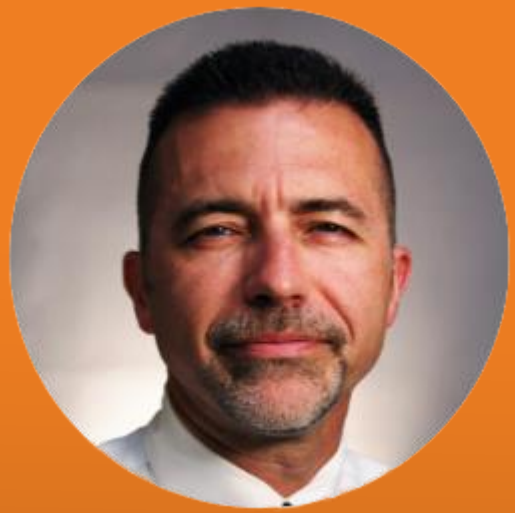
# The Analysis for PFAS in Pennsylvania: An Evaluation of Current Methods, Proposed Methodologies and the Application of New Technologies



PA Chamber Environmental Conference
October 27, 2022

Charles Neslund
*Scientific Officer and PFAS Practice Leader*

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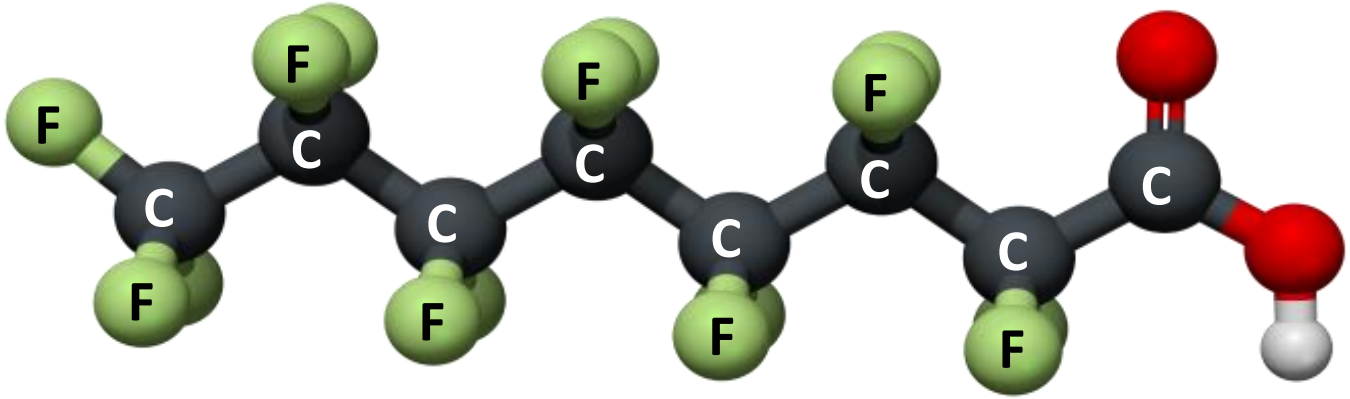
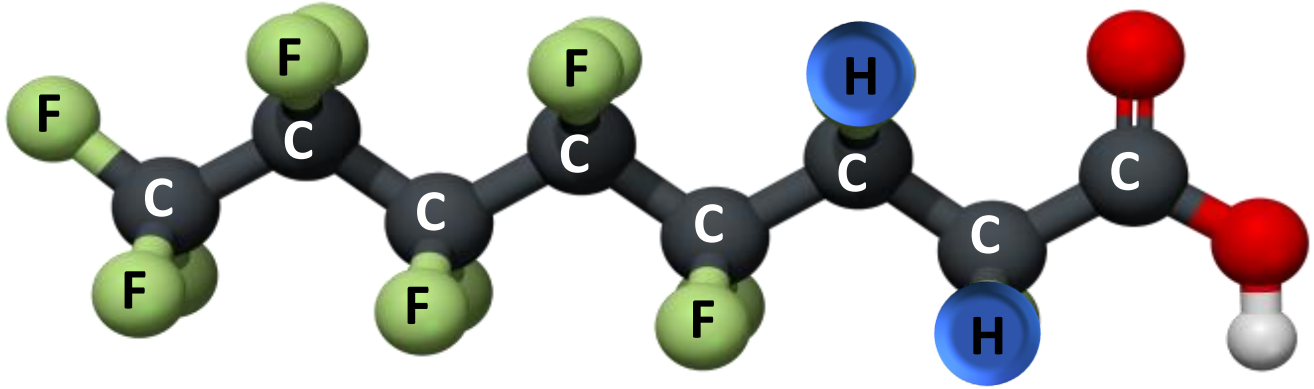
# Per and Poly?

