In-depth Characterization of PFAS in Wastewater, a More Comprehensive Analysis

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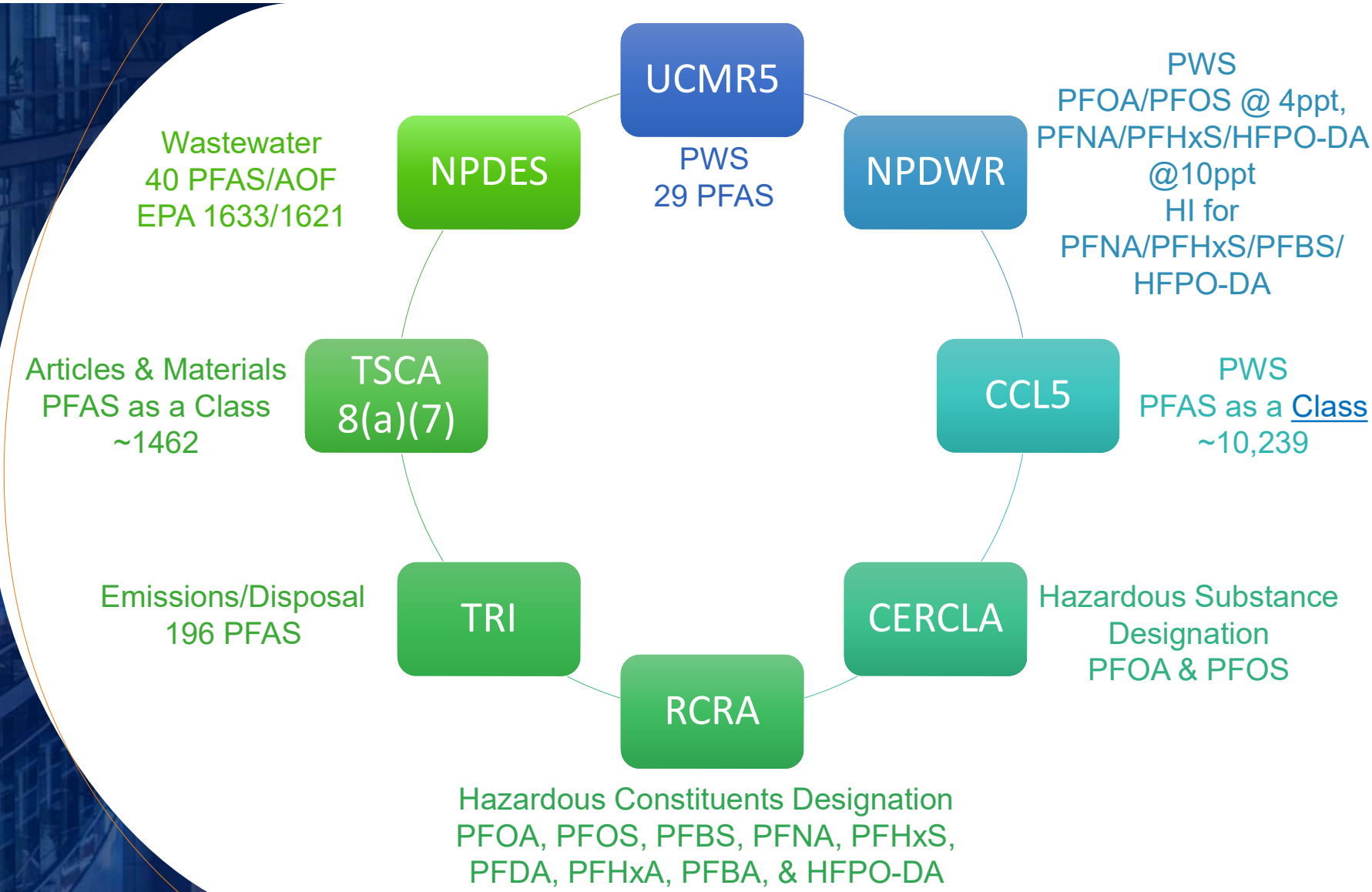
REGULATORY LANDSCAPE

VARIED APPROACH



Key Regulations – ADOPTED

Safe Drinking Water Act

Effective June 25, 2024

- MCLs for PFOA/PFOS at 4 ppt, PFHxS/PFNA/GenX at 10 ppt
- PWSs required to monitor quarterly for first 3 years, compliance required after 5 years
- UCMR5 monitoring for 29 PFAS underway through 2025

CERCLA

Effective July 8, 2024

- Order investigation and remediation of PFOA/PFOS, including cost recovery;
- Re-open closed sites;
- Private parties have cause of action for cost recovery; and
- PFOA/PFOS included in the scope of Phase 1s to satisfy the AAI rule

TSCA

Effective Sept 18, 2023

- Manufacturers and importers required to report regarding PFAS uses, production volumes, disposal, exposures, and hazards
- TRI reporting annually for 196 PFAS, no more de minimis level as of Oct 2023

Key Regulations – IN PROGRESS

Clean Water Act

State Implementation

- EPA issues guidance to state permit writers and pretreatment authorities to address PFAS
- States begin adding 40 PFAS by 1633 to permits in 2024
- EPA develops Effluent Limitation Guidelines

RCRA

Proposed Rule

- PFOA, PFOS, PFBS, PFNA, PFHxS, PFDA, PFHxA, PFBA, & HFPO-DA proposed as RCRA Hazardous Constituents
- Subject to Corrective Action at hazardous waste treatment/ storage/disposal facilities

Clean Air Act

In Development

- EPA publishes OTM-45/50 to measure PFAS in source emissions
- EPA publishes destruction guidance
- EPA lays groundwork to list PFAS as HAPs (a prerequisite to require them in air permits)


WASTEWATER

Effluent Guidelines Program

Program Plan 15

Was with OMB for review…

- ✓ Propose limits for chemical, plastics, synthetic fiber manufacturers (NDAA June 2024)
- ✓ Expand Textiles study (NDAA June 2025) *public comment reopened*
- ✓ Revise ELGs for Landfills category (NDAA June 2025)
- ✓ Not pursuing action for the Electrical and Electronic Components Category (NDAA June 2025)
- ✓ Will monitor the Pulp, Paper, and Paperboard Category and Airports
- ✓ Leather tanning/finishing, paint formulating, and plastics molding categories (NDAA December 2026)

NPDES News

https://www.epa.gov/system/files/documents/2023-01/11143_ELG%20Plan%2015_508.pdf#page=48

