PEOPLE ADVANCING SCIENCE

IRWA
ILLINOIS RURAL WATER ASSOCIATION

PFAS – Technical and Regulatory Update for Wastewater Professionals

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Pace®

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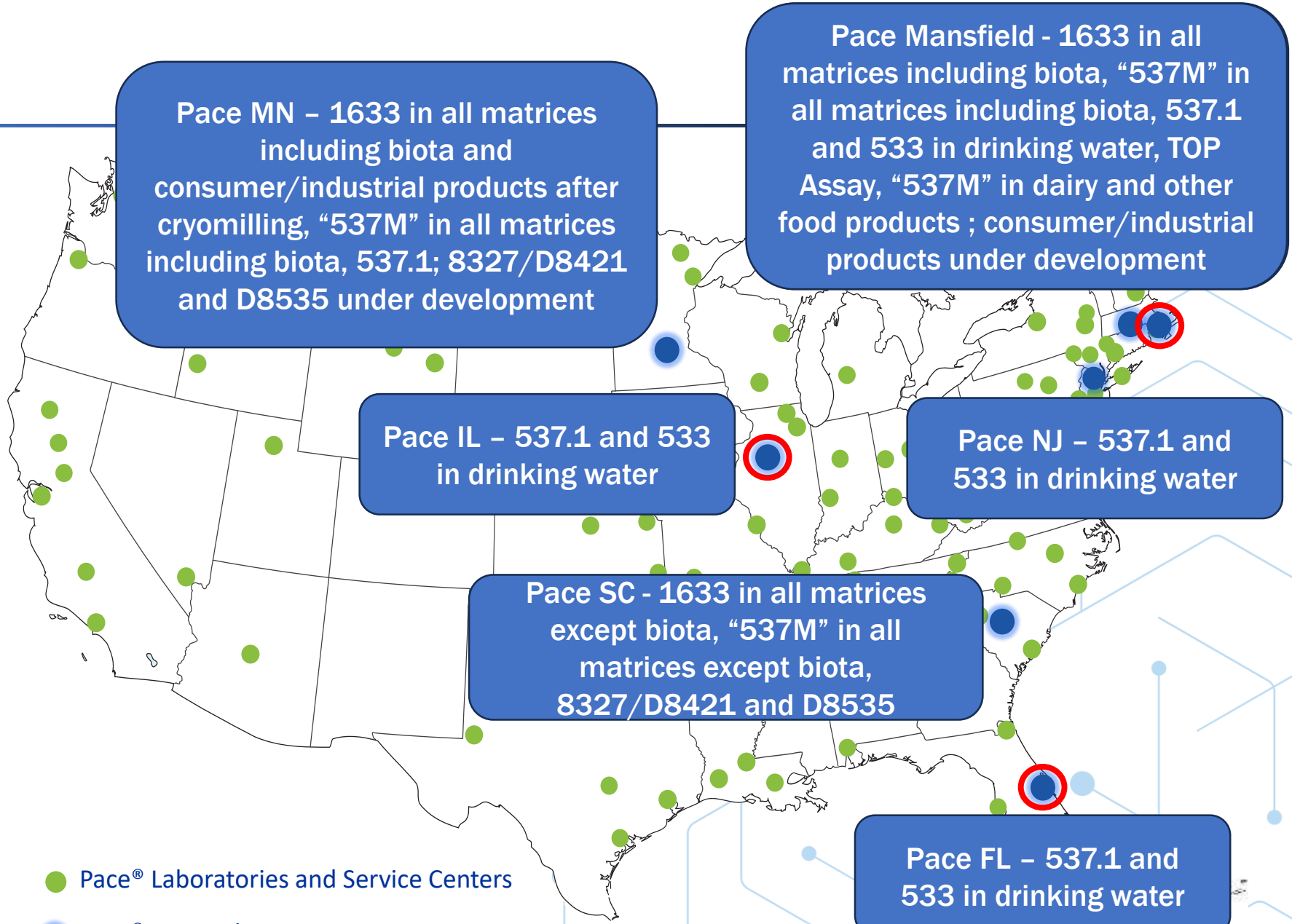


THE PFAS PUZZLE

- Lack of federal regulation
- Non-uniformity of state regulations or test methods
- Lack of environmental test methods
- Variety of compound lists
- Thousands of PFAS compounds
- Low DLs vs. contaminated matrices
- Ultra restrictive field sampling guidance