Perfluorinated = Completely Fluorinated




Polyfluorinated = Incompletely Fluorinated



# Example Uses

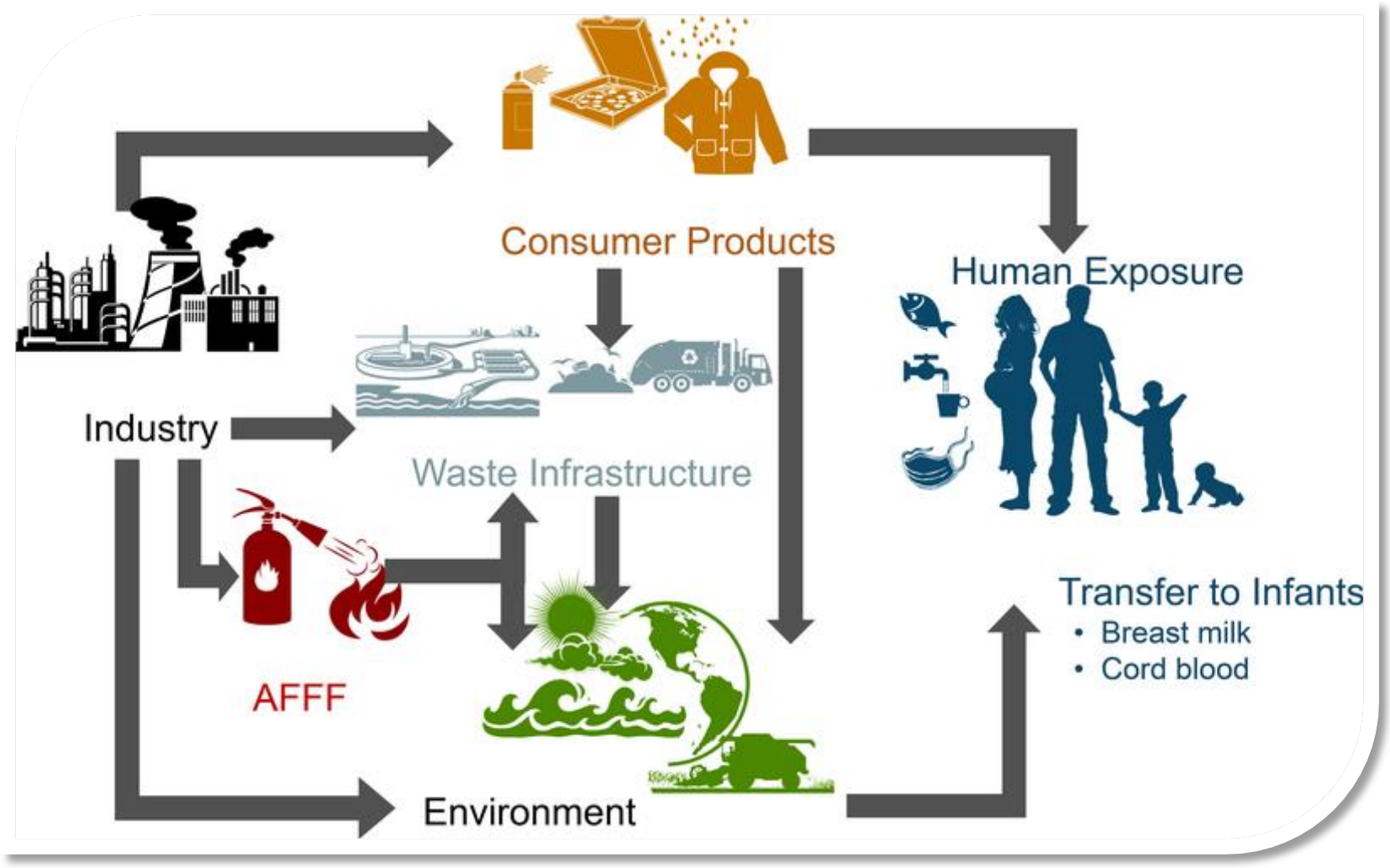
Automotive
Aerospace
Metal Finishers

Textiles
Carpet/Furniture
Paper/Packaging

Paint
Chemicals
Personal Care

Semiconductor
Mining
Stone Cutting

# How are we exposed to them?




Source: Sunderland et al. (2019)
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6380916/

# FEDERAL ACTIONS

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# PFAS STRATEGIC ROADMAP

## RESEARCH

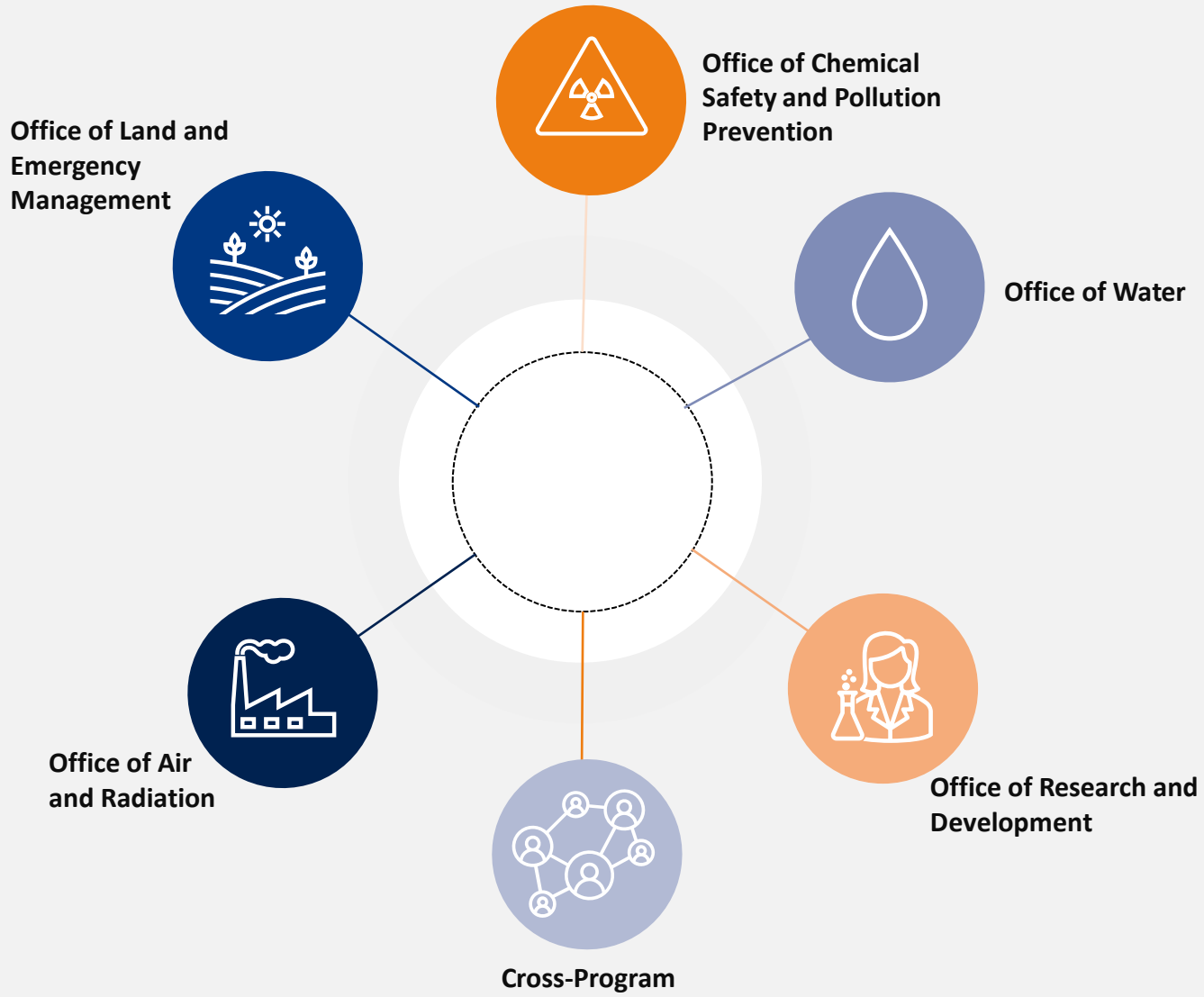
*increase understanding of PFAS exposures and toxicities, human health and ecological effects*

## RESTRICT

*proactively prevent PFAS from entering air, land, and water at levels that can adversely impact human health and the environment*

## REMEDIATE

*Broaden and accelerate the cleanup of PFAS contamination to protect human health and ecological systems*



# TASK FORCE

Identify FFF & Monitor health effects

# INCINERATION

Moratorium until guidance is in place

# PROCUREMENT

Study items procured containing PFAS

# REMEDIATION SCHEDULE

For PFAS release sites

# 2022 NATIONAL DEFENSE AUTHORIZATION ACT (NDAA)

The Fiscal Year 2022 NDAA; S. 1605 was signed into law with funding for addressing PFAS with a focus on AFFF and Drinking Water

