Which Method Should/Did You Use for PFAS?

NORTHEAST CONFERENCE
THE SCIENCE OF PFAS:
Public Health & The Environment

April 5, 2022

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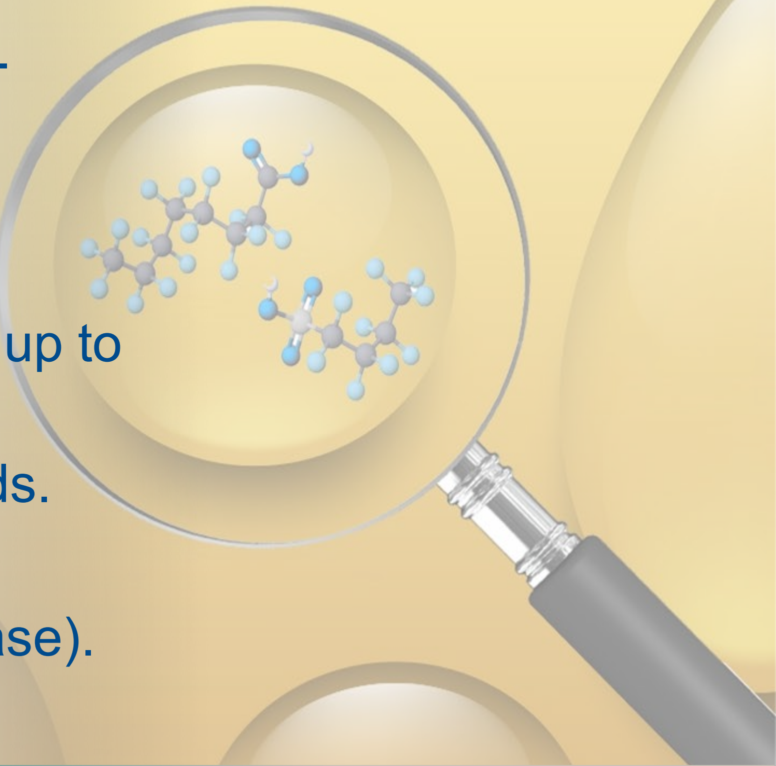
www.envstd.com

Staff photo by Chuck McGowen

Foam fun — Justin Gilday, 3, (left) and his brother Shaun, 4, both of Newark, romp through the residue of "The Blob" in Vilone Park, Elsmere. Firefighters spread the foam as part of the opening-day events at the park. More photos, B1.

Briefly About PFAS
Dramatically Dubbed by the Media as "Forever Chemicals"

- By synthesis design, PFAS repel water and oil and are remarkably thermally stable.
- Forms ions in soil, which are water soluble and then becomes mobile in groundwater and surface water pathways.
  - Does not biodegrade (fluorine bond very strong) but they can bio-transform.
- Found at low levels in the environment – first real "part-per-trillion – OMG!"
  - For perspective, carcinogenic trihalomethanes (THMs) allowable up to 200,000 ppt in drinking water.
- Little toxicity information is known about ~ 99.9% of PFAS compounds.
- Regarding the < 0.1% of the remaining PFAS compounds:
  - PFOA is a (suspected Human) Group 3 carcinogen (thyroid disease).
  - PFOS bioaccumulates in aquatic lifeforms.



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PFAS Uses/Sources

Firefighting (high-temperature fires)

- Airports
- Military (DoD)
- Petroleum Refineries and Terminals

Manufacturing

- Electronics
- Metal Plating
- Aerospace
- Automotive

Non-Industrial

- Wastewater treatment
- Biosolids Application
- Waste Disposal

Commercial and Consumer Products Containing PFAS:

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

Timeline and Known Traits

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Notes:

1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

*From ITRC fact sheet

Regulatory Framework Status

- US EPA *vs.* State proposed guidance or health advisories
- US EPA PFAS advisory is set at 70 ppt (sum of isomers).
  - A screening level was set at 40 ppt.
- US EPA Toxic Release Inventory (TRI) requirements effective January 2020.
  - US EPA added 160 PFAS compounds to the TRI list (analyses by published methods are for a fraction of that list).
  - Reporting threshold is listed as 100 pounds.

Source: https://www.epa.gov/sites/production/files/2020-01/documents/tri_non-cbi_pfas_list_1_16_2020-6.pdf

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Regulatory Framework Status (cont.)

2020 National Defense Authorization Act (NDAA) included PFAS requirements:

- Obligates DoD to phase out PFAS in firefighting foam by October 1, 2024 and to clean up PFAS contamination resulting from DoD activities.
- Directs US EPA to add several PFAS compounds to the TRI.
- Accelerate PFAS drinking water monitoring, and issue guidance on the destruction and disposal of PFAS-containing materials

Source: https://www.epa.gov/toxics-release-inventory-tri-program/addition-certain-pfas-tri-national-defense-authorization-act