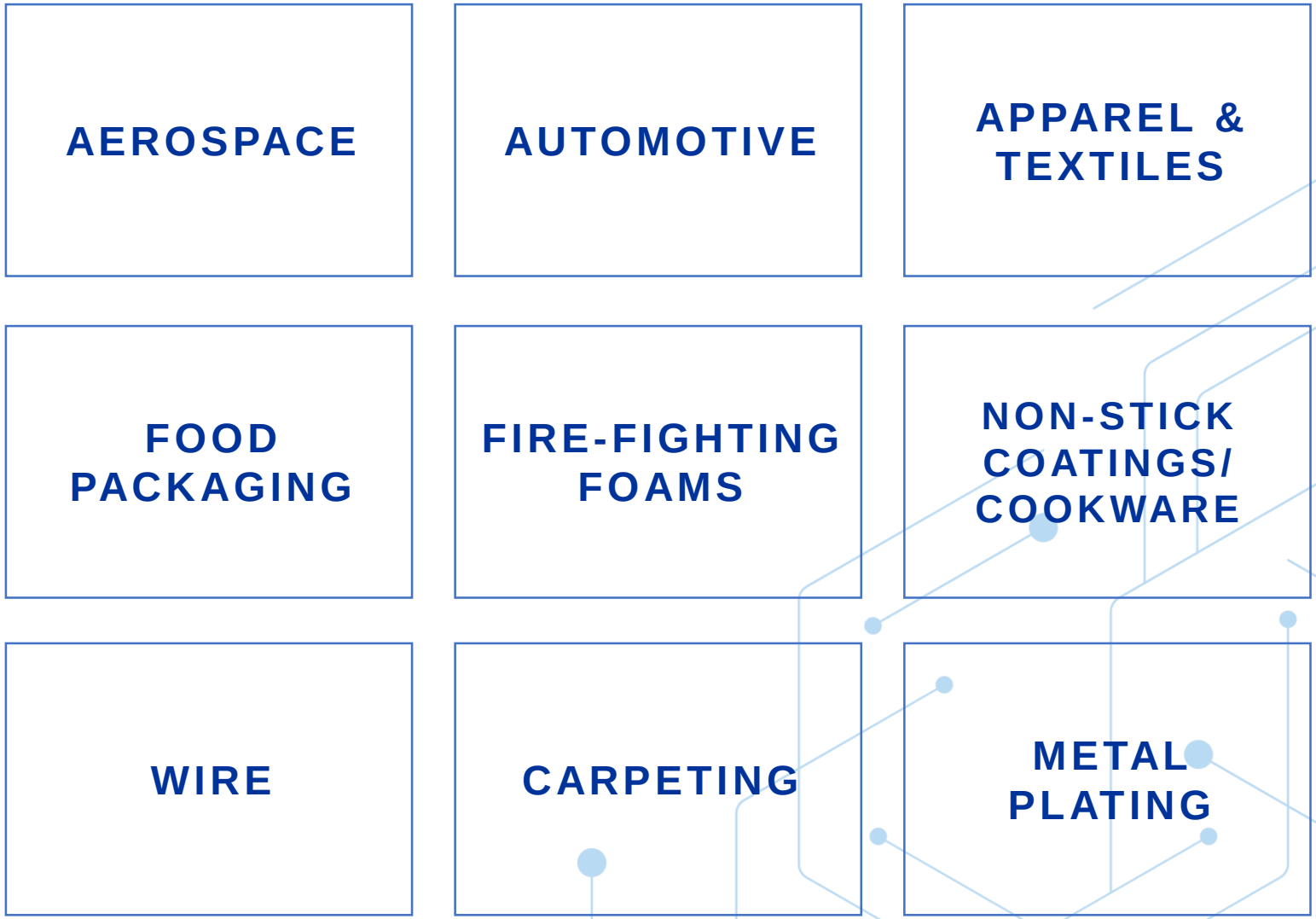
PFAS OVERVIEW

- **PFAS CHEMISTRY**
- **SOURCES & RECEIVERS**
- **TEST METHODS**
- **REGULATORY UPDATE**
- **FIELD SAMPLING & RESOURCES**
- **TAKEAWAYS**

WHAT ARE PFAS?

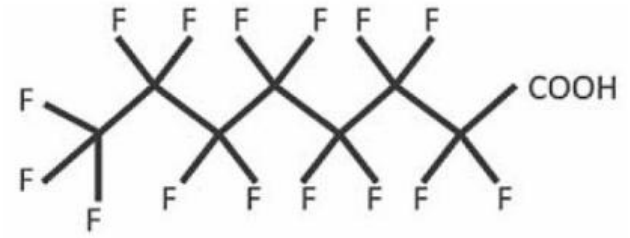
A large, diverse group of manufactured compounds that have been used for decades for many industrial applications and consumer products

- Oil/Water/Grease/Heat resistant properties
- Mist and fume suppressant
- Surfactant
- Entirely man-made
- Bioaccumulative
- Hydrophilic
- Have documented health impacts



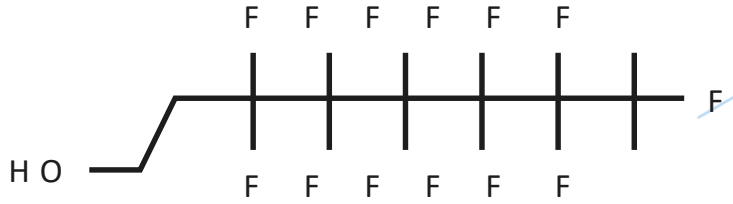
Per- and Polyfluoroalkyl Substances

CLASSES OF PFAS



PERFLUOROALKYL

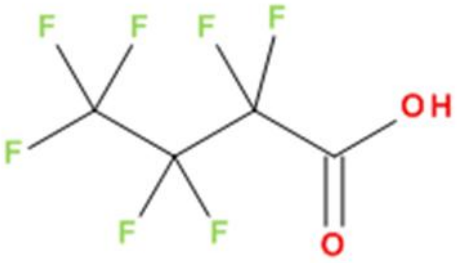
- All hydrogens on the carbons are replaced by fluorine
- Strongest chemical bond in nature
- Difficult to treat
- PFCAs and PFSAs



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

Replacement or Precursor PFAS



PFBA

PFBS

6:2 Fluorotelomer acrylate

- Industry claims they are safer
- Some precursors are longer chain C8 compounds
- PFBA used in food packaging and film
- PFBS used in surfactants/repellents, metal plating, pesticides, and flame retardants