https://www.epa.gov/system/files/documents/2023-01/11143_ELG%20Plan%2015_508.pdf

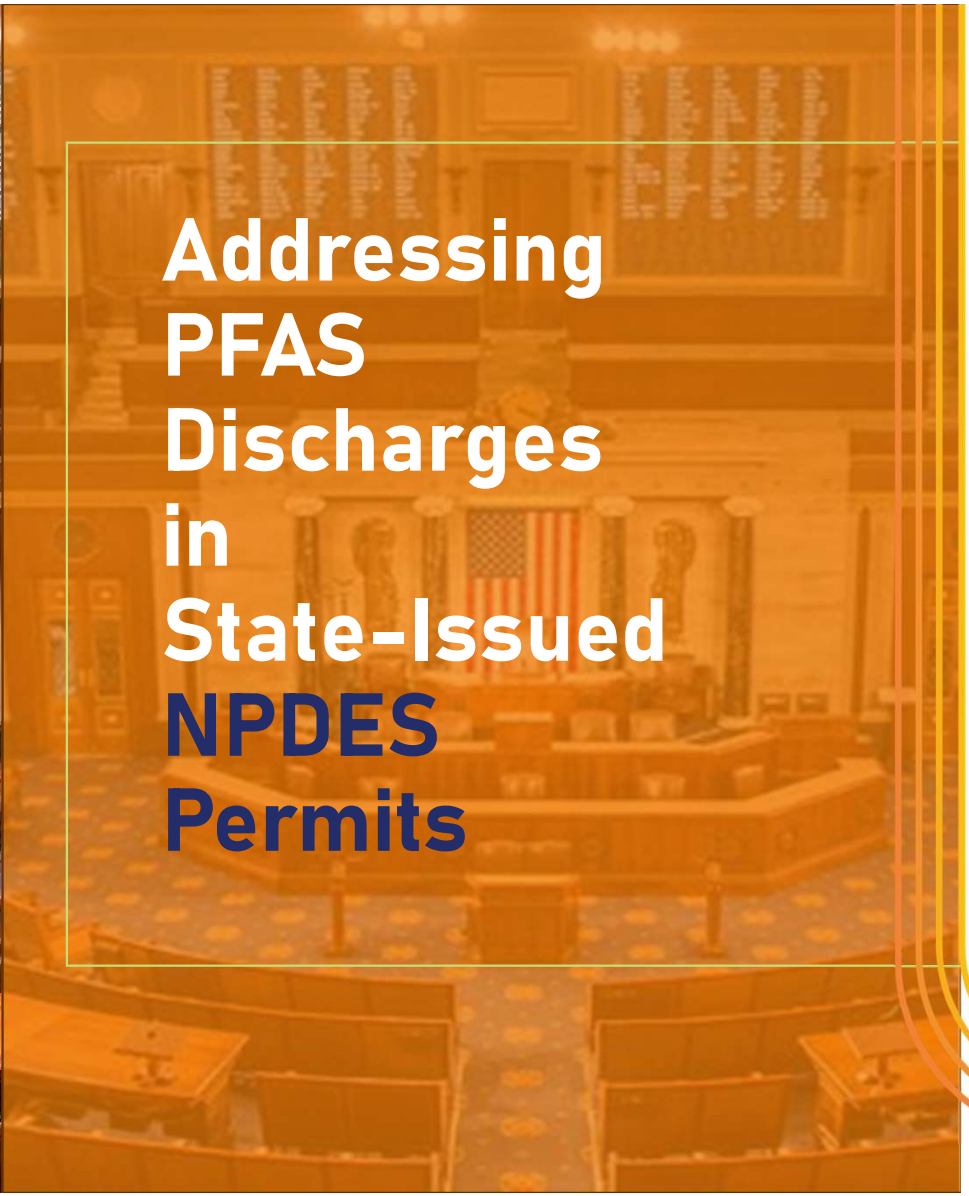
2023 NDAA, SEC. 5883. CLEAN WATER ACT EFFLUENT LIMITATIONS GUIDELINES
The Administrator shall publish in the Federal Register effluent limitations guidelines and standards for priority industry categories, not later than the following dates…

Effluent Guidelines Program

Program Plan 15

- ✓ EPA to initiate a Publicly Owned Treatment Works (POTW) influent study of PFAS
- ✓ Information Collection Request (ICR) initiated. Submitted to OMB for review
- ✓ Public comments closed May 28, 2024. *EPA reopened public comments in Oct 2024 for additional 30 days*
- ✓ Collect data in *2025-2026*
- ✓ Sampling and analysis via EPA 1633 and 1621

https://www.govinfo.gov/content/pkg/FR-2024-03-26/pdf/2024-06408.pdf



Addressing PFAS Discharges in State-Issued NPDES Permits

EPA issues guidance to state permit writers and pretreatment authorities to address PFAS in 2022 and 2025

EPA United States Environmental Protection Agency

Implementing Case-by-Case Technology-Based Effluent Limitations in NPDES permits for Pollutants of Emerging Concern

A "How-To" for NPDES Permit Writers

Tools and Resources

Example Permit Language, State and Local PFAS Strategies, and Other PFAS Permitting Resources

BMP and Source Reduction Resources

- Fact Sheet: Pollution Prevention Strategies for Industrial PFAS Discharges (pdf) (713.1 KB)

https://www.epa.gov/npdes/industrial-wastewater#pfas

RISK ASSESSMENT PFOA & PFOS IN BIOSOLIDS

https://www.epa.gov/biosolids/draft-sewage-sludge-risk-assessment-perfluorooctanoic-acid-pfoa-and-perfluorooctane

EPA United States Environmental Protection Agency

EPA Releases Draft Risk Assessment to Advance Scientific Understanding of PFOA and PFOS in Biosolids

January 14, 2025

Risk assessment only. First step of many towards any regulation.

Modeling only of hypothetical human health risks.

Focused on a specific and narrow population i.e. those living on or near impacted properties

Modeling suggest under certain conditions, land-applying sludge with a detectable level (≥1 ppb) of PFOA or PFOS could result in human health risks exceeding the agency's acceptable thresholds.

METHOD OPTIONS

Where to Begin?