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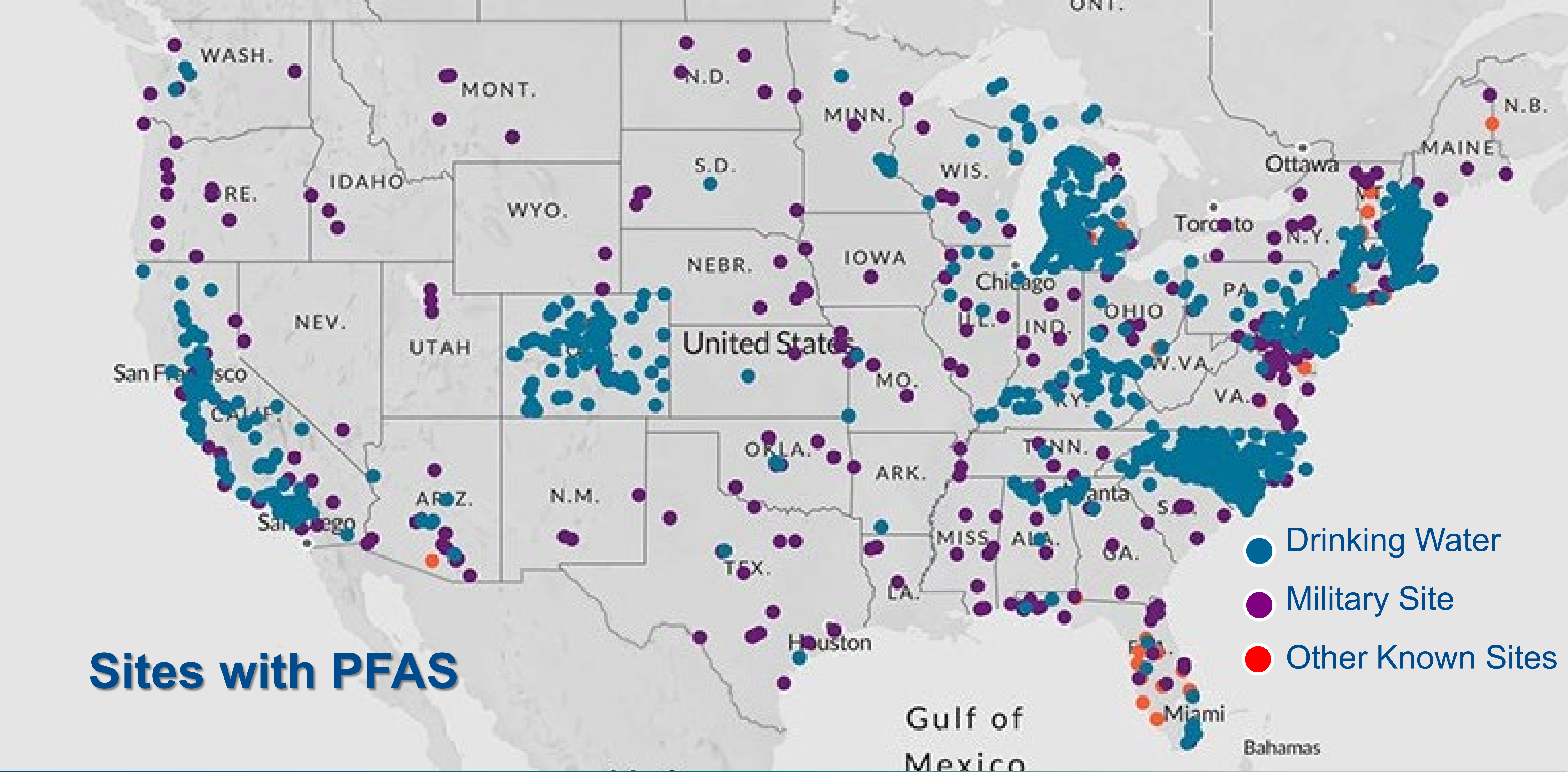
Sites with PFAS



https://www.ewg.org/interactive-maps/2019_pfas_contamination/map/#.W3rwWPZFzIU

Feb. 28, 2019

States Forge Ahead with PFAS Regulations

As EPA dithers on setting standards for PFAS contaminants in drinking water, states are stepping in to set their own guidelines.

EPA acknowledges that its monitoring data for PFAS is flawed, but an outside group estimates that as many as a third of Americans could be drinking water contaminated with the extremely persistent, highly fluorinated chemicals that are linked to kidney and liver cancer, thyroid problems, lowered fertility and diminished effectiveness of vaccines in children. PFAS chemicals have been released into the environment by firefighting foams, certain manufacturing processes and laundering of PFAS-treated clothes. Nearly all Americans have PFAS in their blood, according to CDC.

