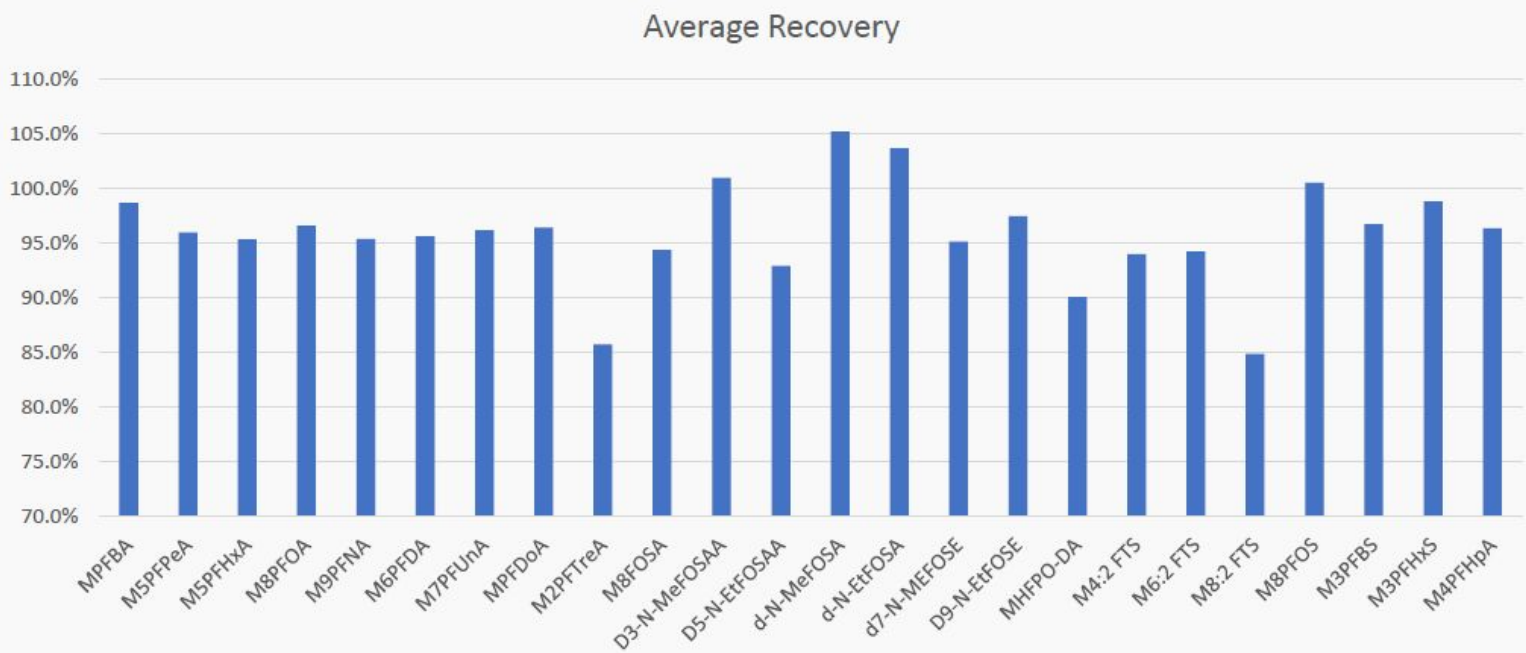
Eleven Matrices



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

Average Surrogate Recovery
All Eleven Matrices Combined Amongst Eight Labs



D8421 vs. 1633: PACE CASE STUDY

Sample ID	PFOA (1633)	PFOA (D8421)	PFOS (1633)	PFOS (D8421)
1	720	700	29000	29000
2	2.8	3.9 J	6.1	7.8 J
3	94	80	710	620
4	13	9.6	47	40
5	79	77	28	27
6	15	17	220	200
7	6.5	6 J	3.5	3.3 J
8	16	15	190	190
9	3.8	4 J	12	11 J
10	55	49	790	770
	PFOA		PFOS	
R-Squared	0.999656228		0.999990751	

- TEMP GW Wells
- Multiple depths
- Multiple locations throughout site

WHEN CAN I USE THESE TARGETED METHODS?

Drinking Water Compliance?

Data Submitted to State? If so, state guidance or certification requirement?

Permit Compliance?

Rapid TAT CRITICAL?

Screening Level DQO? Collaborative sampling strategy??

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SOLIDS in MY SAMPLE – OH MY!

Why Solids Content Matters…….

- Representative?
- Lab/ Method Challenges
- Bias/ PFAS Profile

SOLIDS in MY SAMPLE – OH MY!

Lab/ Method Challenges

- Clogging SPE
- 1633 Requirements
- Not all samples with high solids content centrifuge sufficiently

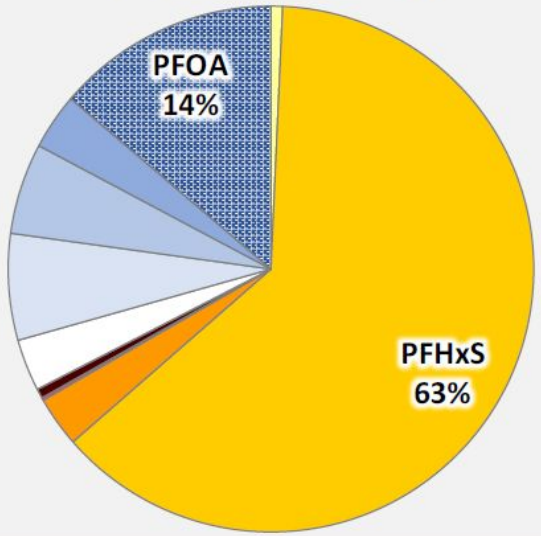
SOLIDS in MY SAMPLE – OH MY!