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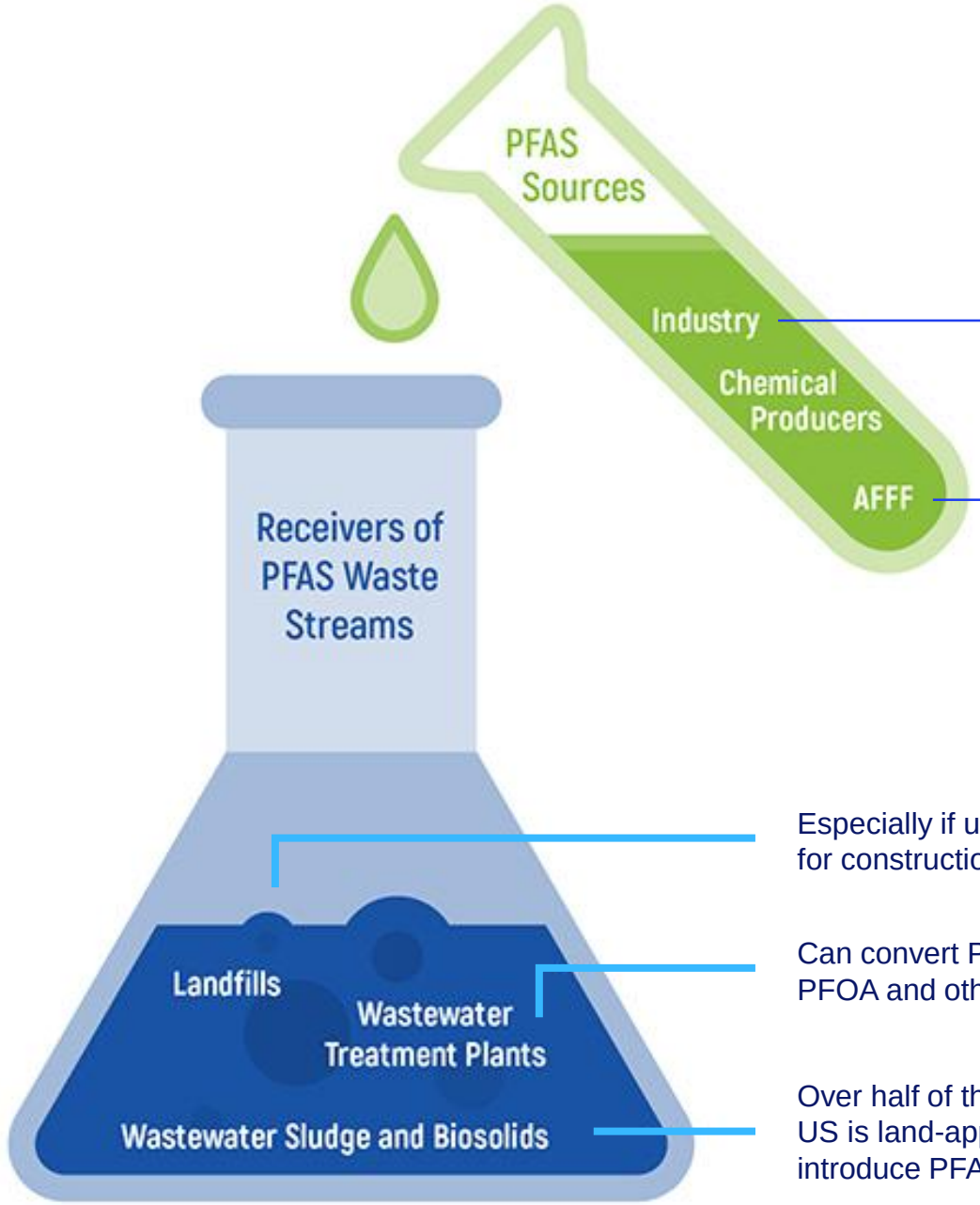
THE PFAS LIFECYCLE

- Industry is the most common source of PFAS contamination - both the manufacturers of PFAS chemicals and those that use them in the products they make
- PFAS do not degrade naturally, chemicals can remain in the surrounding soil for decades
- Industrial discharge and consumer/industrial waste that contain PFAS are received by solid waste facilities and wastewater treatment plants
- All the above impact drinking water sources



- Textile manufacturing
- Certain paper food wrapping
- Metal plating & etching
- Wire manufacturing
- Pesticides
- Personal care products
- Non-stick cookware

Department of Defense and other users of AFFF (Aqueous film forming foam)

Especially if unlined, such as those used for construction and demolition debris

Can convert PFAS precursors into PFOA and other PFAAs

Over half of the sludge produced in the US is land-applied as biosolids and may introduce PFAS into the food chain

PFAS IN WWTP BIOSOLIDS & SLUDGE

- PFAS have been widely found in wastewater sludge and biosolids
- Some states have moved to restrict and ban land application of PFAS-containing biosolids
- More than half of the sludge produced in the United States is applied to agricultural land as biosolids

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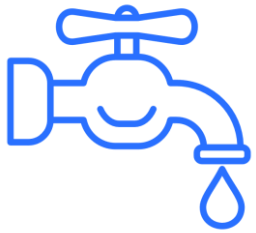
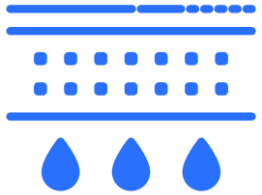
MATRICES

CHOOSING THE RIGHT TEST METHODS

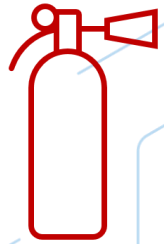


Drinking water



Groundwater, surface water, & leachate

Wastewater, sludge & biosolids



AFFF – concentrate & diluted

Soil, sediment, solid waste & other solids

Biota – plant & animal tissue

Consumer & Industrial Products

TEST METHODS

DRINKING WATER

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.**

TEST METHODS

NON-POTABLE WATER & LEACHATE

SOIL & OTHER SOLIDS

BIOTA – PLANT & ANIMAL TISSUE

METHOD	PFAS by Isotope Dilution/"537M"/ DOD QSM B-15	EPA 1633/ DOD QSM B-24
MATRICES	Non-potable water, leachate, solids, biota	Non-potable water, leachate, solids, biota
COMPOUNDS	40	40
HOLDING TIMES, DAYS	28/28	Water: 28/28 or 90/90 (frozen on receipt) Solid: 90/28 or 90/90 (frozen on receipt)
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	Now a final method

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

- More sample volume required for water – 2 x 500 r containers and 1 x 125 mL container
- Additional QA/QC (Bile salt resolution, new branch isomers, duplicate LCS)
- More aggressive solid sample extraction than "modified" method SOPs - three-fold solvent extraction (Methanolic NH4OH) – shake/centrifuge/decant; dGCB cleanup
- More costly than "modified" method/lab-specific SOPs
- Prep restrictions:
  - Water TSS >100 mg/L requires extra measures
  - Extract dilutions >10X require re-extraction