PFAS contamination

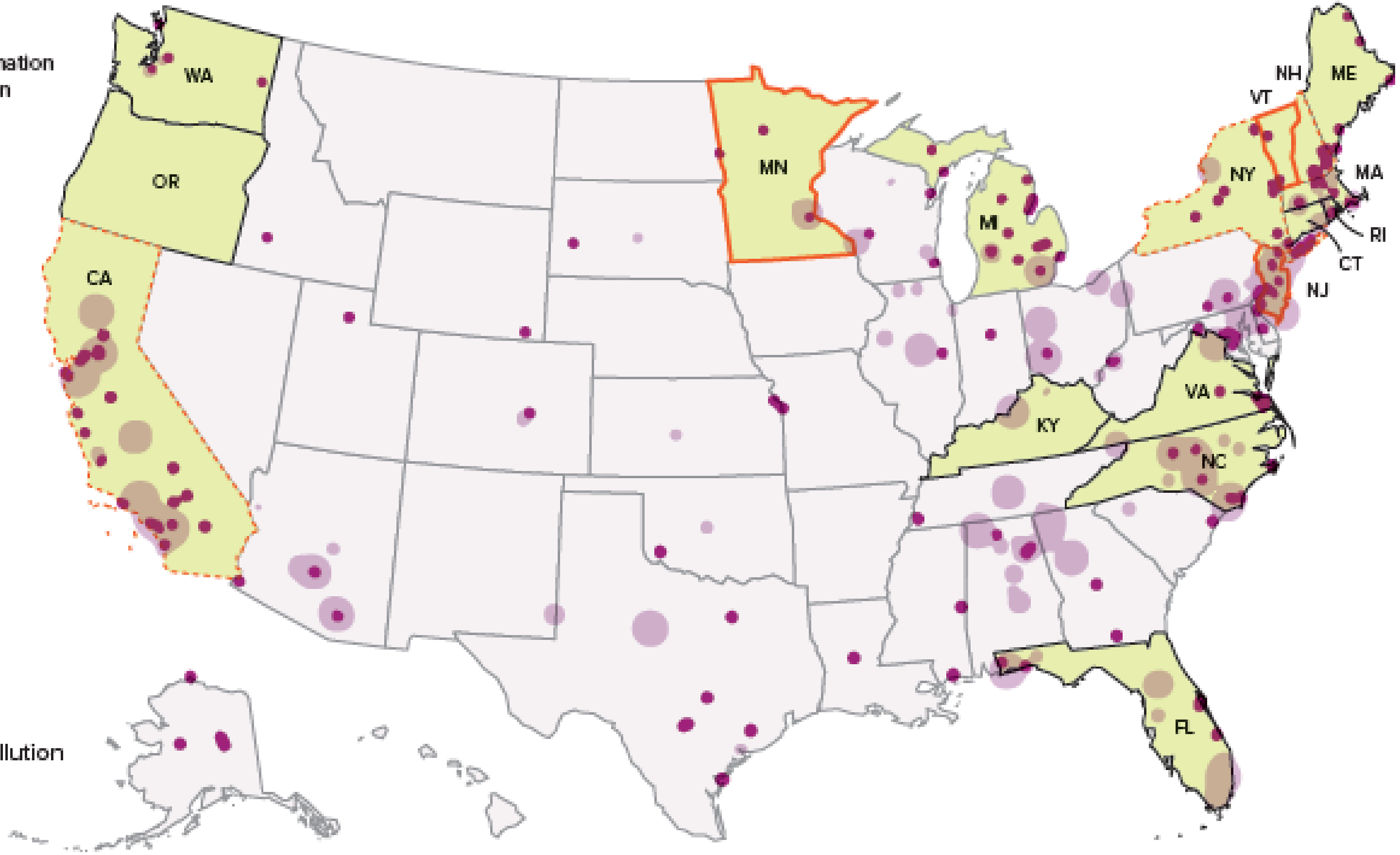
40 states bear **172** known PFAS contamination sites, including **78** military sites. More than **1,500** drinking water systems serving as many as **110 million** Americans might be contaminated with PFAS.

- PFAS contamination site
- Public water systems with detectable PFAS
  - Serving fewer than 30,000
  - Serving more than 60,000