WHAT WILL THE DATA BE USED FOR

Developing a Conceptual Site Model

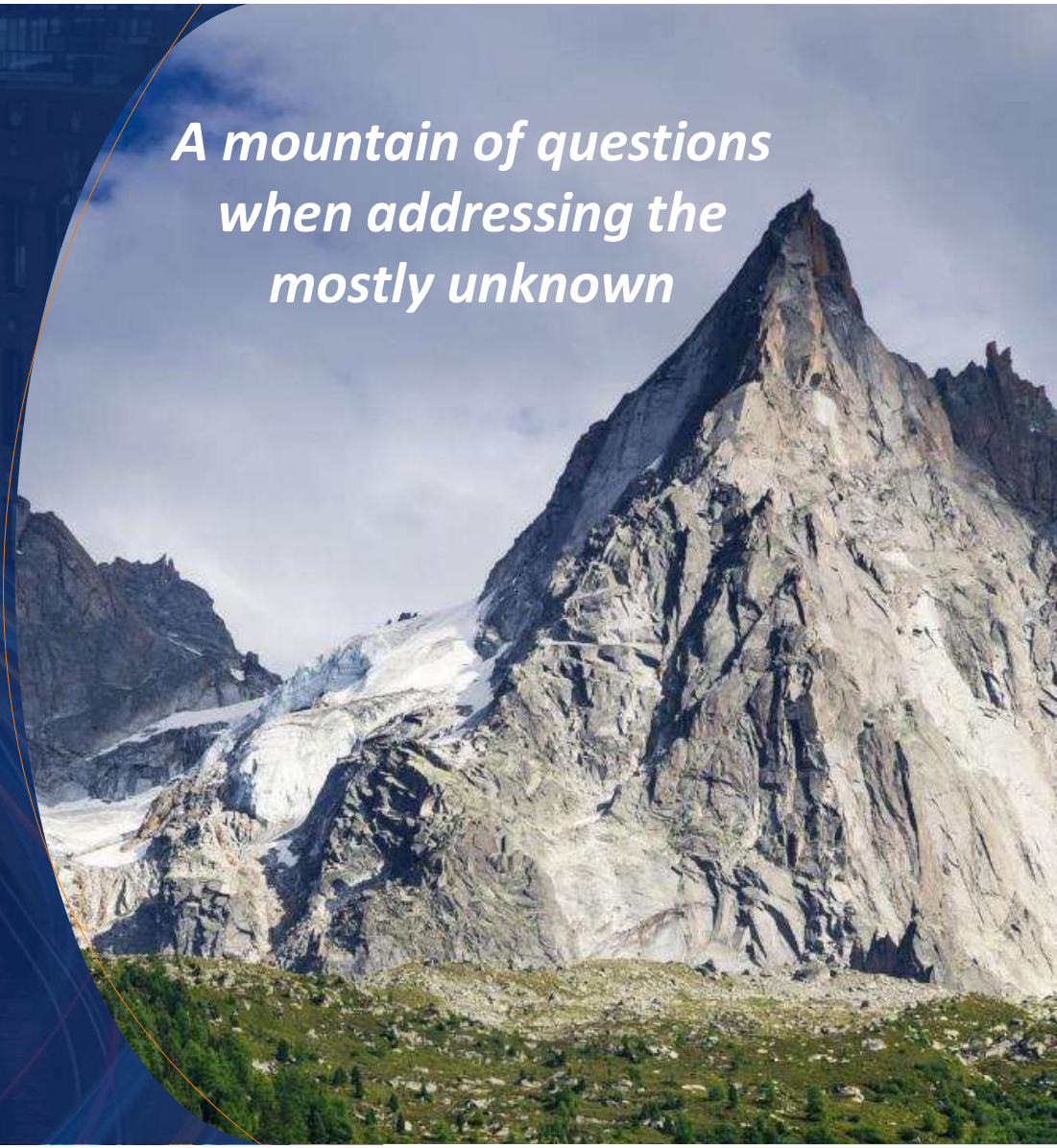
Determining the extent of contamination

Investigating sources of contamination

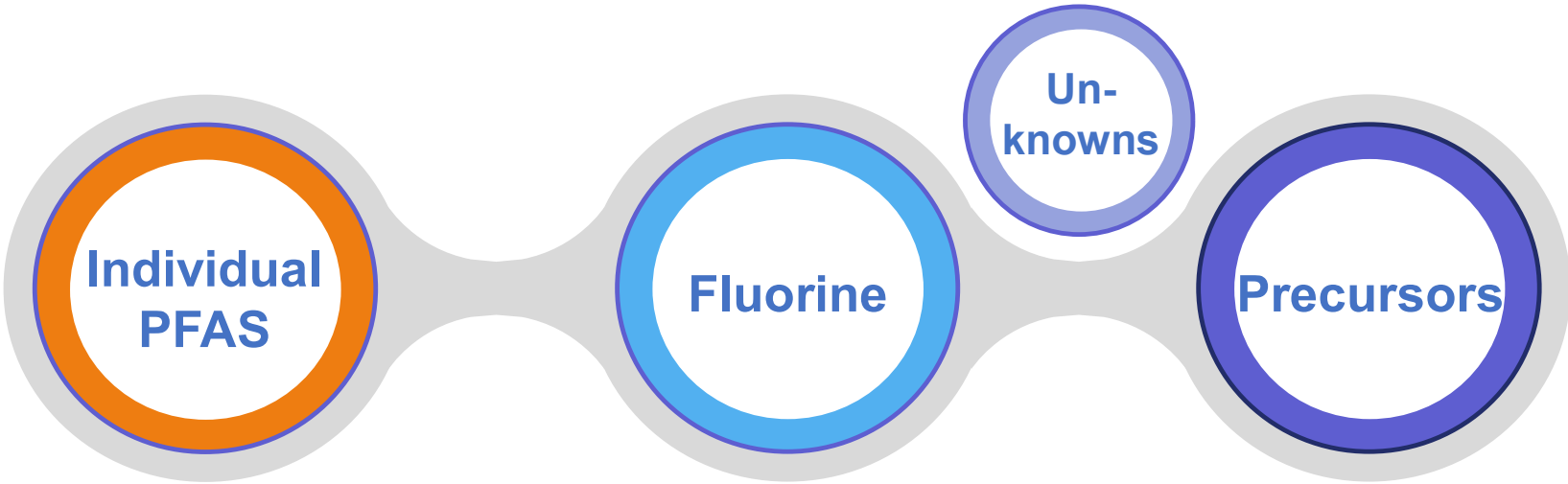
Assessing human health impacts

Implementing a remediation plan

Assessing efficacy of a treatment system



Analyzing for PFAS We've got options



Targeted PFAS by LC/MS/MS
537.1, 533, 537M & 1633A

Up to ~100
non-polymer PFAS

Fluorine by CIC
CIC-TOF & EPA 1621

Total Fluorine
Extractable Organic Fluorine (EOF)
Adsorbable Organic Fluorine (AOF)

Precursors by LC/MS/MS
"TOP Assay"

Unknown PFAA
precursors

CONVENTIONAL TOOLS

TARGETED ANALYSIS

The analysis of specific target analytes with known CAS numbers and analytical reference standards

- EPA Standard Methods
- ASTM Methods
- User-Defined Methods

  - Regulatory derived target analyte lists
  - Laboratory derived target analyte lists
  - Site-specific target analyte lists

EPA Methods

EPA 537.1(2020)

EPA 533 (2019)

EPA 8327 (2021)

EPA 1633A (2024)

User-defined Methods

"537 / 1633A Modified"

Laboratory SOP

EPA PFAS Methods

Drinking Water

533	537.1
Drinking Water	Drinking Water
Branched/Linear Isomers -YES	Branched/Linear Isomers -YES
Compounds: 14 the same / 15 unique	Compounds: 14 the same / 4 unique
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