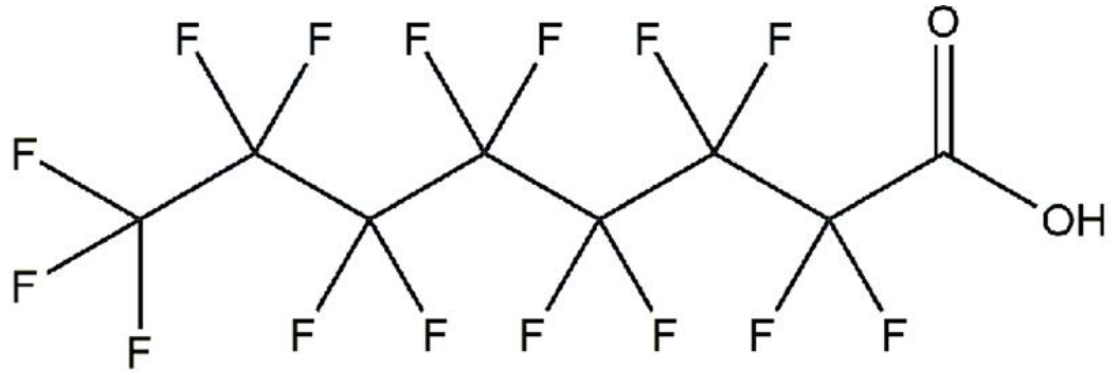
EPA 1633 – Lower Detection Limits

	Water, ng/L		Solids, µg/kg	
Acronym	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
PFTrDA	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

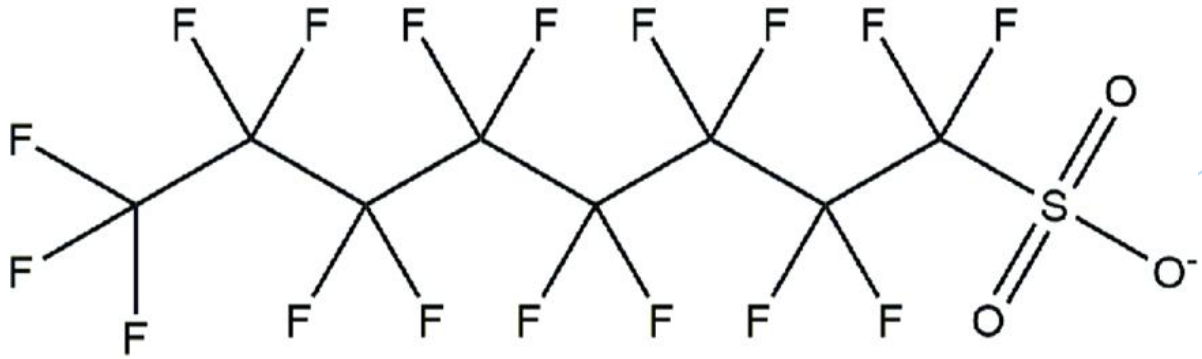
	Water, ng/L		Solids, µg/kg	
Acronym	LOQ	DL	LOQ	DL
NEtFOSA	1	0.14	0.2	0.06
NMeFOSA	1	0.15	0.2	0.03
NEtFOSE	10	2.36	2.0	0.44
NMeFOSE	10	1.52	2.0	0.40
NEtFOSAA	1	0.28	0.2	0.03
NMeFOSAA	1	0.19	0.2	0.05
4:2 FTS	4	0.63	0.8	0.15
6:2 FTS	4	0.95	0.8	0.14
8:2 FTS	4	0.54	0.8	0.13
PFMPA	2	0.32	0.4	0.04
PFMBA	2	0.30	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
9Cl-PF3ONS	4	0.73	0.8	0.08
11Cl-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×

Organic Fluorine…TOF, AOF, and EOF



Perfluorooctanoic acid (PFOA)



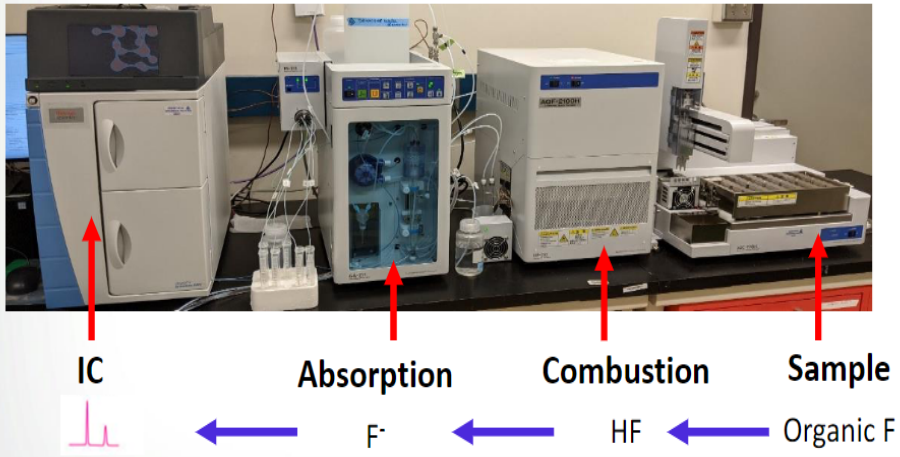
Perfluorooctane sulfonate (PFOS)

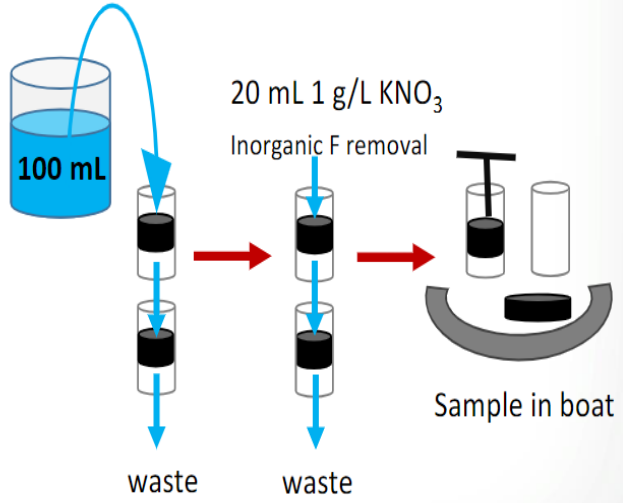
Adsorbable Organic Fluorine (AOF) EPA 1621