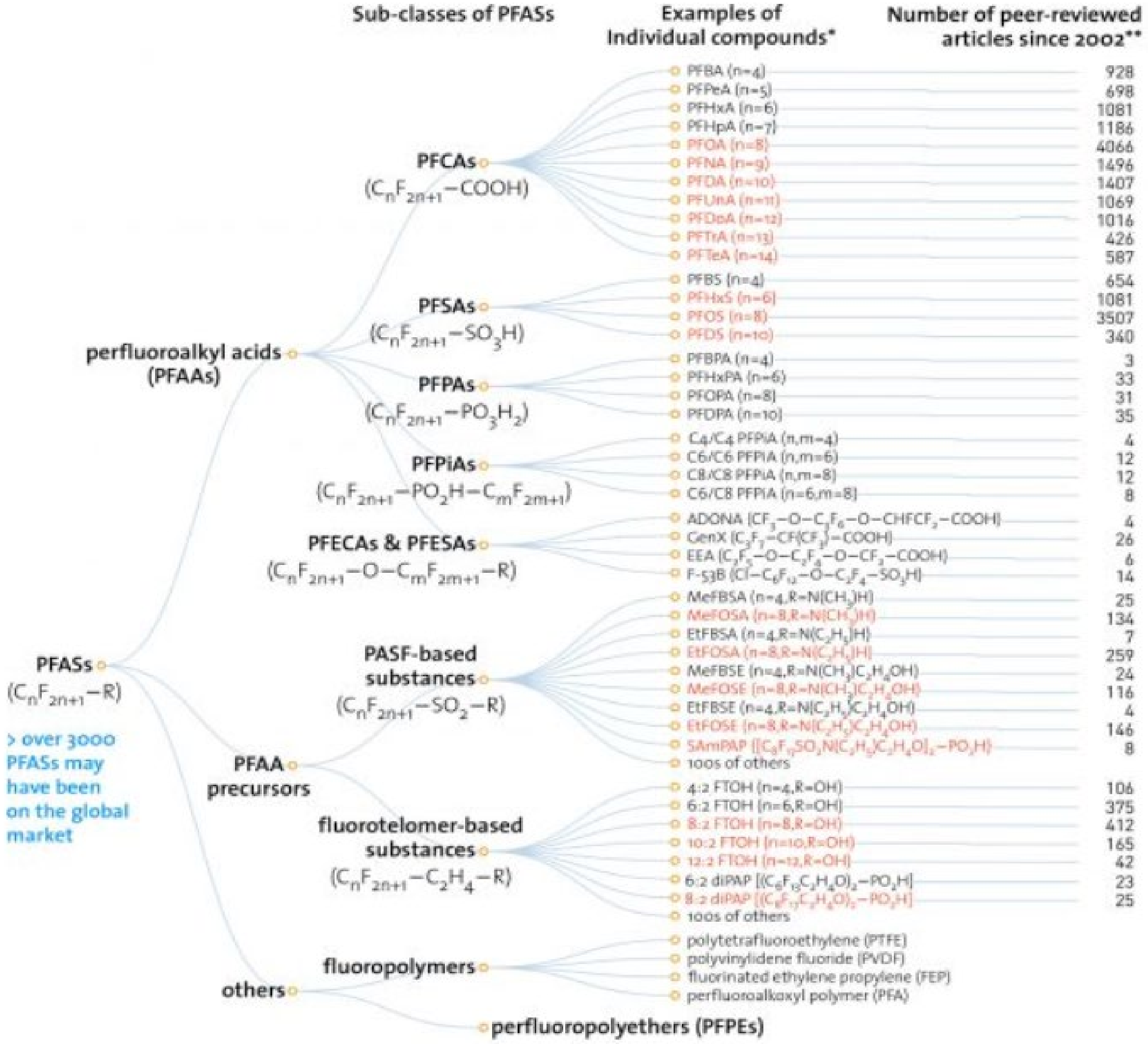
State PFAS policies

- Adopted levels lower than EPA health advisory levels
- Proposed levels lower than EPA health advisory levels†
- No state policies on PFAS pollution

† As of Jan. 8



Complicating Factors – There Are a LOT of PFAS



6,330 PFAS CAS - named substances

* Diagram from centerforenthnography.com

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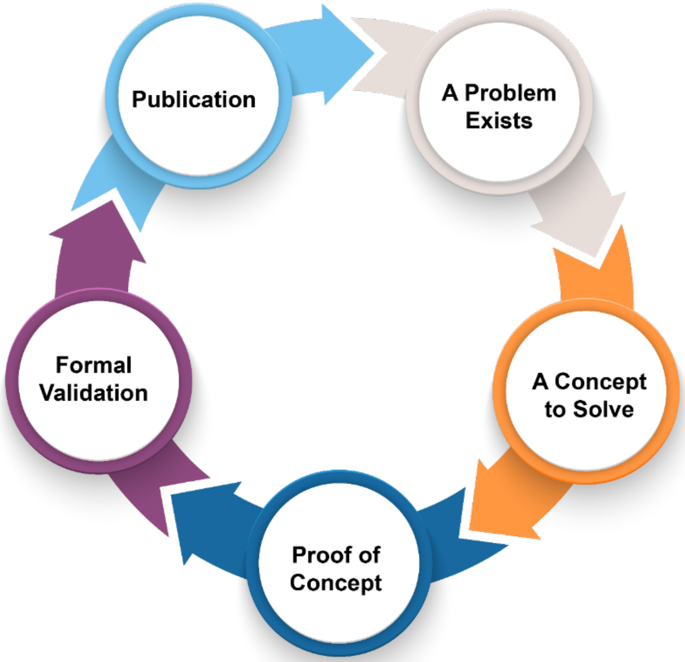
US EPA Regulatory Framework Status

- Validating analytical methods for surface water, groundwater, wastewater, soils, sediments and biosolids.
- Developing new methods to test for PFAS in air and emissions.
- Improving laboratory methods to identify unknown PFAS.
- Developing exposure models to understand how PFAS moves through the environment to potentially impact people and ecosystems.
- Continuing to assess and review treatment methods for removing PFAS in drinking water.
- Working to develop tools to assist stakeholders with the cleanup of PFAS at contaminated sites.