## Temporary Moratorium on Incineration of PFAS Materials

until DoD publishes guidance on destruction and disposal or EPA publishes in the Federal Register a final rule regarding destruction and disposal

## Directs GAO to Audit DoD Procurement

of certain items that contain PFAS substances, to assess the extent to which information is available, and the feasibility of prohibiting said items

## Creation of a PFAS Task Force

to identify an effective alternative to PFAS firefighting foam and monitor the health aspects of exposure to PFAS

## Completion of Remediation Schedule

and associated cost estimates must be submitted within 270 days for DoD sites identified as having a release of PFAS

https://www.govinfo.gov/app/details/BILLS-117s1605enr

# HAZARDOUS SUBSTANCES - CERCLA

## EPA Takes Steps to Designate PFOA and PFOS as Hazardous Substances Under CERCLA

**Propose to designate PFOA and PFOS as CERCLA hazardous substances**

**Issue advance notice of proposed rulemaking on various PFAS under CERCLA**

https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024

## Proposed Rule

EPA Submits to OMB, 1/10/22

## OMB Review

90 days on average

## Comments

Public comment period, Spring 2022

## Final Rule

Summer of 2023

# HAZARDOUS CONSTITUENTS - RCRA

EPA proposes to add PFOA, PFOS, PFBS, and GenX as RCRA "hazardous constituents."

**In an EPA letter to NM Gov. this will be based on EPA's evaluation of existing data alongside the establishment of a record to support the proposed rule.**

**Those chemicals listed are subject to corrective action requirements under RCRA at hazardous waste treatment, storage, and disposal facilities.**

PFOA

PFOS

PFBS

GenX

https://www.epa.gov/newsreleases/epa-responds-new-mexico-governor-and-acts-address-pfas-under-hazardous-waste-law

https://www.jdsupra.com/legalnews/epa-announces-plans-for-waste-rules-3519848/

# Method Selection

## Pre-Planning

## Quality, Regulatory & Laboratory Drivers

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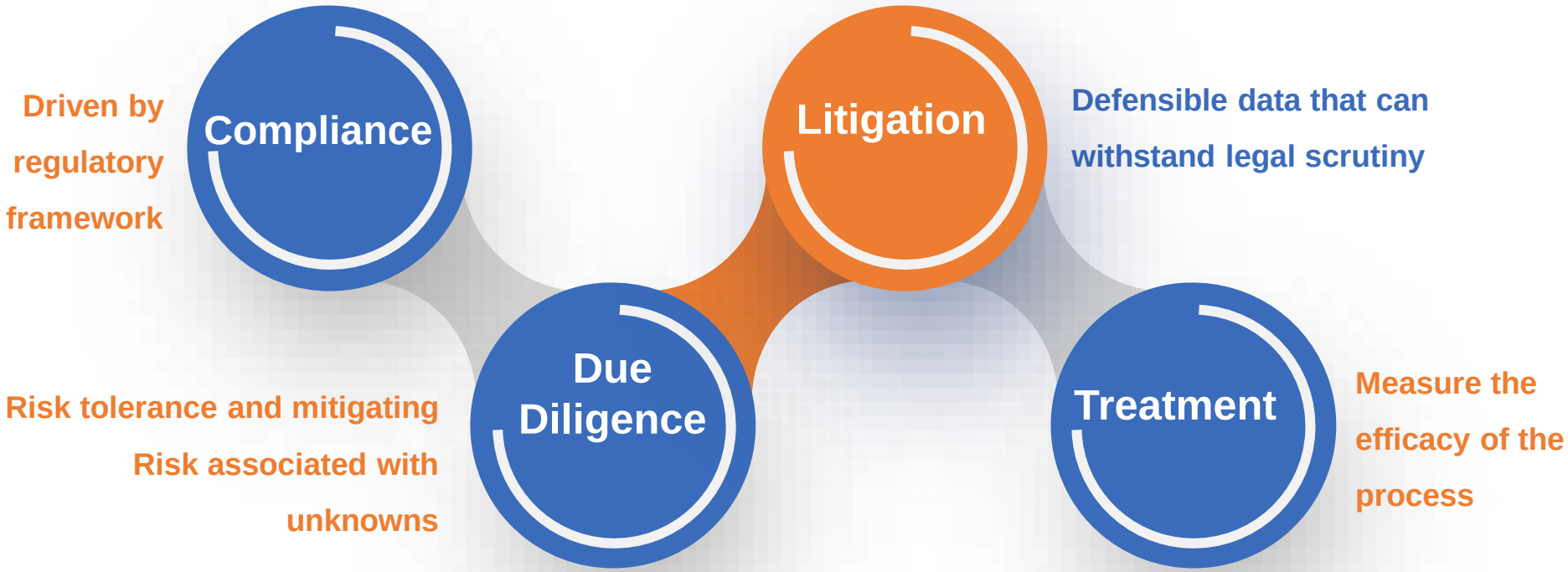
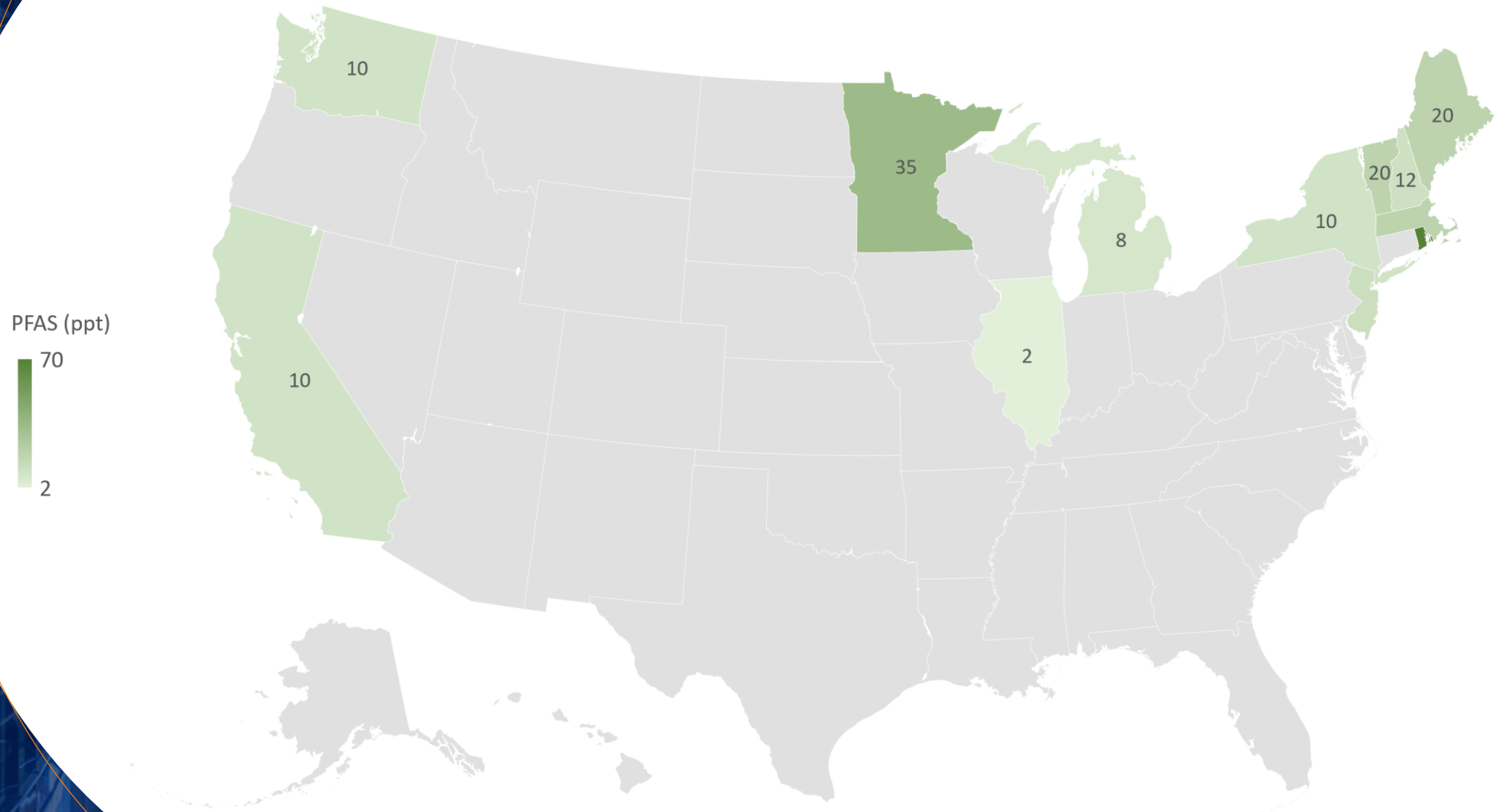
QUALITY DRIVERS