EPA Approach – AOF/CIC

How:

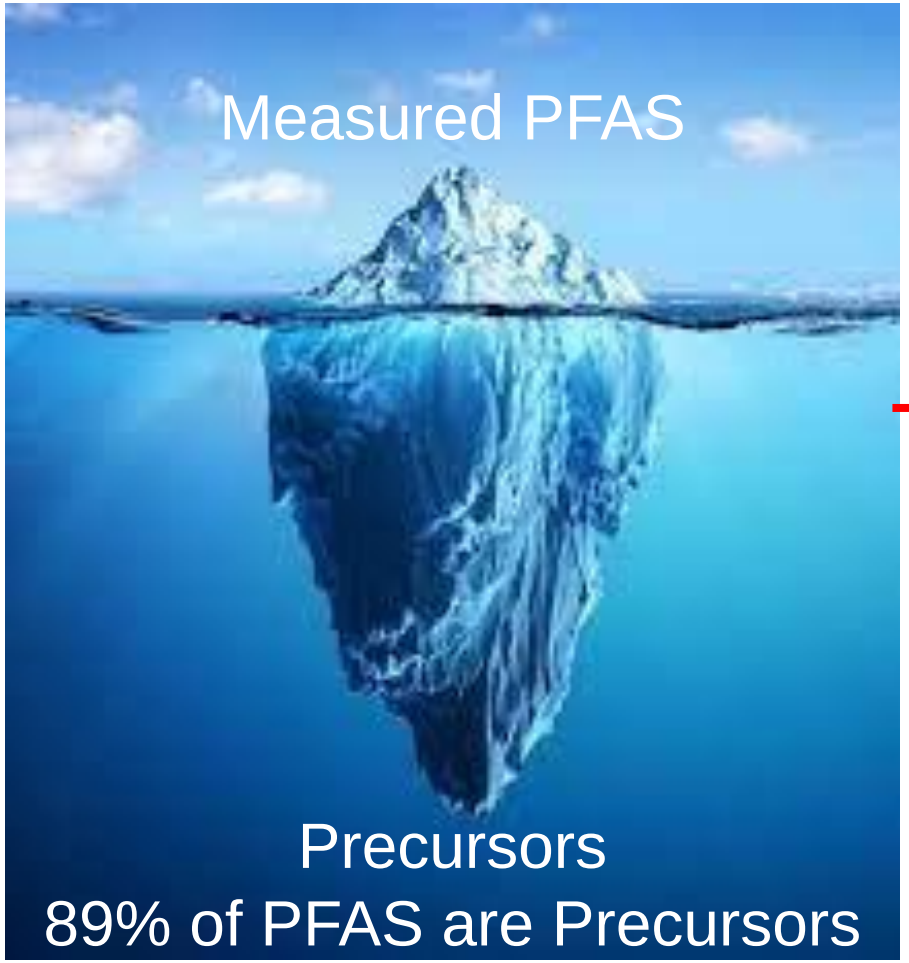
- Screening method adsorbs contaminants onto granular activated carbon, removal of inorganic fluoride with nitrate solution, followed by combustion of the carbon
- Organofluorine compounds are converted to fluoride in the combustion process and measured by ion chromatography





Reporting Limit - 2µg/L

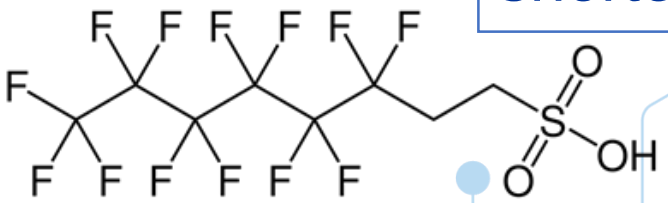
Total Oxidizable Precursor (TOP) Assay



Heat/Oxidation

Under TOP Assay oxidation, conversion occurs of known and unknown precursors to terminal PFAS (PFCA).

Degradation of any precursor would be to an equal or shorter chain length.