EPA Method for NPW/Solids

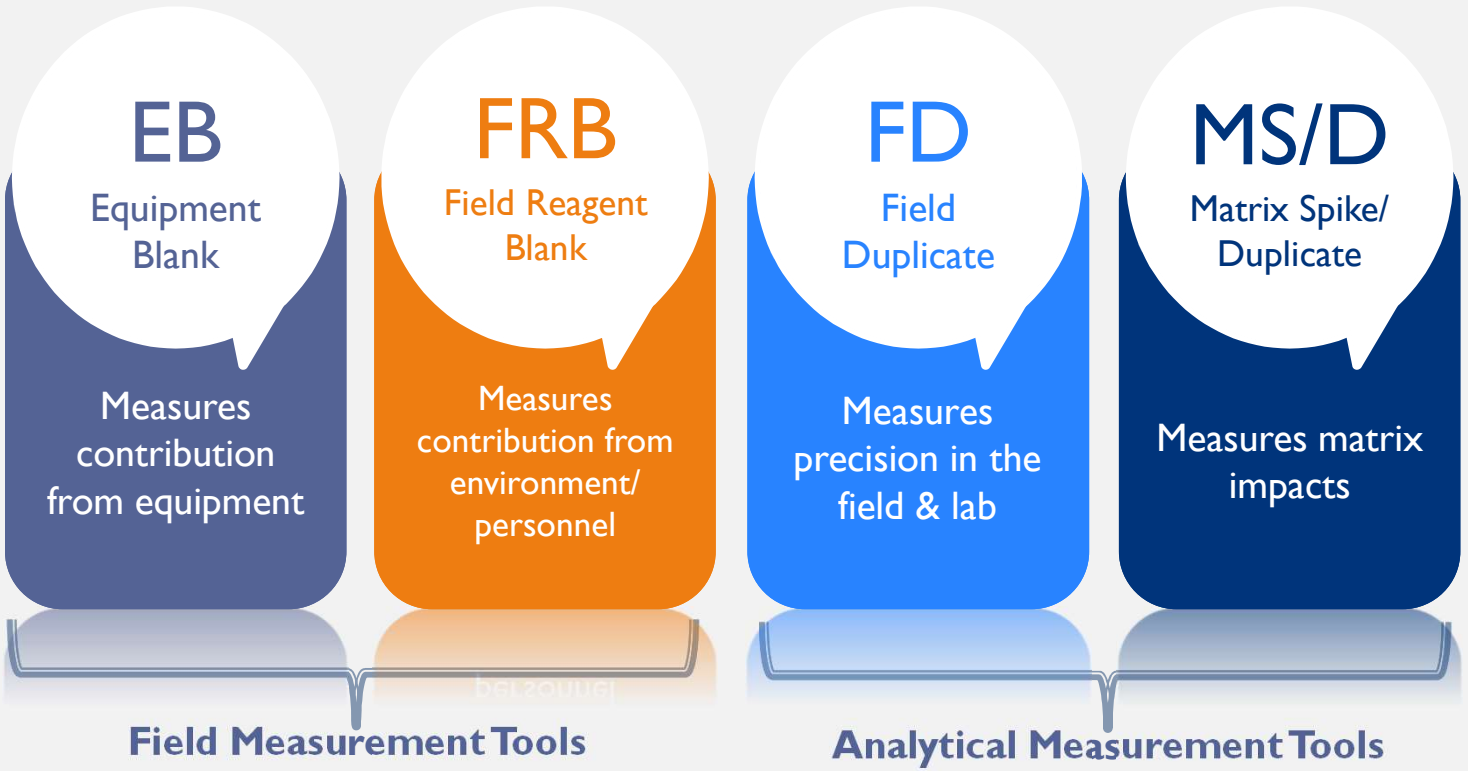
EPA 1633A

Final version released in Dec 2024, NOT PROMULGATED

- Targeted Analysis of 40 PFAS
- Non-Potable Water, Soil, Sediment, Biosolids, Leachate, Tissue
- WAX Solid Phase Extraction (SPE)
- LCMSMS with Isotope Dilution Quantitation
- Detection limits: 0.4-10 ng/L (aqueous) / 0.05-2 ng/g (solids)
- Multi-Lab Validated

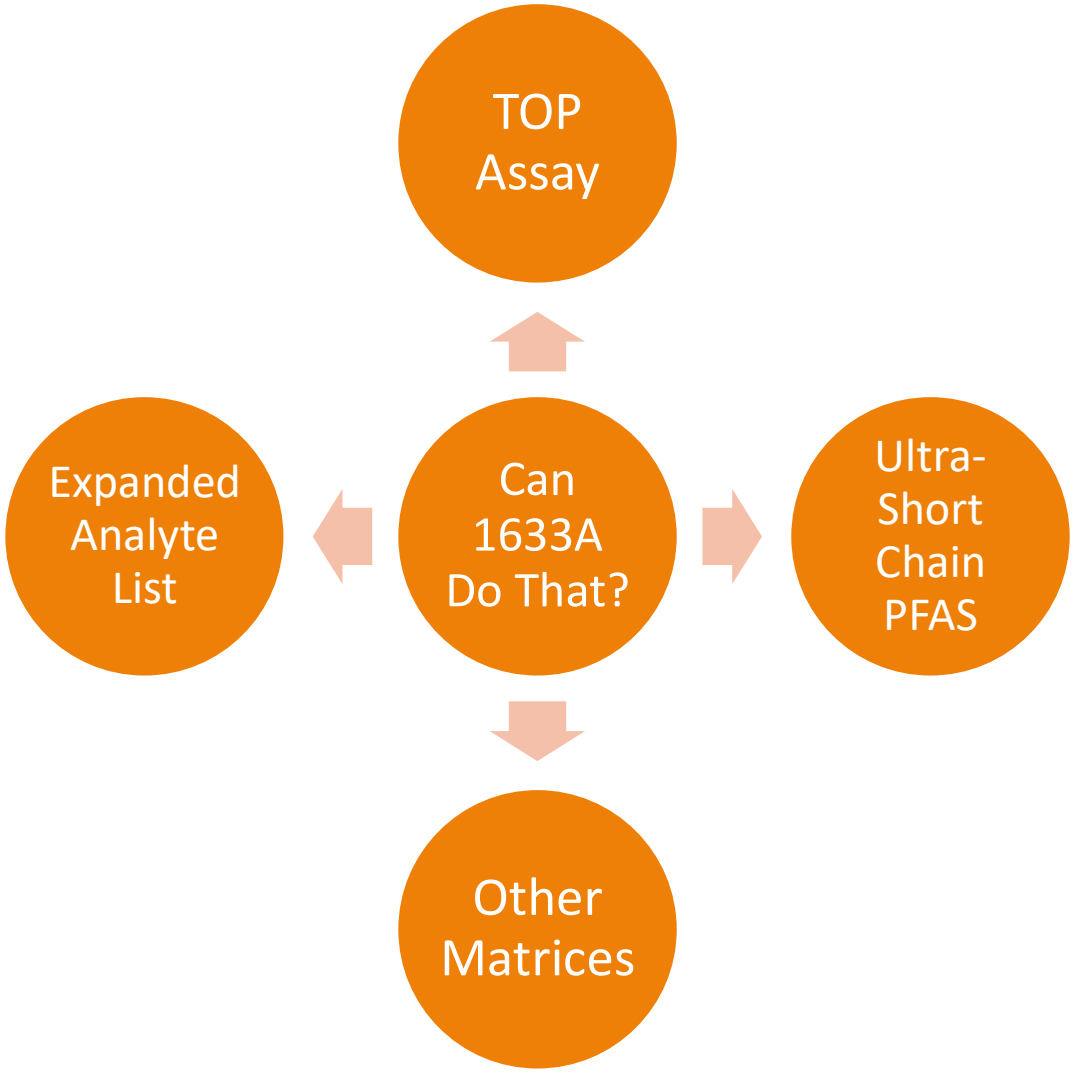
https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

Recommended Field Quality Control



FIELD QC

Scope of 1633 Testing



LCMSMS/GCMSMS Analysis

Compounds Included in EPA 1633A

- 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 1633A

- 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)

EMERGING TECHNOLOGIES

The analysis of analytes or matrices beyond what is supported by standard published EPA methods

- Draft or Non-Standard Methods
- User-Defined Methods
  - Program specific targets
  - Screening applications
  - Litigation derived targets

PFAS in Air

Source & Ambient

Neutral PFAS

FTOHs
FTAcs
FTMAcs

Ultra-Shorts

C2-C4

NON-TARGETED TECHNOLOGIES

The analysis of analytes without known CAS numbers or analytical reference standards, or the analysis of a proxy analyte(s)

- Draft or Non-Standard Methods
- User-Defined Methods
  - Program specific targets
  - Screening applications
  - Litigation derived targets

TOP Assay

Total Oxidizable Precursors

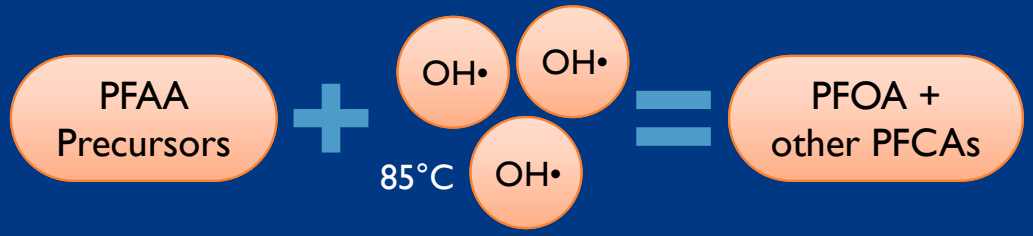
AOF/EOF/TF

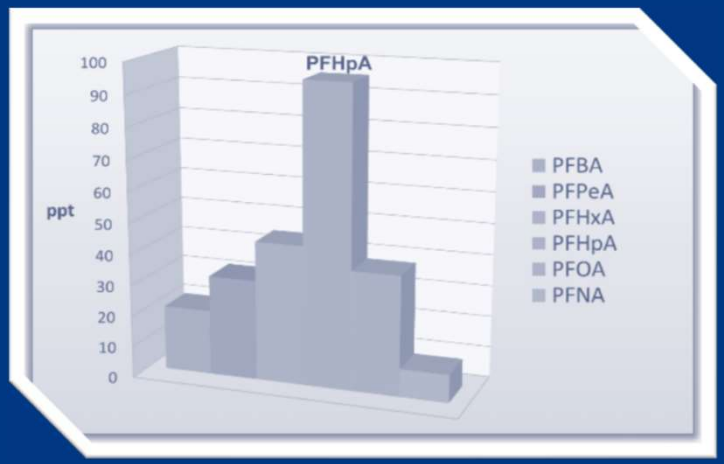
Adsorbable Organic Fluorine
Extractable Organic Fluorine
Total Fluorine