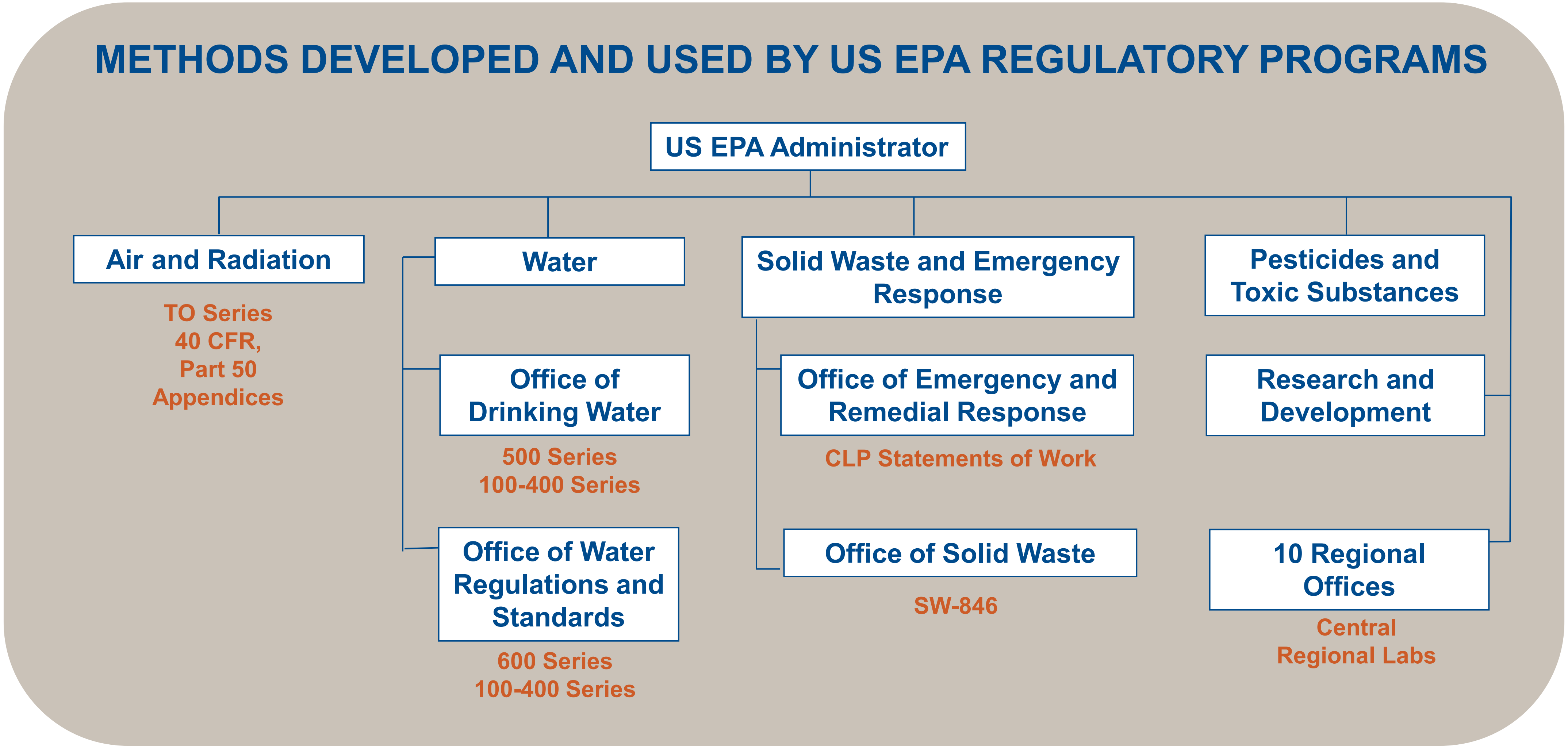
Source: https://www.epa.gov/sites/production/files/2019-12/documents/pfas_groundwater_fact_sheet.pdf

Methods Development, Validation, Promulgation

- US EPA Generic Process for Development, Validation, Publication/Promulgation
  - “It is EPA’s philosophy that all methods of analysis should be validated prior to issuance as an agency Method.” (Directive FEM-2005-01)



Briefly – The World of US EPA Methods



Current US EPA PFAS Methods

- US EPA Method 537.0 – Drinking Water 2009
- US EPA Method 537.1 – Drinking Water 2018 - *Same* as 537.0, but added four PFAS
- US EPA Method 533 – Drinking Water - December 2019
  - Added 11 PFAS (shorter chains) – Finally, isotope dilution quantitation
- US EPA SW-846 Method 8327 – Non-DW Aqueous
  - June 2019 (draft) - Direct injection, screening only *and not usable*
    - Environmental Standards draft method comments can be found at *https://www.regulations.gov/document?D=EPA-HQ-OLEM-2018-0846-0103*
  - September 2021 (Rev 0) (and Method 3512) – Addressed many comments, still screening level
- US EPA Method 1633 - Non-DW Aqueous, Solids/Biosolids – August 2021
  - Posted on the US EPA website, not even a formal draft method, single-laboratory study
  - Environmental Standards drafted method comments on behalf of industrial and advocacy groups.
    - Inconsistencies and major problems (e.g., branched/linear analysis/reporting)
  - DOD currently accrediting laboratories and yet the multi-laboratory is far from complete
  - US EPA anticipates Final Rule for Method 1633 to be 2024
- Ambient Air: No published/validated US EPA methods yet
- Many commercial laboratories are still “making up” analytical methods for PFAS analysis in non-DW matrices.

PFAS Analytes *vs.* Method

PFAS Class	533	537.1	537 Modified*
Number of Analytes	25	18	18-34?
A (Carboxylates)	9 (C4-C14)	9 (C4-C14)	Yes
B (Sulfonates)	8 (3 with ether group)	5 (2 with ether group)	Yes
C (Fluorotelomer)	3	0	Likely
D (Sulfonamido Substances)	0	2	Likely
E (Other)	5	2	?
Notes		Attempted to include more analytes, poor SPE recovery	As a standard becomes available

Other: ADONA, HFPO-DA (GenX component), etc. (contain carboxylate and ether groups)