# What Are The Data Being Used For?



DRINKING WATER

# STATE ACTIONS: DRINKING WATER LIMITS



# Pennsylvania Limits

| PFAS | MCLG (ng/L) | MCL (ng/L) | MCLs Protective Of |
|---|---|---|---|
| PFOA | 8 | 14 | Adverse developmental effects (including neurobehavioral and skeletal effects) |
| PFOS | 14 | 18 | Adverse immune system effects (including immune suppression) |

MCLG = maximum contaminant level goal
MCL = maximum contaminant level
ng/L = nanograms per liter = parts per trillion (ppt)

# Pennsylvania vs Other States

| | NY | MI | NJ | NH | PA | MA | VT | WA |
|---|---|---|---|---|---|---|---|---|
| **PFOA** | 10 | 8 | 14 | 12 | **14** | 20* | 20* | 10 |
| **PFOS** | 10 | 16 | 13 | 15 | **18** | 20* | 20* | 15 |

*The MCL for MA & VT is for a group of five (VT) or six (MA) PFAS, including PFOA and PFOS (not individual contaminants).

# EPA DRINKING WATER METHODS

## EPA 537.1
## EPA 533

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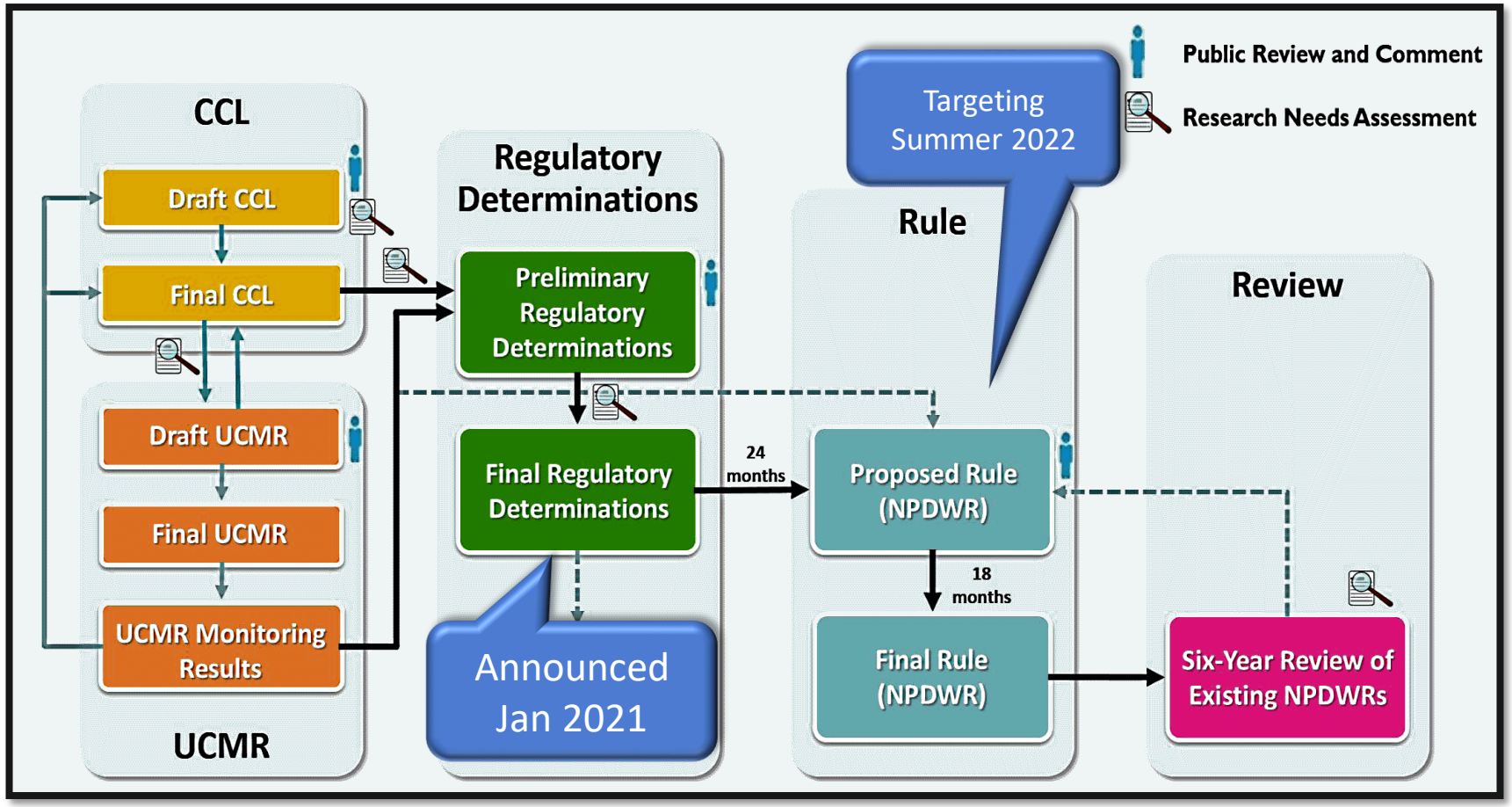
DRINKING WATER