NTA

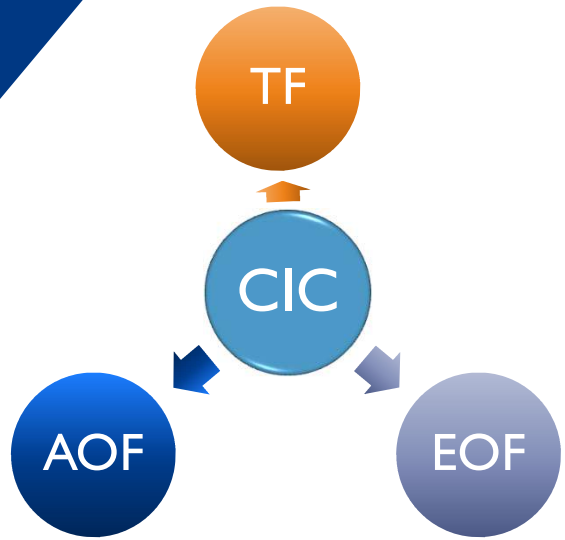
Non-Target Analysis

Total Oxidizable Precursors
TOP Assay





TOP Conversion of 8:2 FTS



CIC: Combustion Ion Chromatography

Total Organofluorine Analysis

EPA Method 1621

Final version released in Dec 2024, NOT PROMULGATED

- Adsorbable Organic Fluorine (AOF)
- Screening analysis for 'Total PFAS'
- Applies to aqueous samples
- Multi-lab validated

- Adsorbs contaminants onto granular activated carbon, removal of inorganic fluoride with nitrate solution, followed by combustion of the carbon
- Method Detection Limit: 1.5 µg F-/L