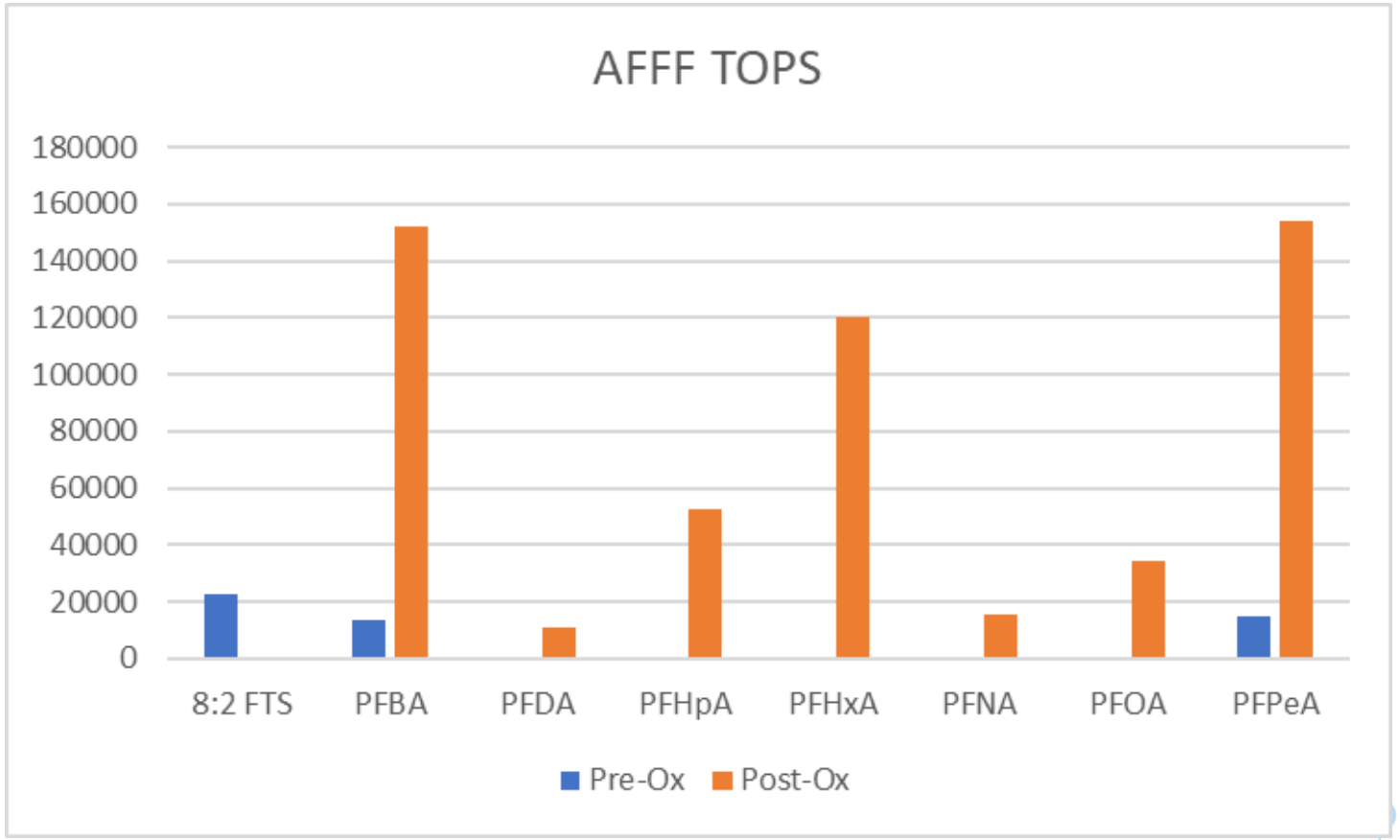


6:2 FTS

PFBA, PFPeA, PFHxA, PFHpA

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

TOP Assay - Pre-Oxidation and Post-Oxidation Comparison



	Pre-Ox	Post-Ox
8:2 FTS	22,300	ND
PFBA	13,700	152,000
PFDA	ND	10,900
PFHpA	ND	52,600
PFHxA	ND	120,000
PFNA	ND	15,500
PFOA	ND	34,500
PFPeA	14,900	154,000
Total	50,900	539,500

All units of measure are expressed in ppt/ng/L

TEST METHODS

WATER

SOIL & OTHER SOLIDS

Image: Pittsboro, NC GAC system

EPA 8327/ASTM D8421 & D8535

- Detection Limits of 10 ng/L for aqueous, 0.1 ug/kg for soil
- Lower cost
- Faster lab turnaround time (TAT)
- 44 compound list
- 3 x 5 mL water, 50 g soil sample volume
- Under review by CWA for inclusion in 40CFR Part 136 and RCRA for inclusion in SW-846

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REGULATORY UPDATE

Federal

- PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024 https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024
- Whole-of-agency approach
- Set timelines for specific actions and establishing new policies for SDWA, CWA, CERCLA, RCRA programs
- EPA Goals
  - Research – invest in research, development, innovation
  - Restrict – prevent PFAS from entering air, land, water
  - Remediate – clean up contamination, human and ecological health

REGULATORY UPDATE

Federal

- RCRA – January 2024 - EPA proposed rule to designate 9 PFAS as hazardous constituents
- CERCLA – April 2024 - EPA finalized rule to designate PFOA and PFOS as hazardous substances with carve-outs for farmers, municipal landfills, water utilities, municipal airports, and local fire departments
- Toxics Release Inventory (TRI) - Tracks industries' use and discharge of 196 PFAS
- UCMR 5 – January 2023 - December 2025 – sample >10,000 Public Water Systems for 29 PFAS compounds (EPA 537.1 and EPA 533)
- SDWA – April 2024 – EPA finalized rule to set enforceable Maximum Contaminant Levels (MCLs) for PFOA, PFOS, and 4 PFAS replacement chemicals "GenX" HFPO-DA, PFBS, PFNA, PFHxS in the nation's Public Water Systems

Sources: https://www.regulations.gov/document/EPA-HQ-OLEM-2022-0922-0001; https://www.epa.gov/eg/current-effluent-guidelines-program-plan; https://www.epa.gov/toxics-release-inventory-tri-program; https://www.epa.gov/newsreleases/epa-issues-guidance-states-reduce-harmful-pfas-pollution

REGULATORY UPDATE

Federal

- CWA NPDES – December 2022 - EPA issues guidance that signals their intent to start including PFAS in discharge permits of these industries:
  - Organic chemicals, plastics & synthetic fibers (OCPSF)
  - Metal finishing and electroplating
  - Electric and electronic components
  - Landfills
  - Pulp, paper & paperboard
  - Leather tanning & finishing
  - Plastics molding & forming
  - Textile mills
  - Paint formulating
  - Airports
  - Others are under consideration, such as Centralized Waste Treatment (CWT) facilities that receive wastes from these industries