# PFAS Maximum Contaminant Levels (MCLs)



DRINKING WATER

# SDWA: UCMR 5

## Unregulated Contaminant Monitoring Rule


**Final Rule Adopted, Dec 2021**

UCMR 5 period spans

2022–2026

**29 PFAS Analytes**

Includes all analytes from

537.1 & 533

**Will occur 2023 - 2025**

PWS serving >10,000

PWS serving 3,300-10,000

Small systems serving < 3,300

https://www.epa.gov/newsreleases/epa-announces-nationwide-monitoring-effort-better-understand-extent-pfas-drinking

DRINKING WATER

# SDWA: UCMR 5

## PFAS Analyte List

| 537.1 Analytes | | |
|---|---|---|
| PFBS | PFUnA | DONA |
| PFHxA | PFDoA | HFPO-DA |
| PFHxS | PFTA | |
| PFHpA | PFTrDA | |
| PFOA | NMeFOSAA | |
| PFOS | NEtFOSAA | |
| PFNA | 11Cl-PF3OUdS | |
| PFDA | 9Cl-PF3ONS | |

| 533 Analytes |
|---|
| NFDHA |
| PFBA |
| PFEESA |
| PFHpS |
| PFMPA |
| PFMBA |
| PFPeA |
| PFPeS |
| 4:2 FTS |
| 6:2 FTS |
| 8:2 FTS |

https://www.epa.gov/dwucmr/fifth-unregulated-contaminant-monitoring-rule

EPA PFAS Methods

# Drinking Water

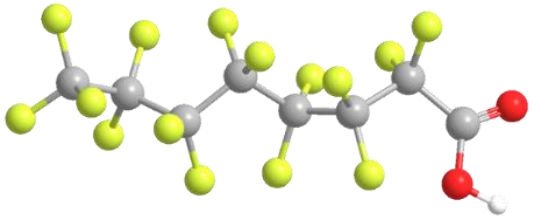
| 533 | 537.1 |
|---|---|
| Drinking Water | Drinking Water |
| Branched/Linear Isomers -YES | Branched/Linear Isomers -YES |
| 14 of the same and 15 unique compounds | 14 of the same and 4 unique compounds |
| SPE WAX | SPE SDVB |
| Hold Time: 28/28 days | Hold Time: 14/28 days |
| LCMSMS with confirmation ion | LCMSMS - no confirmation ion |
| Isotope Dilution | Internal standard |
| Recovery Correction - YES | Recovery Correction – NO |
| RLs: Not defined | RLs: 2ppt - 40ppt |

# Labeled Analogues

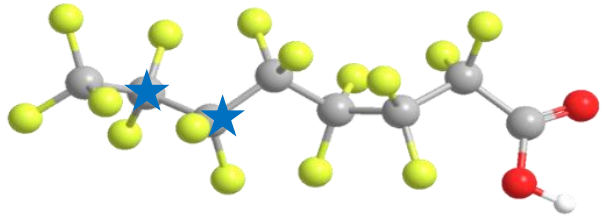
The Parr Family = Native PFOS

+ =

The Incredible Family = Labeled PFOS



+ ★=



★ = $^{13}C$

Isotope Dilution

# Benefits of Isotope Dilution

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***What affects the native analyte will equally affect the isotope***

**Calibration**

Most accurate and precise method

Target analytes are quantitated against structurally similar materials, the isotopes themselves

**Matrix Mitigation**

Expands ability to process a broader range of matrices

**Compound Identification**

Reduces the potential for false positives

Reduces the potential for error; corrects for retention time shifts

# NON-POTABLE WATER & SOLIDS

## User-Defined Isotope Dilution Method
## EPA 8327
## EPA Draft 1633 Method
## Air Methods

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# Comprehensive PFAS Testing

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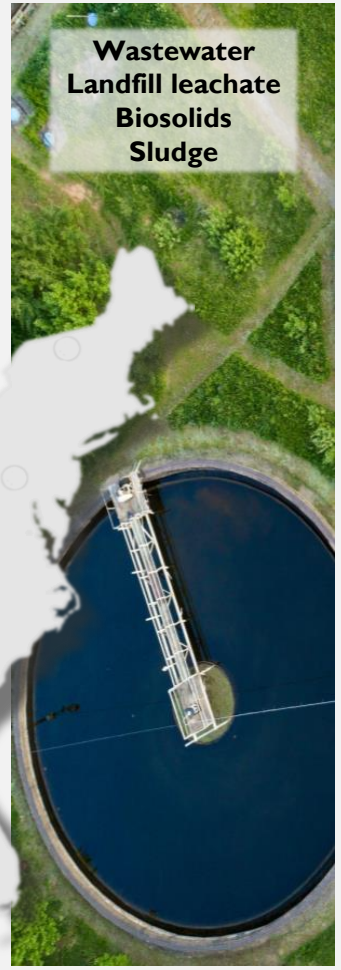