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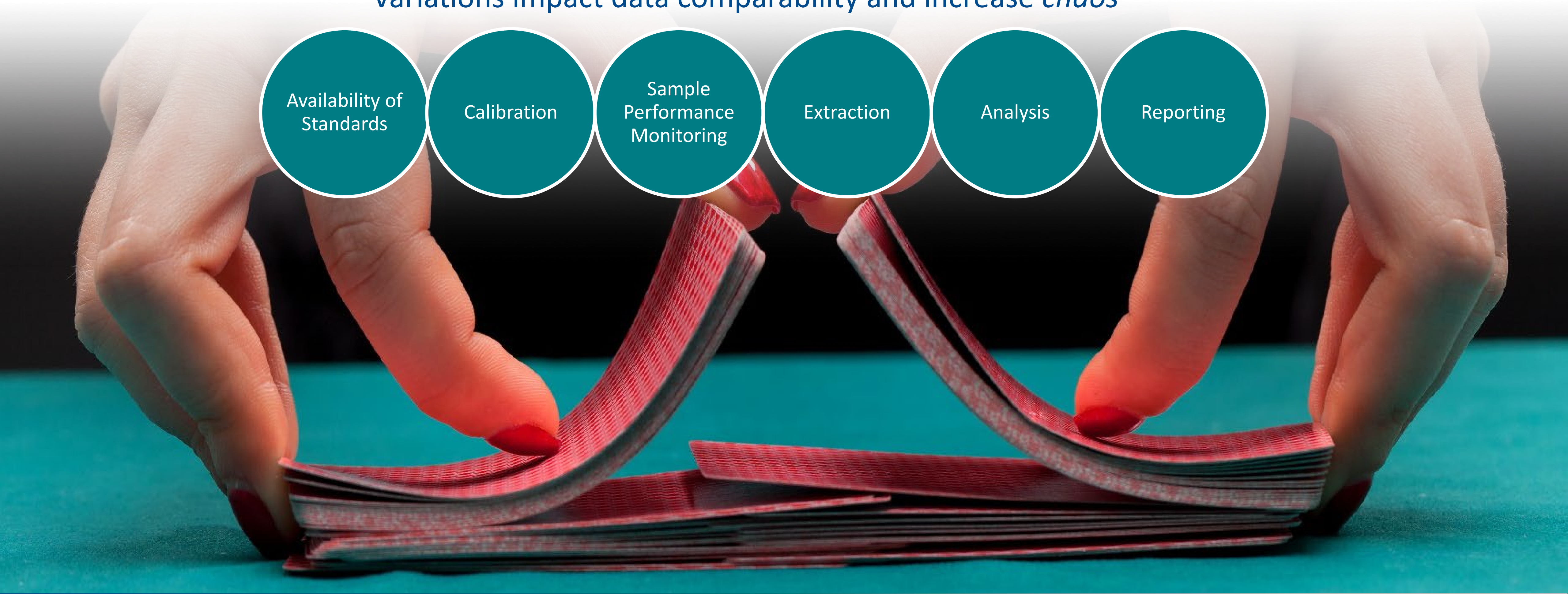
PFAS Analytes *vs.* Method (Cont.)

PFAS Class	DoD QSM 5.2	SW-846 8327	ASTM D7968-17a	ASTM D7979-17
Number of Analytes	Per laboratory	24	21 +	21 +
A (Carboxylates)	Yes	11 (C4-C14)	11 (C4-C14)	11 (C4-C14)
B (Sulfonates)	Yes	7 (2 with ether group)	3 (C4, C6, C8), + 1 cyclic	3 (C4, C6, C8), + 1 cyclic
C (Fluorotelomer)	Likely	3	6	6
D (Sulfonamido Substances)	Likely	3	0*	0*
E (Other)	?	0	0	0
Notes	Prescribed QC Table B.15		Performance based, could add	Performance based, could add

* Listed as likely applicable analytes

Laboratories "Making Up" Their Own Analytical Methods for Non-Drinking Water Matrices

Variations impact data comparability and increase *chaos*



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Reference Materials and Standards

- US EPA Method 537, 533, 1633 and DoD QSM indicate that standards “should” include linear and branched isomers *unless unavailable*.
- Standards are not available for all branched and linear PFAS target compounds.
- There are a limited number of isotope-labeled compounds available, and the list of PFAS analytes being requested is growing quickly.

Calibration Models – External, Internal *or* Isotope dilution

- Calibration models:
  - Average repose factor (RF) or relative response factor (RRF) or linear
  - Quadratic equation with or without weighting
- Forcing the calibration curve through the origin (or not)

Sample-specific Performance Monitoring

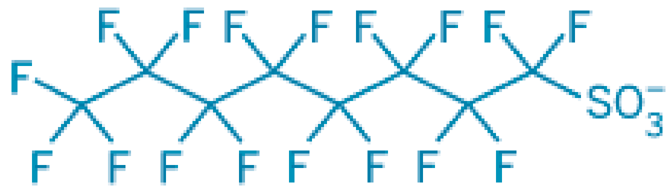
- External standard technique or internal standard technique
  - Surrogate compounds added prior to extraction monitors extraction performance.
  - Internal standard added immediately prior to instrument analysis monitors the instrument.
- Isotope dilution technique – this is the *Gold* Standard
  - FINALLY, in Method 533 and 1633, but was not in Method 537 or 537.1.
  - Labeled isotopes added prior to extraction
  - Labeled compounds are used to calculate target results.
  - Labeled compounds mathematically corrects for losses
  - Internal standard is added prior to analysis to quantitate labeled compounds (well, not all laboratories).