https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

Non-Target Analysis

LC-QToF-MS

Liquid Chromatography
Quadrupole Time of Flight
Mass Spectrometry

Targeted Analysis

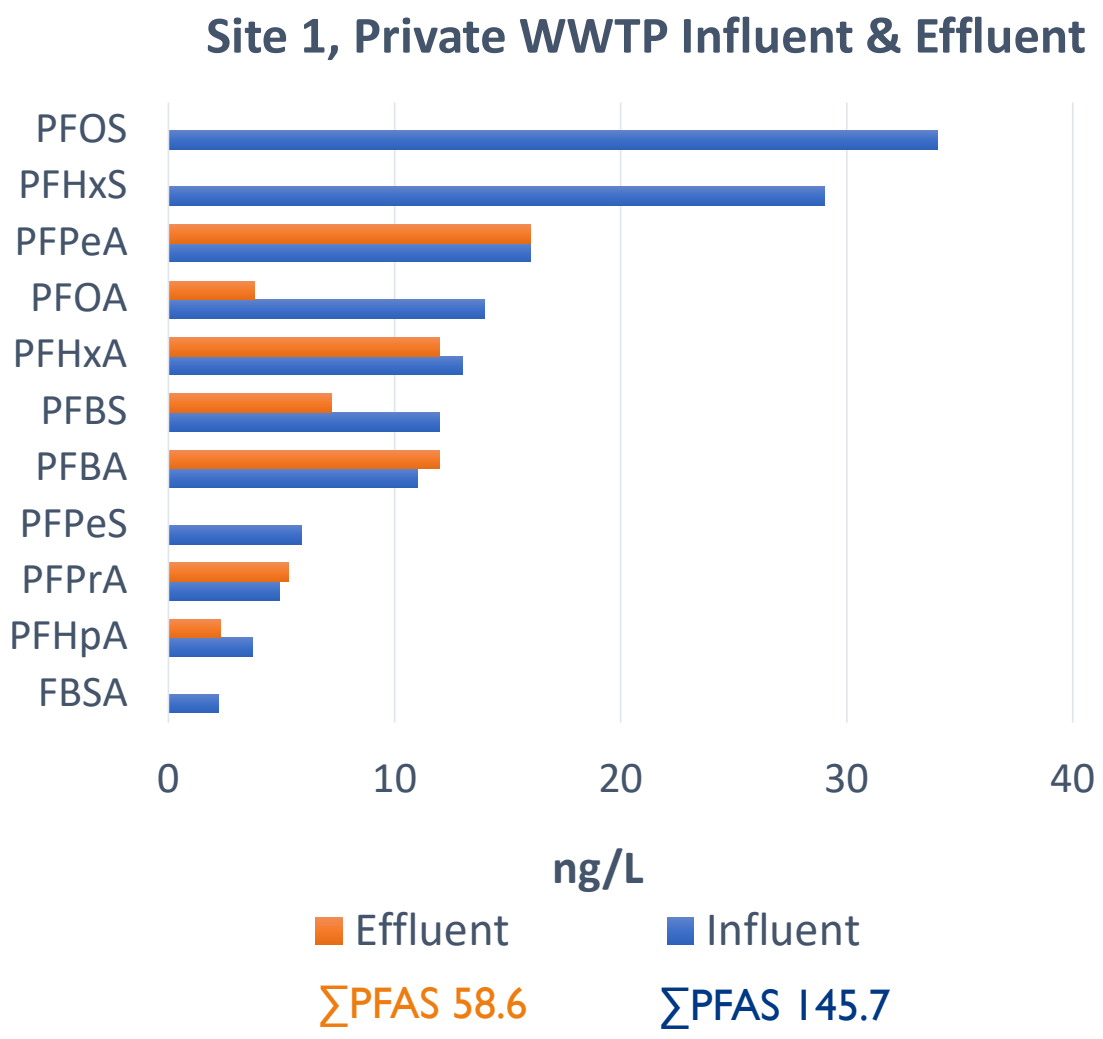
Suspect Screening Analysis

Non-Targeted Analysis

COMPARING ANALYTICAL TOOLS

WWTP Study

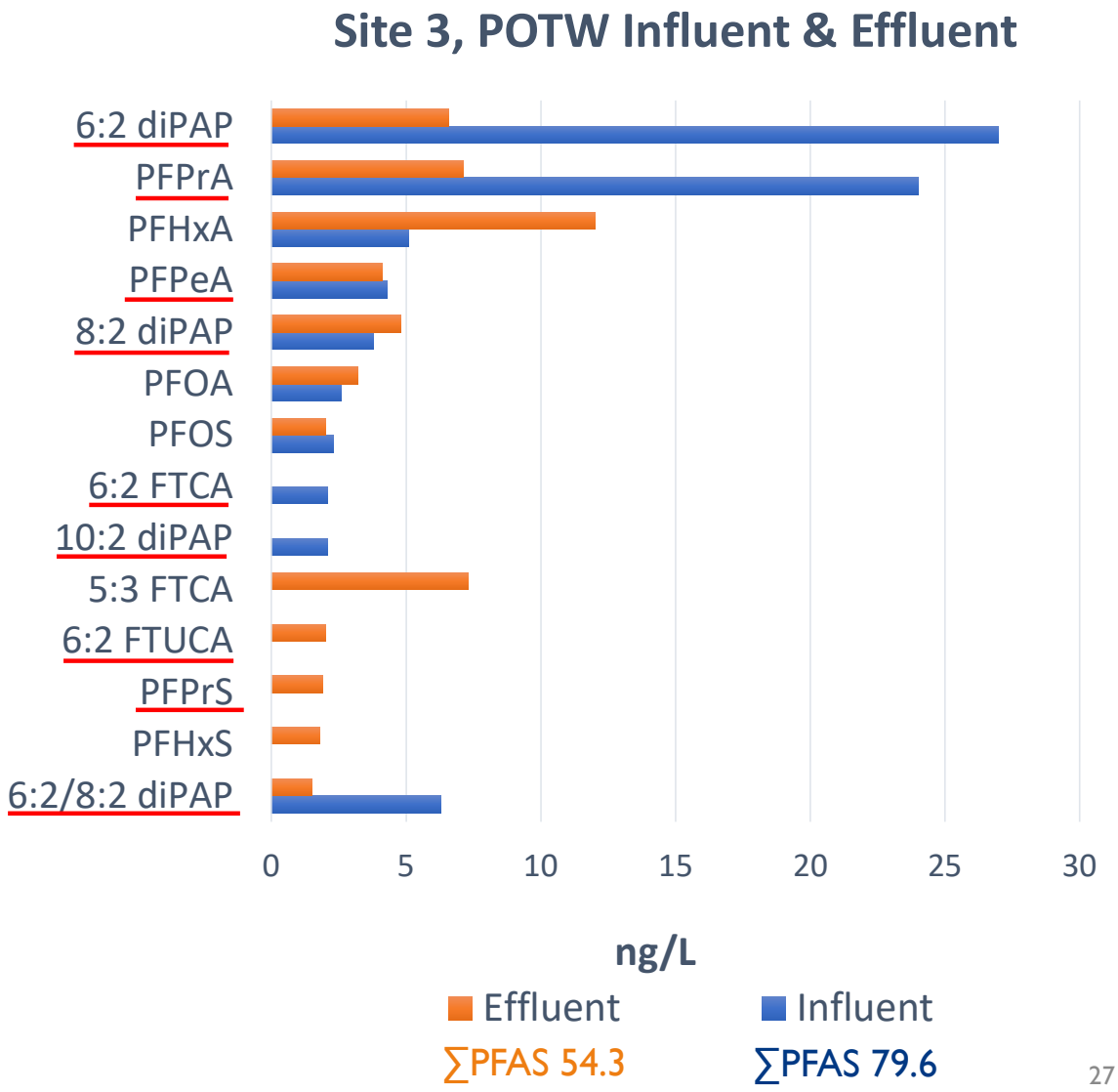
Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	1,300	110
Influent Dup	1,300	120
Effluent	1,500	220
Effluent Dup	1,100	230



AOF Equivalent for these samples is 63%

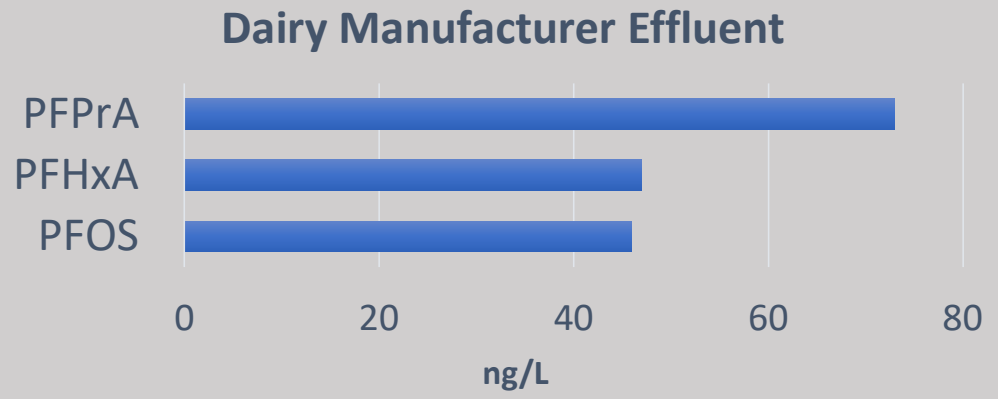
POTW

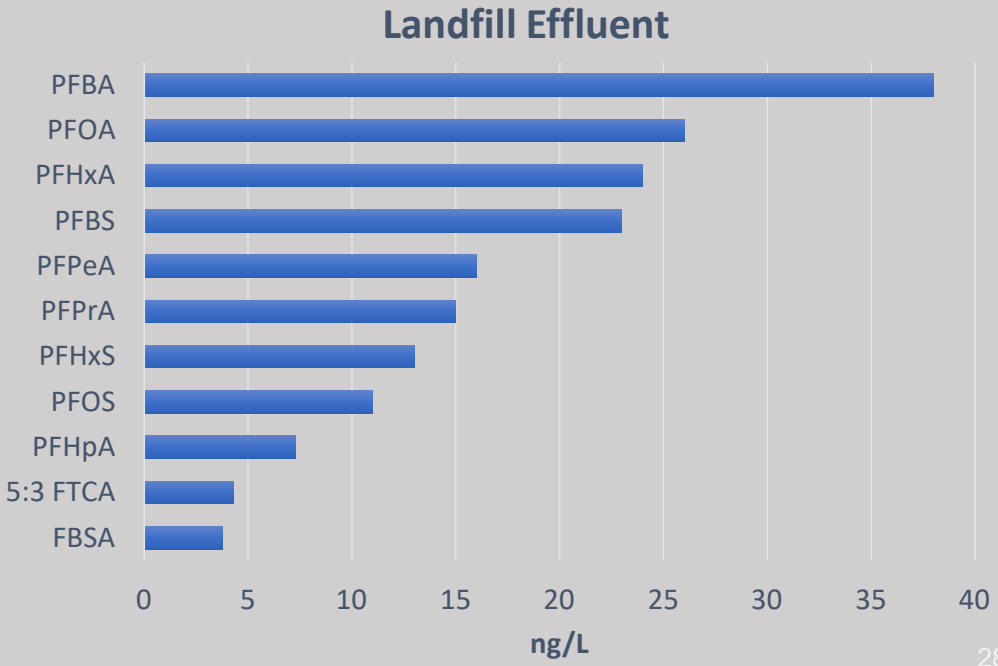
Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	5,200	170
Influent Dup	4,600	170
Effluent	3,100	94
Effluent Dup	1,800	85



WWTP Study
Site 4 – Industrial Discharge

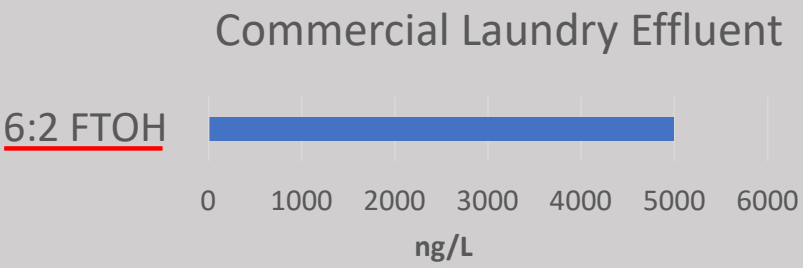
Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Dairy Manufacturer, Effluent	33,000	360
Landfill, Effluent	1400	100