In-line SPE

LEAF

537.1

QSM

ISM

Isotope Dilution

Direct Injection

533

SPLP

# Methods Distribution

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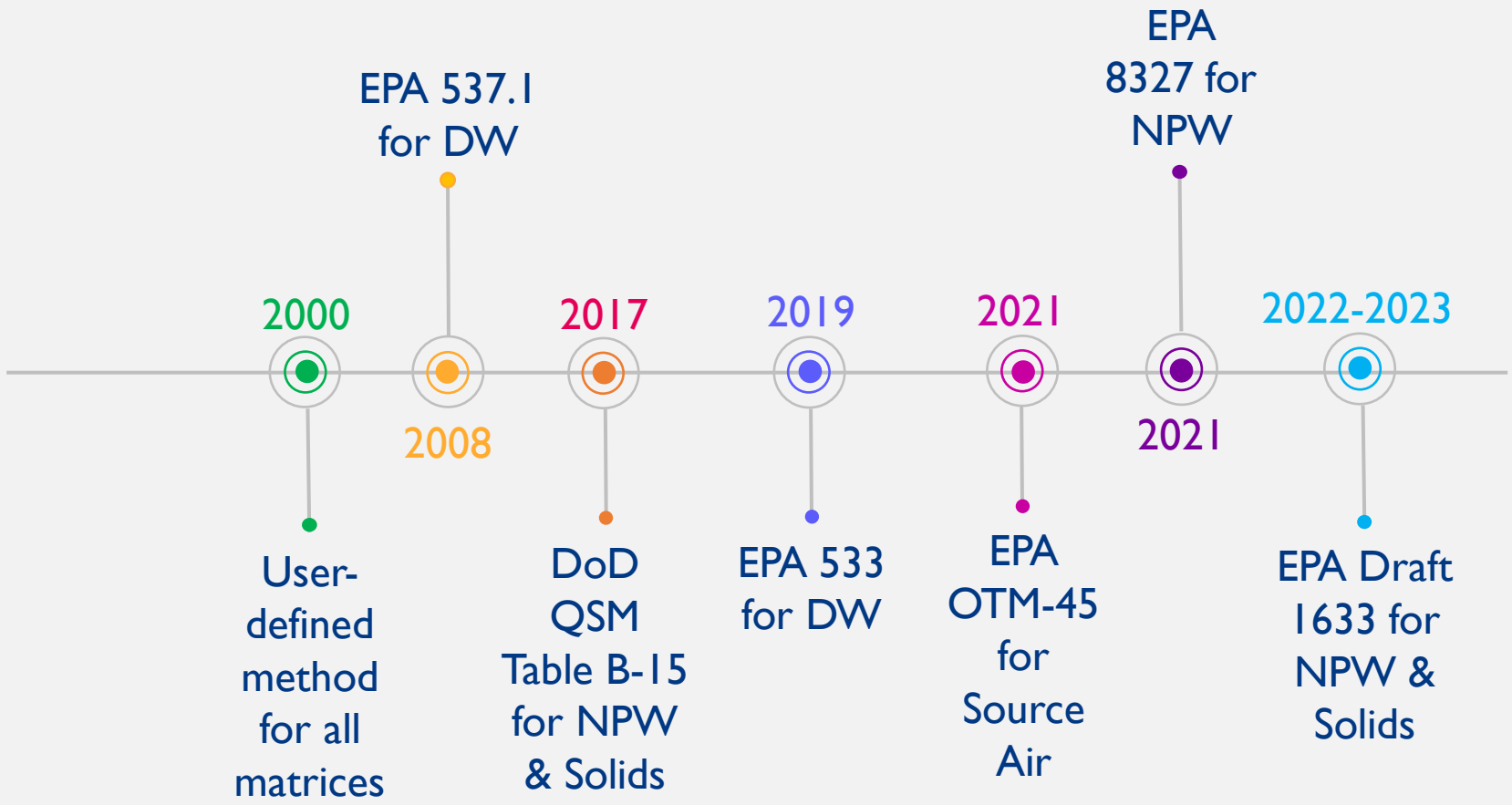
Utilizes Internal/ External Std. Quantitation and unique techniques

Utilizes Isotope Dilution and other consistent techniques



# User-Defined Methods: PUT TO THE TEST!




**Complex Matrices**

- Biphasic
- Biosolids
- Tissues
- Dispersions
- Activated Carbon
- Cosmetics
- Concrete

**Audits & PTs**

- NELAC
- DoD ELAP
- Client/Program Specific Audits
- Semiannual PT
- NMI International Round Robin
- DOW Study

**3rd Party Validation**

- >85% of all PFAS data includes a validation package
- >300,000 sample data validated

# LCMSMS/GCMSMS Analysis

## Compounds Included in EPA Draft 1633 (RLs = 2-5ng/L)

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPeA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnA)
- Perfluorododecanoic acid (PFDoA)
- Perfluorotridecanoic acid (PFTriA)
- Perfluorotetradecanoic acid (PFTeA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluoropentanesulfonic acid (PFPeS)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluoroheptanesulfonic Acid (PFHpS)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorononanesulfonic acid (PFNS)
- Perfluorodecanesulfonic acid (PFDS)
- Perfluorododecanesulfonic acid (PFDoS)
- Perfluorooctanesulfonamide (FOSA)
- NEtFOSA
- NMeFOSA
- NMeFOSAA
- NEtFOSAA
- NMeFOSE
- NEtFOSE
- 4:2 FTS
- 6:2 FTS
- 8:2 FTS
- 9Cl-PF3ONS
- 11Cl-PF3OUdS
- DONA
- HFPO-DA (GenX)
- 3:3 FTCA
- 5:3 FTCA
- 7:3 FTCA
- NFDHA
- PFMBA
- PFMPA
- PFEESA

## Target Compounds Not Part of EPA Draft 1633 (RLs = 2-5ng/L)

- 10:2 FTS
- 6:2 FTCA
- 8:2 FTCA
- 10:2 FTCA
- 6:2 FTUCA
- 8:2 FTUCA
- 10:2 FTUCA
- PFECHS
- PFPrS
- PFPrA
- PFMOAA
- PFECAG
- PFO4DA
- PFO3OA
- PFO2HxA
- R-EVE
- NVHOS
- Hydro-EVE Acid
- Perfluoro-n-octadecanoic acid (PFODA)
- Perfluoro-n-hexadecanoic acid (PFHxDA)
- EVE Acid
- PFO5DA
- PMPA
- PEPA
- MTP
- PS Acid
- Hydro-PS Acid
- R-PSDA
- Hydrolyzed PSDA
- R-PSDCA
- 6:2 diPAP
- 8:2 diPAP
- 6:2/8:2 diPAP
- 10:2 diPAP
- 10:2 FTOH (RL=1ug/L)
- 8:2 FTOH (RL=1ug/L)
- 7:2 FTOH (RL=1ug/L)
- 6:2 FTOH (RL=1ug/L)
- 4:2 FTOH (RL=1ug/L)

# EPA *Draft* 1633 for Non-Potable Water & Solids

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Compared to: User-Defined Methods and DoD QSM Table B-15

## SIMILARITIES

- Applicable to a variety of solids and aqueous matrices
- Solid Phase Extraction using WAX
- Isotope Dilution Quantitation using all available isotopes
- Ion Transitions, monitoring ratios
- *Using non-Extracted Internal Standards (NEIS) for quantitation of extracted internal standards (EIS)
- **Use of carbon cleanup

*QSM 5.3 dropped it, but they are bringing it back with B-24

**User-defined methods use stacked carbon vs. loose carbon

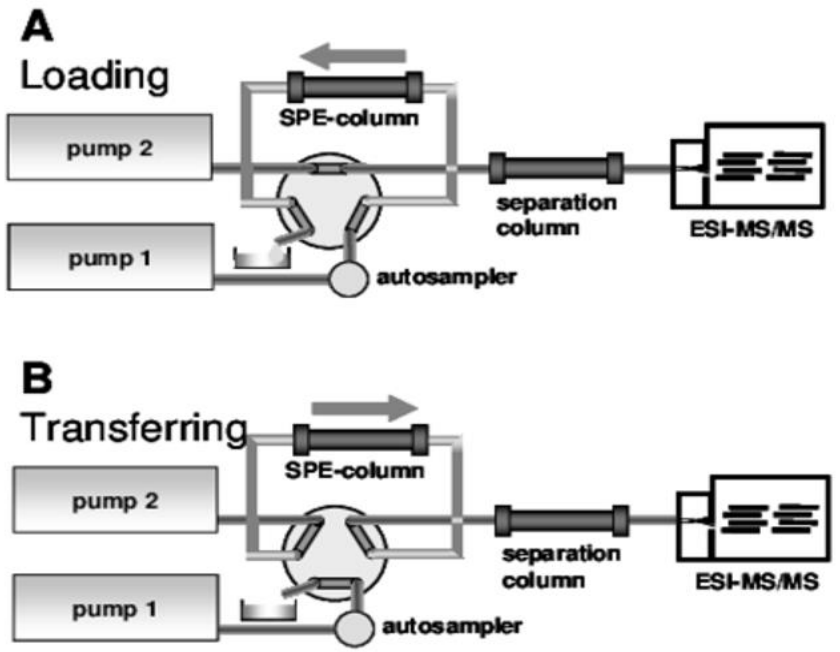
## DIFFERENCES

- Frozen storage requirements
- Soil/Tissue Prep: concentration step
- S/N Ratio
- Waters Oasis WAX SPE Cartridge with loose carbon cleanup
- TDCA Check: 60 sec window specification
- E-flagged results: complex dilution scheme
- Mass transitions vary for some