Solid Matrix Extraction Techniques

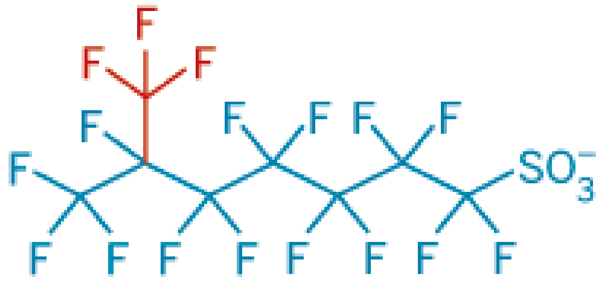
- ASTM Method D7979-16 and D7979-17 – methanol shake/vortex (aqueous and sludge)
- ASTM Method D7968-17 – methanol and vortex
- DoD QSM 5.3 - not specified for solids/sediments
- Laboratory-specific modified methods - ***anything*** goes
- Solid (Soils/Sediments/Biomass) extractions may include:
  - Shake/Vortex Sonicate, automated extraction or microwave
- Extraction solvents (reagent water, methanol, acetonitrile)
- Extract cleanups – important in complex solids (biomass)
- Extract blowdowns:
  - Concentrated to dryness, then transferred into final solvent
  - Concentrated, but not to dryness … or not at all

Down in the PFAS Isomer Weeds

- Integration of PFAS Chromatographic Peaks
  - There are many PFAS analytes – some have lots of isomers.
  - We have branched and linear isomers.
  - Integration of the isomer peak(s) *is not straightforward*
- Synthesis by Electrochemical Fluorination (historic)
  - Mix of branched and linear isomers
  - Odd & even number carbon chain lengths
  - Manufacturer- 3M
- Synthesis by Telomerization
  - Results in an “Isometrically pure” product
  - Maintains the geometry of starting telogen
  - Major product C8 or C9
  - Manufacturer- DuPont



PFOS linear isomer

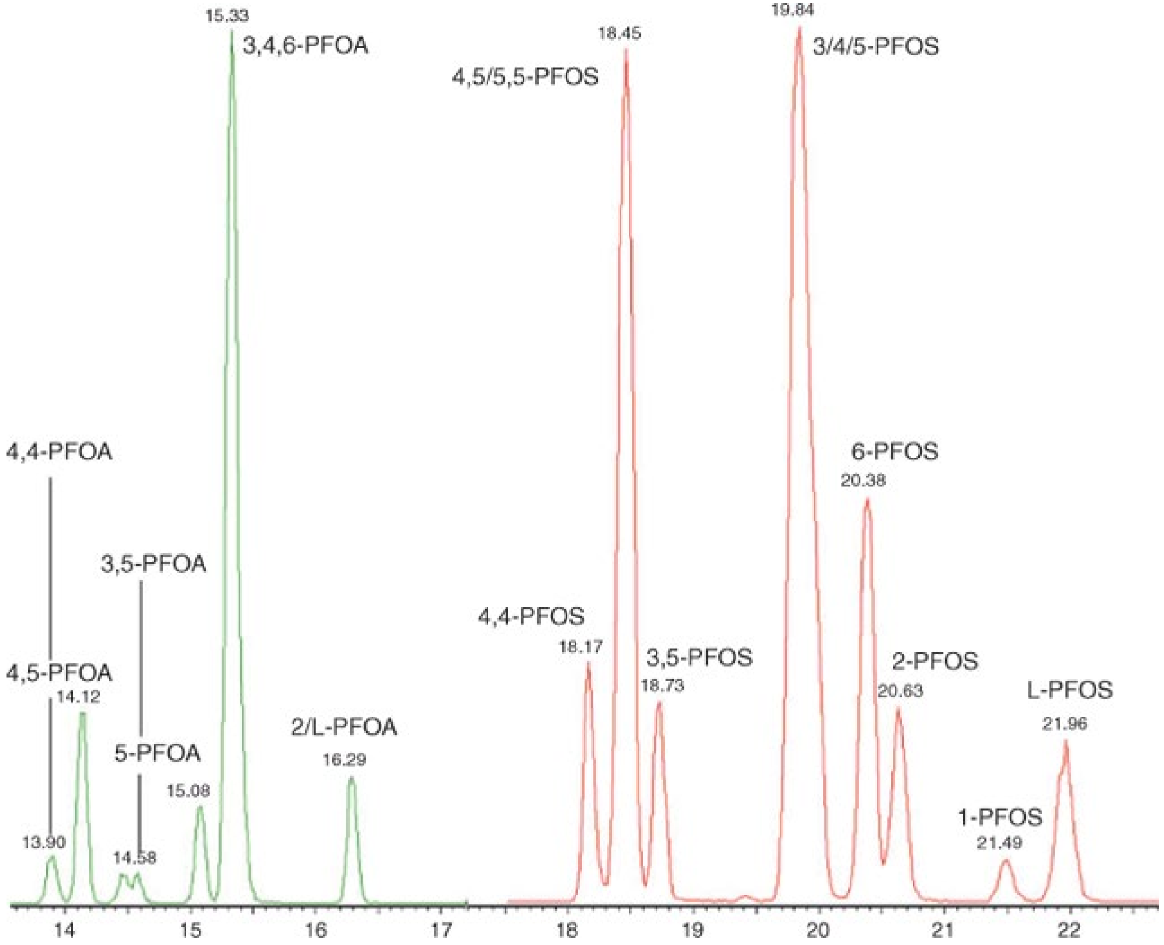


PFOS branched isomer

Branched/Linear Configurations

PFOS Anion ($C_8F_{17}O_3S$) for Example

- There are 89 structural isomers.
- There are 11 isomers in most current reference standards.
- Technical-grade standard
  - 68.3% linear
  - 30.1% methyl isomers
  - 1.6% dimethyl isomers
- Quantitation-grade standard
  - 78.8% linear
  - 20.4% methyl isomers
  - 0.7% dimethyl isomers