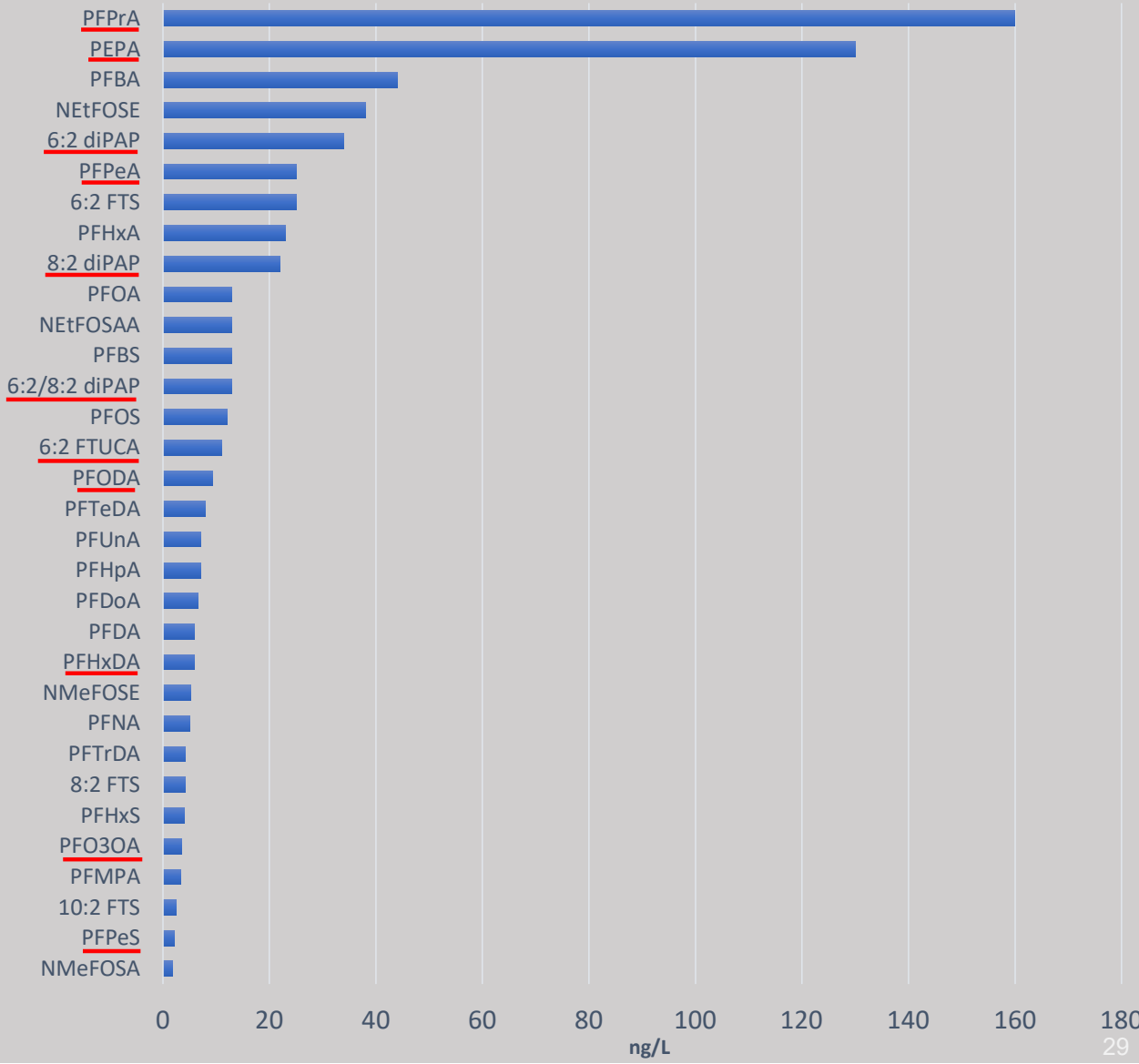




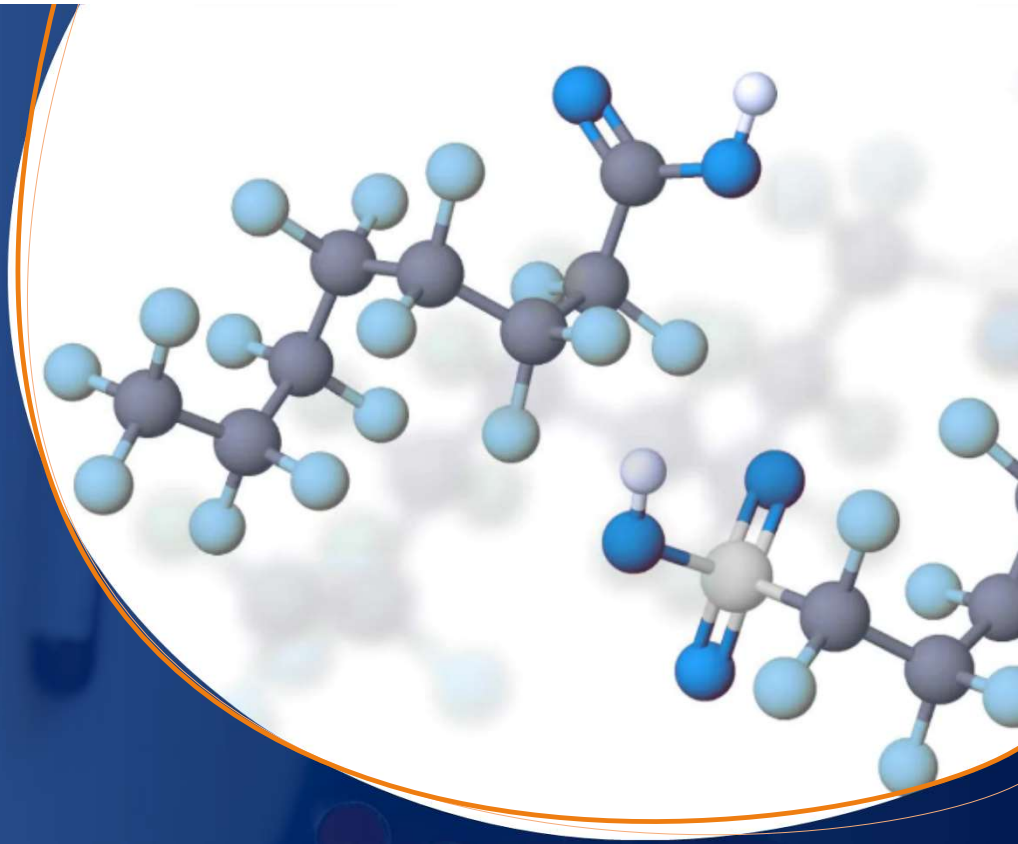
Site 4 – Industrial Discharge

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Effluent Commercial Laundry	39,000	6,100





ASSESSING PFAS DESTRUCTION



DESTRUCTION

Destruction

"Mineralization of PFAS" means all PFAS, not just the few PFAS routinely measured for in environmental matrices