# How 8327 Compares to Draft 1633

## EPA 8327

| Specifications |
|---|
| Applies to non-potable water (NPW) |
| Applies to 24 compounds |
| External Standard |
| Direct Injection – no SPE |
| Recovery Correction - NO |
| Hold Time: 28/30 days |
| LCMSMS with confirmation ion |
| Branched/Linear Isomers -YES |
| RLs: 10ppt |




## EPA Draft 1633

| Specifications |
|---|
| Applies to NPW, soil, tissue |
| Applies to 40 compounds |
| Isotope Dilution |
| SPE WAX |
| Recovery Correction - YES |
| Hold Time: Varies, 90/90 days option when frozen, 7/28 days when refrigerated |
| LCMSMS with confirmation ion |
| Branched/Linear Isomers -YES |
| RLs: 2ppt |

# Source Air

## EPA OTM 45

Application: Semivolatile and particulate-bound PFAS from Source Air Emissions

Sample Collection: Based off of EPA Method 0010

Sample Preparation: Based off of 3542

Analysis: LCMSMS with Isotope Dilution based off of EPA Method 533

# Ambient Air

## Modified TO-13A / LCMSMS

Application: Semivolatile and particle-bound PFAS in Ambient Air

Sample Collection: PUF/XAD Cartridge based off of EPA Method TO-13A

Sample Preparation: Methanol Extraction based off of User-defined method

Analysis: User-defined method for PFAS by LCMSMS with Isotope Dilution

# Vapor

## Modified TO-17 / GCMSMS

Application: Volatile PFAS in Indoor Air and Soil Vapor

Sample Collection: Thermal Desorption Tube based off of EPA Method TO-17

Sample Preparation: Thermal Desorption based off of EPA Method TO-17

Analysis: User-defined method for PFAS by GCMSMS

https://www.epa.gov/sites/production/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

# AMBIENT AIR

## States Establish Limits

| State | PFOA | PFOS | APFO | 6:2FTS |
|---|---|---|---|---|
| NH | N/A | N/A | 0.024ug/m3 (annual) | N/A |
| TX | 0.005ug/m3 (annual) | 0.01ug/m3 (annual) | 0.01ug/m3 (annual) | N/A |
| MI | 0.07ug/m3 (24hr) | 0.07ug/m3 (24hr) | N/A | 1.0ug/m3 (annual) |
| NY | 0.0053ug/m3 (annual) | N/A | N/A | N/A |
| MN | 0.07ug/m3 (24hr->8yr) | 0.07ug/m3 (24hr->8yr) | N/A | N/A |

https://www.dec.ny.gov/docs/air_pdf/dar1proposed.pdf

https://www.health.state.mn.us/communities/environment/risk/guidance/air/table.html#hbvsraas

http://www2.des.state.nh.us/OneStopPub/Air/330110016520060807TypeAOC.pdf

https://www.michigan.gov/documents/deq/deq-aqd-toxics-ITSLALPH_244167_7.pdf

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# 537.1

**Drinking Water –**

**18 Compounds**

SDVB SPE Extraction,

External Standard Quantitation

# 533

**Drinking Water –**

**25 Compounds**

WAX SPE Extraction,

Isotope Dilution Quantitation


A great example of collaboration applied in real world applications

EPA 8327
24 Compounds
Non-Potable Water

# OTM-45

**Source Air –**

**up to 50 Compounds**

Sample collection and analysis references standard EPA methods and isotope dilution

# Draft 1633

**Non-Potable Water & Solids –**

**40 Compounds**

WAX SPE Extraction

Secondary Ion Confirmation

Isotope Dilution Quantitation



https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research

# EMERGING TECHNOLOGIES

TOP Assay
Total Organic Fluorine (TOF)
Non-Target Analysis (NTA)



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# Total Oxidizable Precursors

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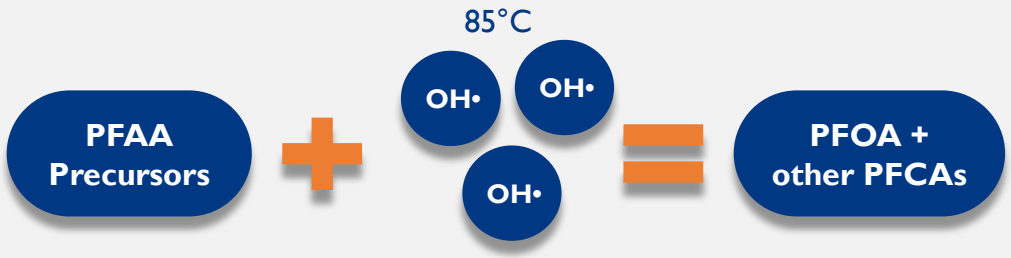
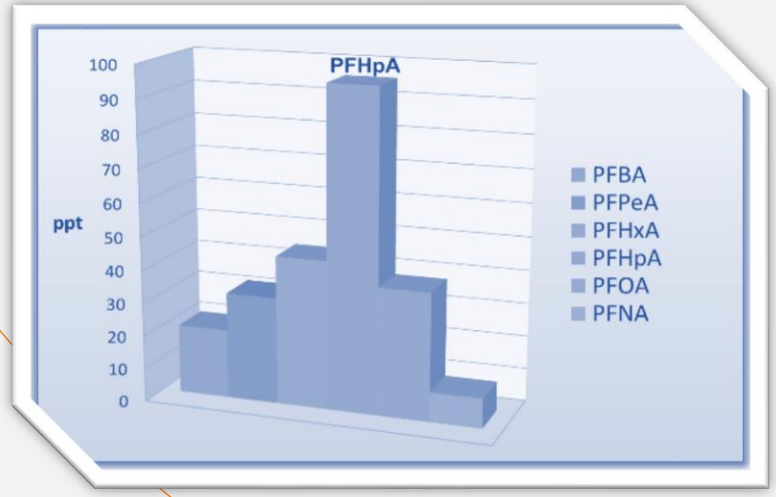
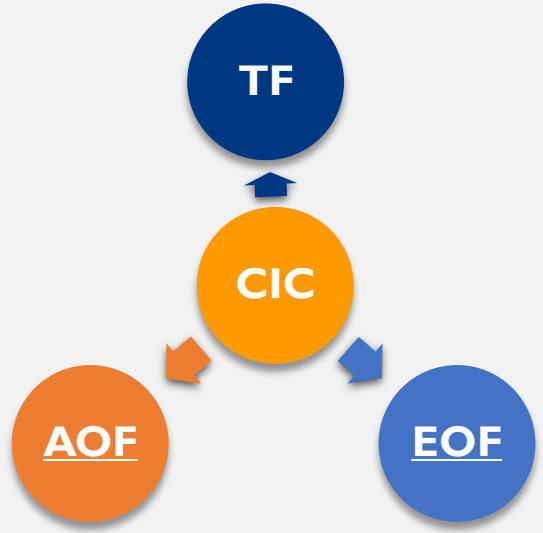
## TOP Assay