REGULATORY UPDATE

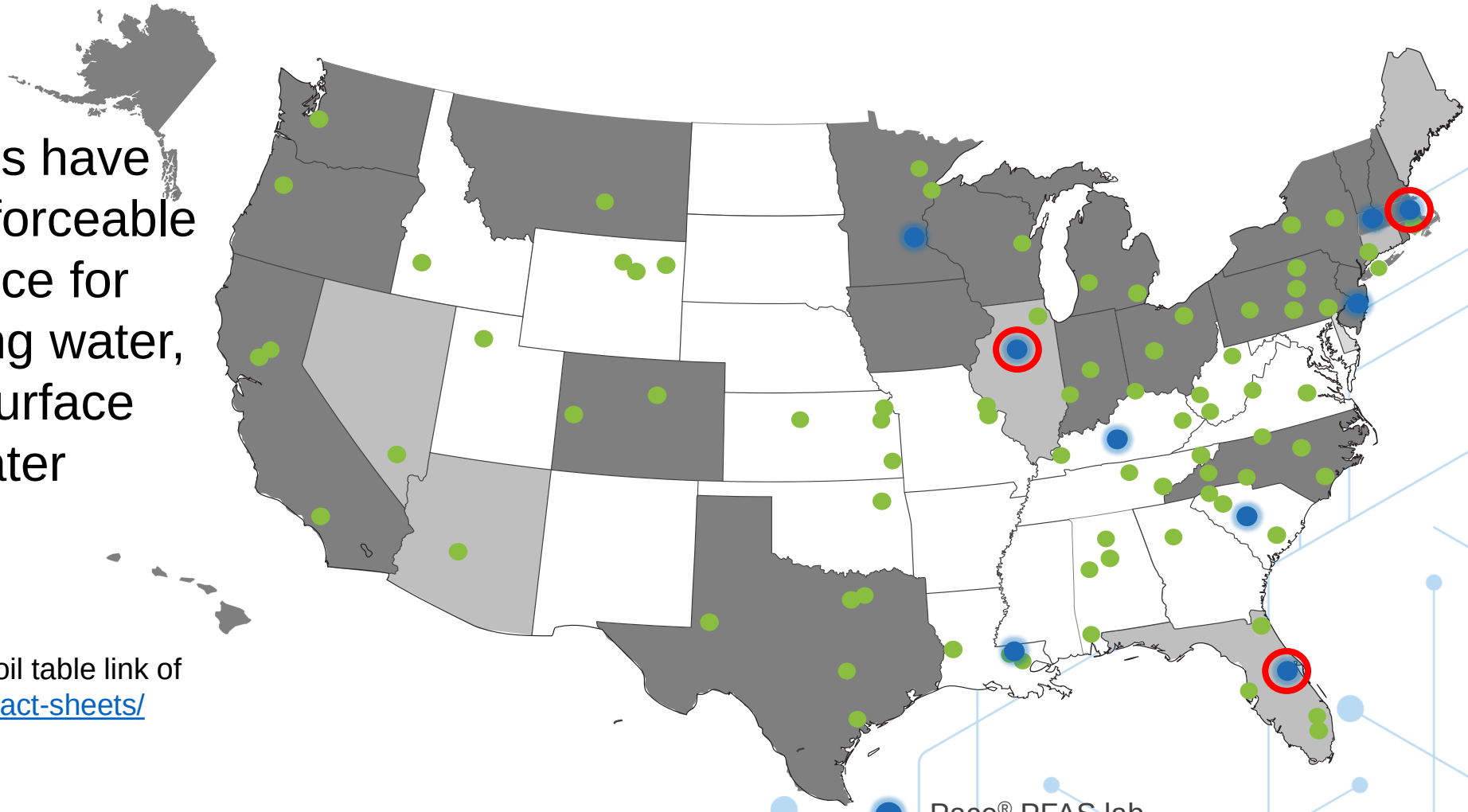
Federal

- CWA NPDES – March 26, 2024
  - US EPA issues request for public comment for proposed Information Collection Rule (ICR).
  - The proposed ICR will survey the largest 400 Publicly Owned Treatment Works (POTWs AKA Wastewater Treatment Plants) to gather data about discharges that may contain PFAS.
  - EPA plans to use that information to require 200-300 POTWS to sample their influent, effluent, and biosolids, and up to 10 industrial wastewater dischargers to those systems for PFAS. 1 sample will also be collected from a wastewater stream identified as domestic, meaning it's municipal human wastewater that includes no industrial discharge.
  - Sampling is expected to occur 2024 to 2025.
  - Delayed implementation due to change in administration?

REGULATORY UPDATE

States

So far, 30 states have established enforceable limits or guidance for PFAS in drinking water, groundwater, surface water, wastewater and/or soil