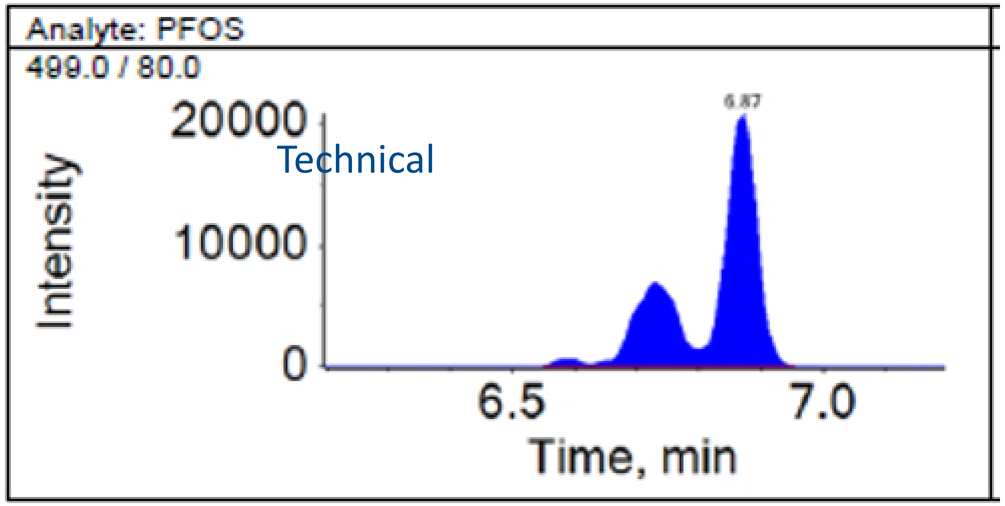


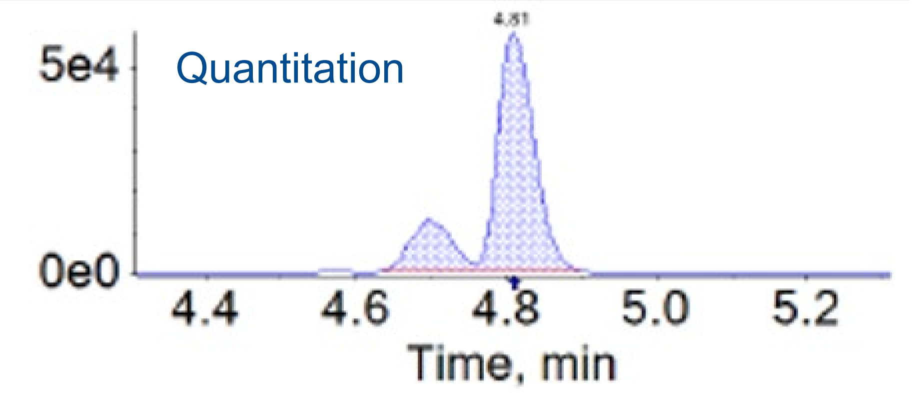
Kärrman, et al., Environmental Chemistry 8(4) 372-380 2011 http://dx.doi.org/10.1071/EN10145

Branched/Linear Configurations (Cont.)

PFOS anion ($C_8F_{17}O_3S$)

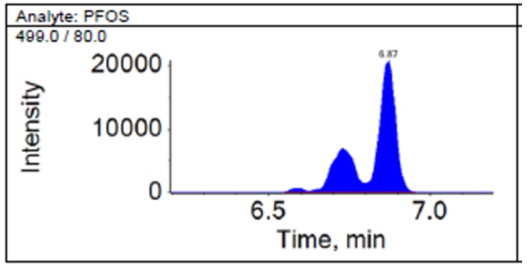
- Technical-grade standard
  - 68.3% linear
  - 30.1% methyl isomers
  - 1.6% dimethyl isomers
- Quantitation-grade standard
  - 78.8% linear
  - 20.4% methyl isomers
  - 0.7% dimethyl isomers
- Dimethyl isomers are often not included for quantitation.





Mission-critical Considerations – Branched/Linear Configurations

- Understand the type of standards that are being used (linear or linear/branched).
- Assess the laboratory's separation based on the mixed linear/branched standards – The methods do not define resolution



- Is total isomer OK ? Or is reported branched/linear needed ?
- Make sure the laboratory stays consistent or communicates changes that will impact historical comparability.

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Best Practices - Proactively Direct, Audit and Manage PFAS Liability

- Critically review consultants' sampling procedures.
- Contractually Mandate laboratory analytical requirements.
- Actively audit sampling and analytical vendors.
- Contract a qualified third-party PFAS chemistry consultant to assess field and laboratory data quality as data are being generated and reported.
- Immediately troubleshoot/correct suspicious data.
- Centralize your sampling and analytical PFAS data using enterprise data management platforms - larger scale programs.

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Thank You

QUESTIONS?

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