TOP Conversion of 8:2 FTS

## Total Organic Fluorine Analysis




CIC: Combustion Ion Chromatography

# Strengths & Weaknesses

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## Strengths & Utility

- AOF/EOF:
  - Proxy for entire class of PFAS
  - Mass balance applications
- TOP Assay:
  - Insight specific to current risk drivers
  - Sensitivity at single digit ppt

## Weaknesses

- AOF/EOF:
  - 1ppb reporting limit
  - Subject to certain interferences
- TOP Assay:
  - Oxidizable precursors only
  - Does not complete a mass balance

# TOF & TOP Standardization Efforts

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HARVARD School of Engineering and Applied Sciences

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ASTM

**Improving Measurement Reliability of the PFAS TOP Assay**

Final | 20 June 2019

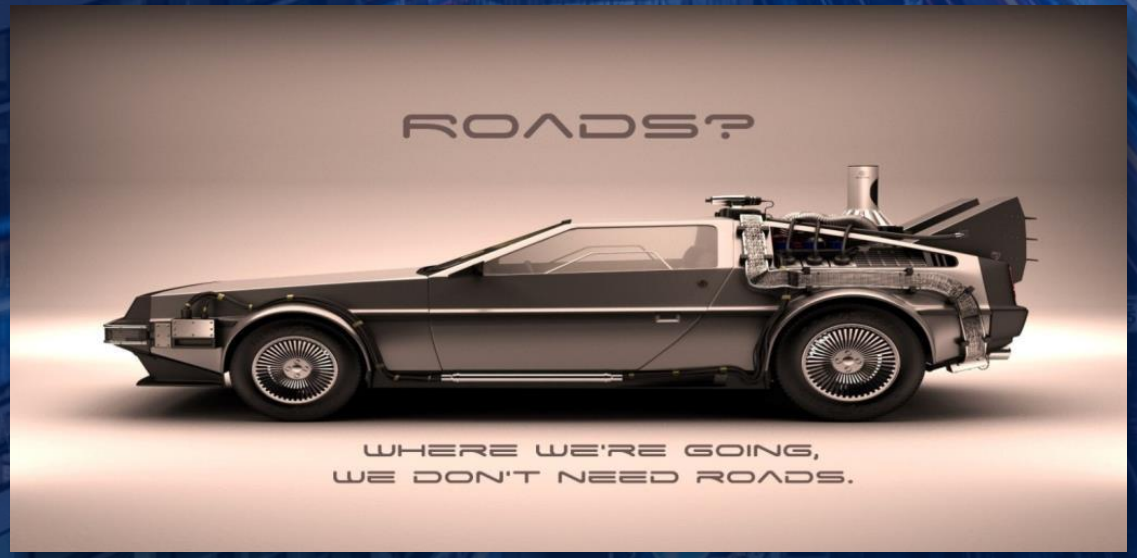
SERDP DOD · EPA · DOE

ESTCP

# Non-Target Analysis

## LC-QToF-MS

Liquid Chromatography
Quadrupole Time of Flight
Mass Spectrometry




Targeted Analysis

Suspect Screening Analysis

Non-Targeted Analysis

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# Targeted PFAS

**All Matrices – Up to 80 Analytes**

**Strengths:** Selectivity

Sensitivity at ~1-5ppt

Can be used for risk assessment

**Weaknesses:** Limited list of compounds

# TOP Assay

**All Matrices – Oxidizable Precursors**

**Strengths:** Sensitivity at ~1-5ppt

Specific to 'unknowns' with potential to convert to risk drivers

**Weaknesses:** Not specific

Does not complete a mass balance


# Non-Target Analysis

**All Matrices – Unknowns**

**Strengths:** Ability to identify 'unknowns' with specificity

Ability to conduct novel compound identification

**Weaknesses:** Limited to current libraries

Limited quantitation

# Total Organic Fluorine

**All Matrices – Organic Fluorine**

**Strengths:** Closest to a mass balance

**Weaknesses:** Sensitivity at ~1ppb

No selectivity



https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research

# THE NEXT FRONTIER

## Sub-ppt Reporting Limits

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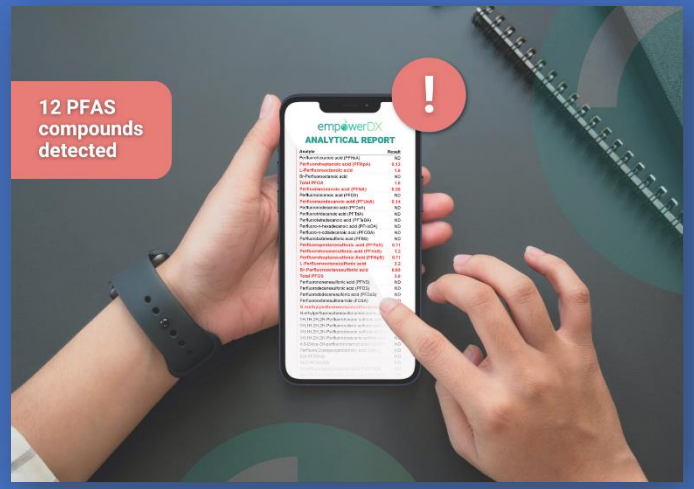
# PFAS in Human Serum / Blood


**PFAS analysis from a single drop of blood, sampled by the end user**

# Ultra-Low Level PFAS

## 7500 LCMSMS


CA PFOA: 0.007ppt
CA PFOS: 1ppt
MN PFOS: 0.05ppt
EPA HA PFOA: 0.004 ppt
EPA HA PFOS: 0.02 ppt
EPA HA GenX: 10 ppt
EPA HA PFBS: 2000 ppt

## What can it do?

- Direct injection valid for 70+ compounds
- 2ppt reporting limits with standard volumes of 250mLs or less
- Sub-ppt analysis in our sights

# QUESTIONS?

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717-799-0439

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