High Biased PFAS Results – Turbidity (AFFF Source)

TRC

Turbidity 1000 NTU

Total – 1,161 ng/L

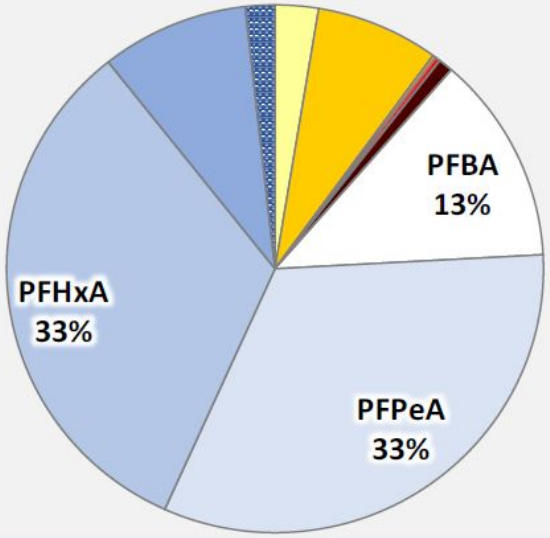


- PFBS - 8.3
- PFHxS - 730
- PFHpS - 36
- PFOS - 1.8
- 6:2 FtS - 7
- 8:2 FtS - N/A
- PFBA - 37
- PFPeA - 76
- PFHxA - 65
- PFHpA - 40
- PFOA - 160
- PFNA - N/A
- PFDA - N/A
- PFUnDA - N/A
- PFDoDA - N/A
- PFTrDA - N/A
- PFTeDA - N/A
- NMeFOSAA - N/A
- NEtFOSAA - N/A

Total PFAS	1,161 ppt
PFHxS	730 ppt
PFOA	**160 ppt**

Turbidity 25 NTU

Total – 338 ng/L



- PFBS - 8.8
- PFHxS - 25
- PFHpS - 0.72
- PFOS - 0.99
- 6:2 FtS - 3
- 8:2 FtS - N/A
- PFBA - 43
- PFPeA - 110
- PFHxA - 110
- PFHpA - 30
- PFOA - 6
- PFNA - N/A
- PFDA - N/A
- PFUnDA - N/A
- PFDoDA - N/A
- PFTrDA - N/A
- PFTeDA - N/A
- NMeFOSAA - N/A
- NEtFOSAA - N/A

Total PFAS	338 ppt
PFHxS	25 ppt
PFOA	6 ppt

PFOA MCL
10 ppt

PFAS Concentrations and PFAS Signatures Affected by Turbidity

Used with permission: Liz Denly, TRC

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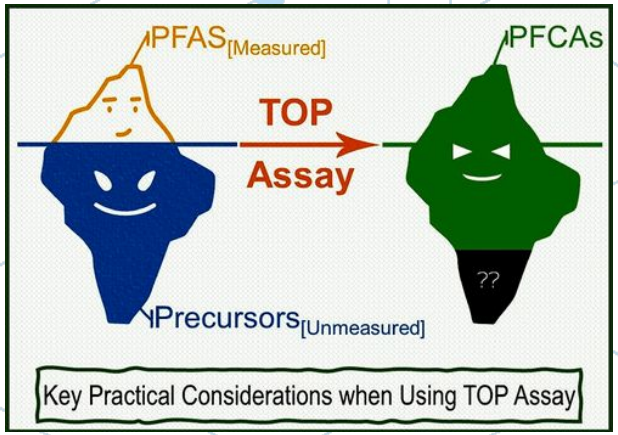
Now That Methods Are ***Final ?***

DRINKING WATER

- **Draft Method 534** □ 9 compounds
  (6 MCL + 3) using co-solvation followed by direct injection
- **Ultra-Short Chain (USC)** □ 6 compounds
  (e.g., <C4 e.g., TFA, PFPrA) using direct-injection
- **EOF/CIC method** □ Lower RL than EPA 1621 AOF

CLEAN WATER ACT

- Update to **EPA 1633**?
- 40 CFR 136 Method Update Rule (early 2025?) adding:
  - ✔ *EPA 1633*
  - ✔ *EPA 1621*
  - ✔ *ASTM D8421*



SW-846 (RCRA/CERCLA)

- Publish an SW-846 version of EPA 1633 (timeframe TBD) □ 8328?

HOPEFUL TAKE-AWAYS

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- ✔ **Turbid/ High TSS GW samples is an important consideration**

Pace® *Favorite* PFAS Resources

Compound Databases

- **EPA CompTox**: https://comptox.epa.gov/dashboard/chemical-lists (in "List Name" search for "PFAS," → 51 lists currently)

Site Maps and Data

- **ECHO PFAS Analytics**: https://echo.epa.gov/trends/pfas-tools
- **EWG**: https://www.ewg.org/interactive-maps/pfas_contamination/

Cleanup Levels

- **ITRC PFAS Water and Soil Values Table Excel File**: LINK (updated frequently) – also includes many other PFAS Fact Sheets
- **EPA RSLs:** https://www.epa.gov/risk/regional-screening-levels-rsls-whats-new

Regulatory/ Legal

- **Safer States**: https://www.saferstates.com/bill-tracker

Toxicity

- **ECOTOX**: https://cfpub.epa.gov/ecotox/explore.cfm?sub=Chemicals

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THANK YOU

Additional resources:

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