Demonstration

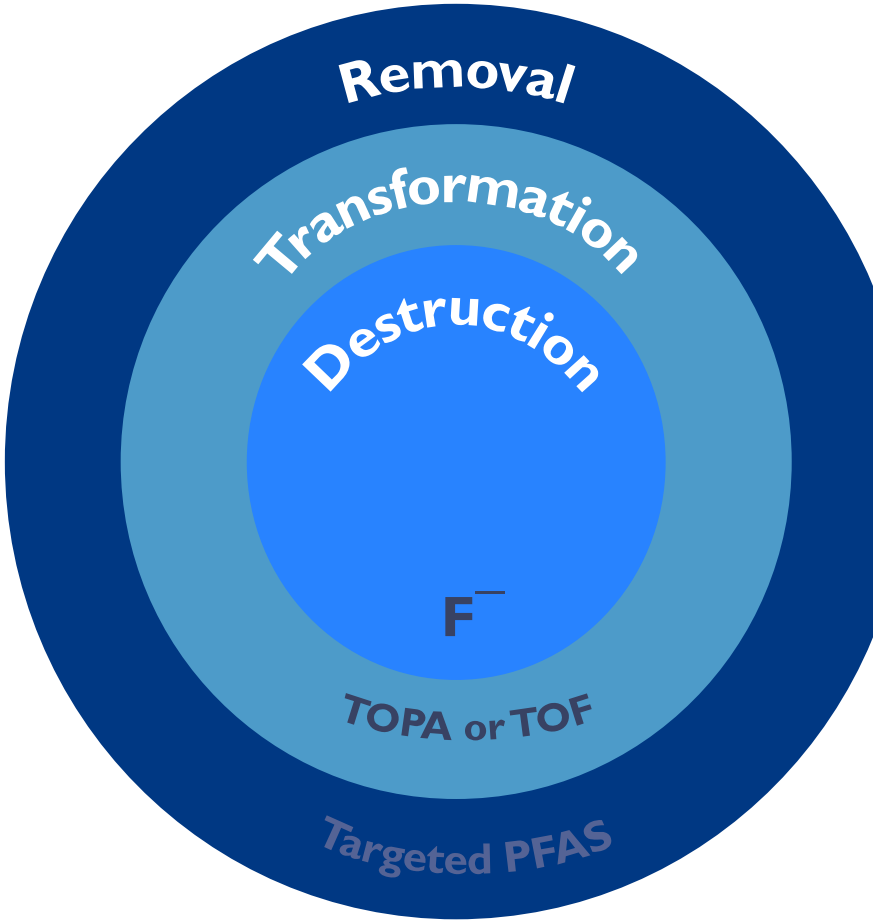
What analytical tools are available to demonstration destruction is complete?

Mass Balance

System-wide mass balances for *all* PFAS not yet achieved; limiting factor is the analytical chemistry

Current Analytical Tools

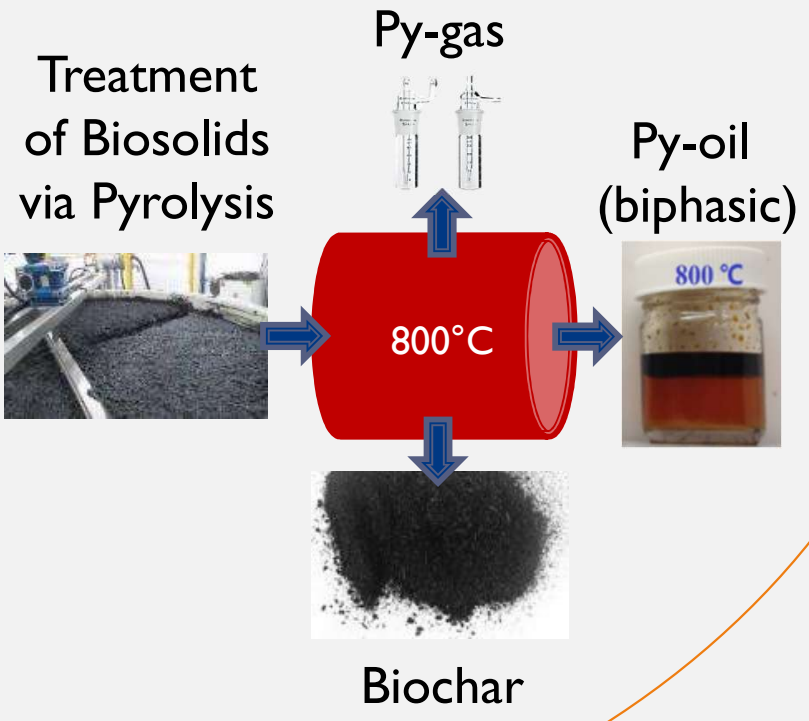
- EPA 1633A for solid/aqueous:
  - **40 anionic PFAS**
  - **C4-C14**
- EPA OTM-45/50 for gaseous
  - **50 anionic, C4-C14 PFAS**
  - **30 non-polar, C1-C8 PFAS**
- TOF for solid/aqueous/gaseous:
  - **Total Oxidizable Precursors (TOP)**
  - **Total Fluorine (TF)**
  - **Total Organic Fluorine (TOF)**



Matrix Specific Challenges

Each matrix requires accurate measurements to determine if complete destruction is occurring or if products of incomplete destruction are generated

These matrices may be biphasic or corrosive, and complex. All requiring tailored analytical techniques to ensure maximum extraction efficiency and matrix mitigation is achieved



Compound Specific Challenges

Compounds Included in EPA Draft 1633 (RLs = 2-5ng/L)		Target Compounds Not Part of Draft 1633 (RLs = 2-20ng/L)	
Perfluorobutanoic acid (PFBA)	NEtFOSA	Perfluoro-n-octadecanoic acid (PFODA)	PEPA
Perfluoropentanoic acid (PFPeA)	NMeFOSA	Perfluoro-n-hexadecanoic acid (PFHxDA)	MTP
Perfluorohexanoic acid (PFHxA)	NMeFOSAA	10:2 FTS	PS Acid
Perfluoroheptanoic acid (PFHpA)	NEtFOSAA	6:2 FTCA	Hydro-PS Acid
Perfluorooctanoic acid (PFOA)	NMeFOSE	8:2 FTCA	R-PSDA
Perfluorononanoic acid (PFNA)	NEtFOSE	10:2 FTCA	Hydrolyzed PSDA
Perfluorodecanoic acid (PFDA)	4:2 FTS	6:2 FTUCA	R-PSDCA
Perfluoroundecanoic acid (PFUnA)	6:2 FTS	8:2 FTUCA	6:2 diPAP
Perfluorododecanoic acid (PFDoA)	8:2 FTS	10:2 FTUCA	8:2 diPAP
Perfluorotridecanoic acid (PFTriA)	9Cl-PF3ONS	PFECHS	6:2/8:2 diPAP
Perfluorotetradecanoic acid (PFTeA)	11Cl-PF3OUdS	PFPrS	12:2 FTOH
Perfluorobutanesulfonic acid (PFBS)	DONA	PFPrA	10:2 FTOH
Perfluoropentanesulfonic acid (PFPeS)	HFPO-DA (GenX)	PFMOAA	8:2 FTOH
Perfluorohexanesulfonic acid (PFHxS)	3:3 FTCA	PFECAG	7:2 FTOH
Perfluoroheptanesulfonic Acid (PFHpS)	5:3 FTCA	PFO4DA	6:2 FTOH
Perfluorooctanesulfonic acid (PFOS)	7:3 FTCA	PFO3OA	4:2 FTOH
Perfluorononanesulfonic acid (PFNS)	NFDHA	PFO2HxA	10:2 FTAc
Perfluorodecanesulfonic acid (PFDS)	PFMBA	R-EVE	8:2 FTAc
Perfluorododecanesulfonic acid (PFDoS)	PFMPA	NVHOS	10:2 FTAcr
Perfluorooctanesulfonamide (FOSA)	PFEESA	Hydro-EVE Acid	8:2 FTAcr
		EVE Acid	6:2 FTAcr
		PFO5DA	4:2 FTAcr
		PMPA	

TARGETED ANALYSIS

Extraction media, columns, solvents, detectors, and instrument parameters used will minimize the range of PFAS identified, typically less than 100 PFAS like the ones listed in this table

Targeted PFAS

All Matrices – ~ 100 PFAS

Strengths: Selectivity Sensitivity at ~1-20ppt

Can be used for risk assessment

Weaknesses: Limited list of compounds

TOP Assay

All Matrices – Precursors

Strengths: Sensitivity at ~1-20ppt

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 & sensitivity

Total Organic Fluorine

All Matrices – Organic Fluorine

Strengths: Closest to a mass balance

Weaknesses: Sensitivity at ~1ppb

No selectivity

Potential for high bias from inorganic fluorine & low bias from sample prep

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THANK YOU

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