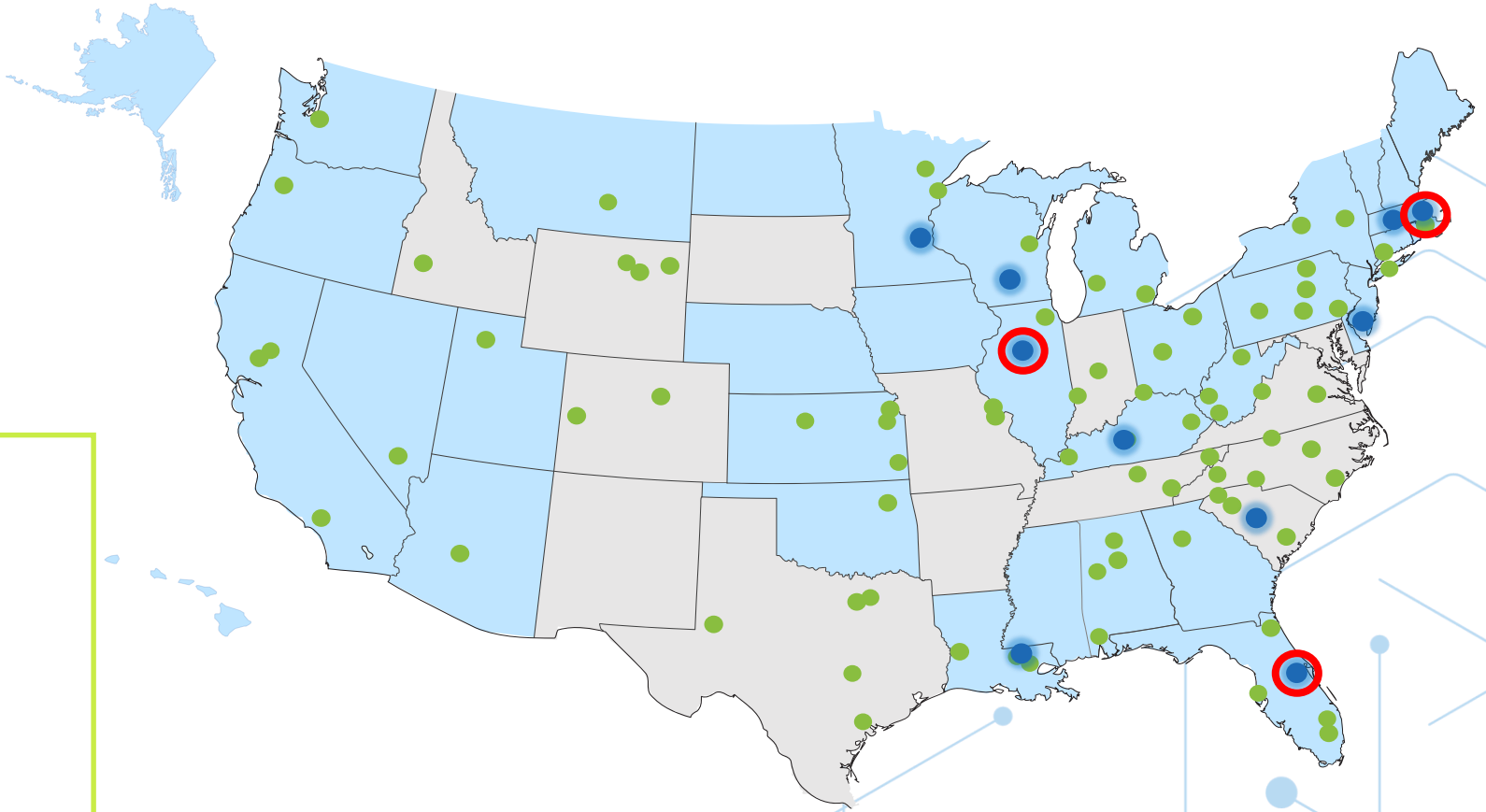


Source: See Water and Soil table link of https://pfas-1.itrcweb.org/fact-sheets/

PACE® PFAS CERTIFICATIONS

PACE PFAS CERTIFICATIONS

- Every state that offers PFAS
- TNI NELAC
- DOD ELAP
- DOE
- ISO
- US EPA – UCMR 5



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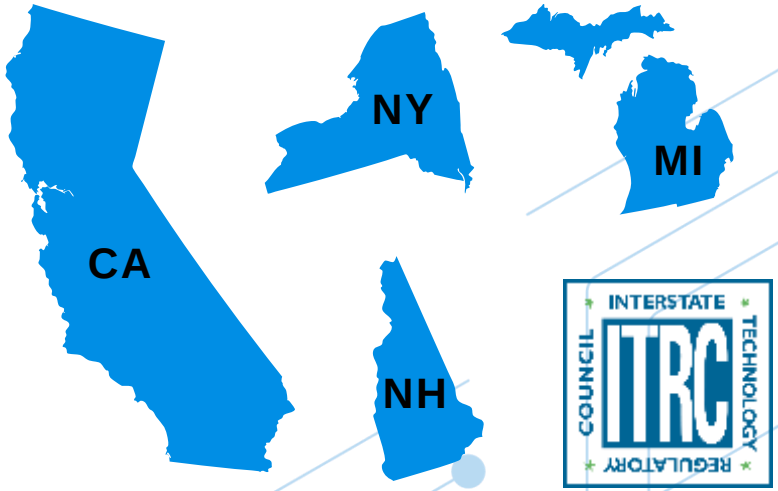
FIELD SAMPLING & RESOURCES

- Traditional sampling materials contain PFAS: clothing, sunscreen, bug repellant, footwear, sampling equipment, waterproof notebooks
- PFAS reporting limits – single digit ppt levels
- More potential for field sampling activity to cause sample contamination
- Take measures to limit sample to PFAS exposure in the field
- Field quality control samples have heightened importance
- Michigan EGLE field sampling - https://www.michigan.gov/pfasresponse/investigations/sampling-guidance



Some states and organizations have published stringent SOPs for drinking water, non-potable water, and soil

links available at the Pace PFAS webpage

FIELD SAMPLING & RESOURCES

Clothing and Hygiene

- No clothing or boots containing Gore-Tex™
- Safety boots must be made from polyurethane or PVC
- No materials containing Tyvek®
- Do not use fabric softener on clothing to be worn in field
- Do not use cosmetics, moisturizers, hand cream, or other related products the day of sampling
- Do not use unauthorized sunscreen or insect repellant
- Wet weather wear - made of polyurethane and PVC only
- Wash hands and put on powderless nitrile gloves
- No food or drink at the sampling site
- No use of Sharpies®

FIELD SAMPLING & RESOURCES

Field QC Samples

FIELD BLANK (FB) or FIELD REAGENT BLANK (FRB)

meant to validate that field sampling activity did not cause sample contamination

EQUIPMENT/ RINSATE BLANK (EB)

meant to validate cleanliness of sampling equipment before sampling and between sampling points

TRIP BLANK (TB)

meant to validate that samples were not cross-contaminated in route to lab

FIELD SAMPLING & INFORMATION RESOURCES

Compound Databases

- **EPA CompTox**: https://comptox.epa.gov/dashboard/chemical-lists (in “List Name” search for “PFAS” lists (47 lists currently)
- **OECD PFAS Database**: https://www.oecd.org/chemicalsafety/risk-management/global-database-of-per-and-polyfluoroalkyl-substances.xlsx

Site Maps and Data

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

Regulatory Limits and Guidance Levels

- **ITRC PFAS Water and Soil Values Table Excel File**: LINK (updated frequently) – also includes many other PFAS Fact Sheets

Regulatory/Legal

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

Toxicity

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

Sampling

- https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/#11_1

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TAKEAWAYS

- PFAS are now well down the path to become regulated in drinking water, wastewater, groundwater, soil solid waste
- Industrial dischargers contributing to PFAS POTW can significantly impact land application of biosolids
- Choosing the right PFAS method and compound lists is crucial
- EPA 1633 and 1621 are now final methods
- US EPA is moving to add PFAS to NPDES, RCRA and CERCLA programs
- US EPA finalized the National Primary Drinking Water Regulation (NPDWR) to set MCLS for 6 PFAS MCLs under the SDWA
- Field QC samples sampling considerations are important
- Carefully consider detection limits, upstream sources, consumer perception, financial and legal implications, treatment options
- Pace® Analytical is your source for the most current information and full-service laboratory testing

PEOPLE ADVANCING SCIENCE

QUESTIONS?

THANK YOU

Additional resources:

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

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Program Manager, Emerging Contaminants & Environmental Compliance

CONTACT ME: