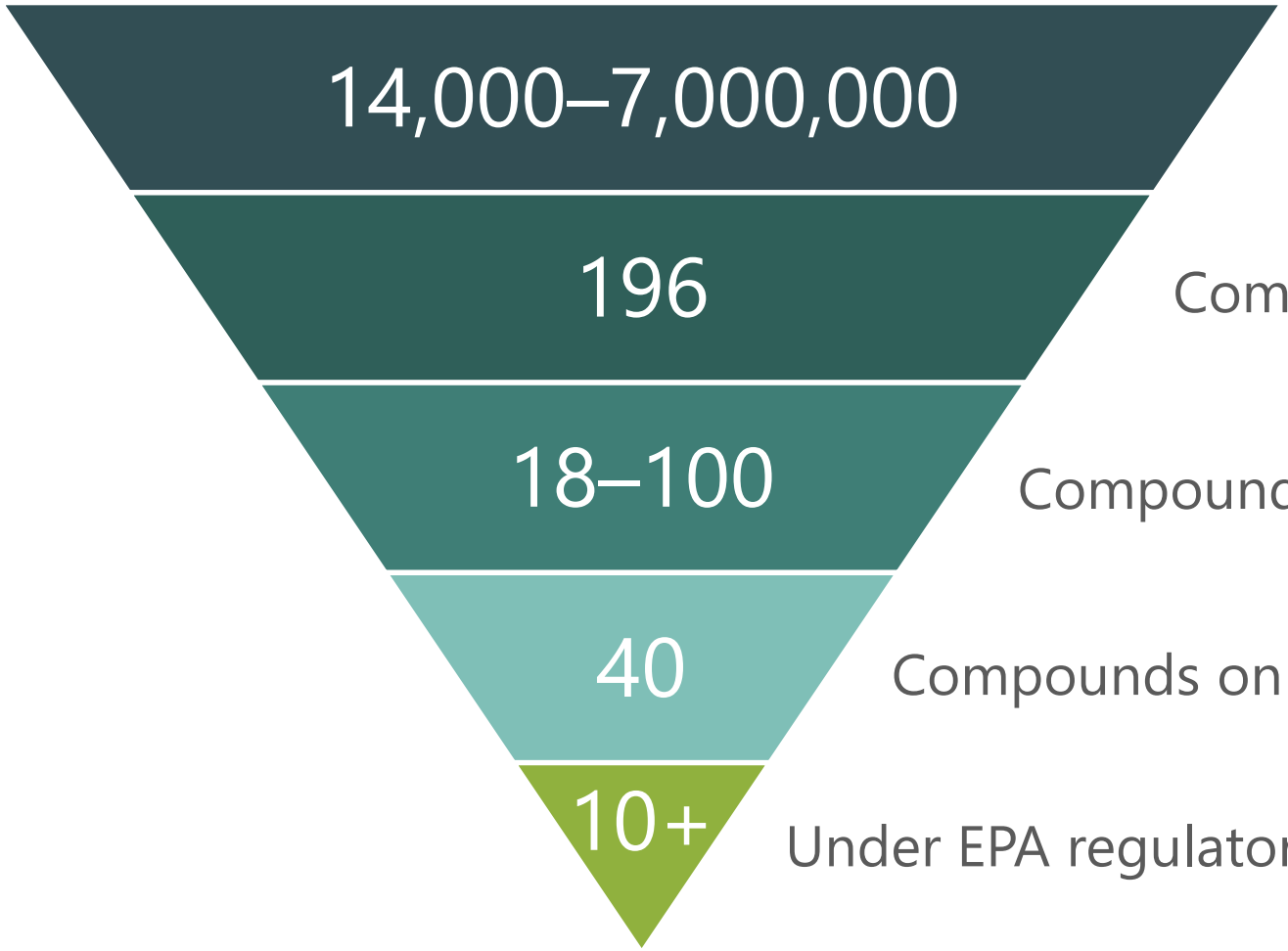
2025 WISCONSIN DNR PFAS EXTERNAL ADVISORY GROUP MEETING

Introduction to PFAS Forensics: Source Characteristics and Analytical Considerations

Presented by Sarah LaRoe, PhD, Anchor QEA

ANCHOR QEA

PFAS



PFAS compounds

Commercially available analytical standards*

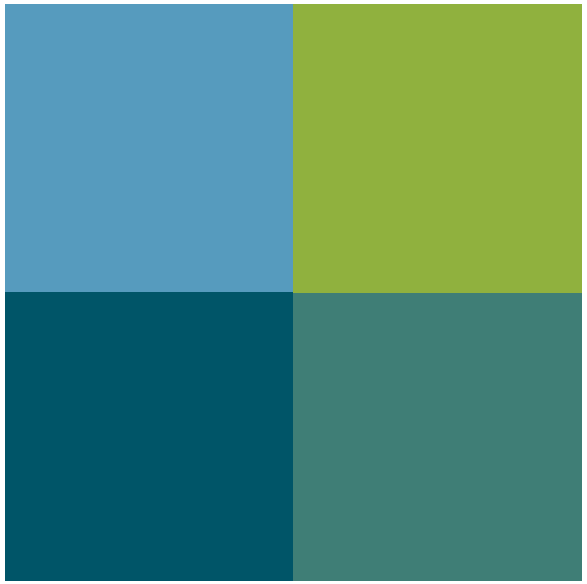
Compounds on commercial laboratory analyte lists

Compounds on EPA Method 1633A analyte list

Under EPA regulatory attention

*Estimated by Trier, X., S.J.P van-Leeuwen, G. Brambilla, R. Weber, and T.F. Webster, 2025. "The Critical Role of Commercial Analytical Reference Standards in the Control of Chemical Risks: The Case of PFAS and Ways Forward." *Environmental Health Perspectives* 133(1).

Forensics = Pattern Recognition



More Data =
More Unique Patterns

Types of Laboratory Analyses

Method 1633A

Target Analyses

Non-Target Analyses

Total Oxidizable Precursor (TOP)

Method 1621

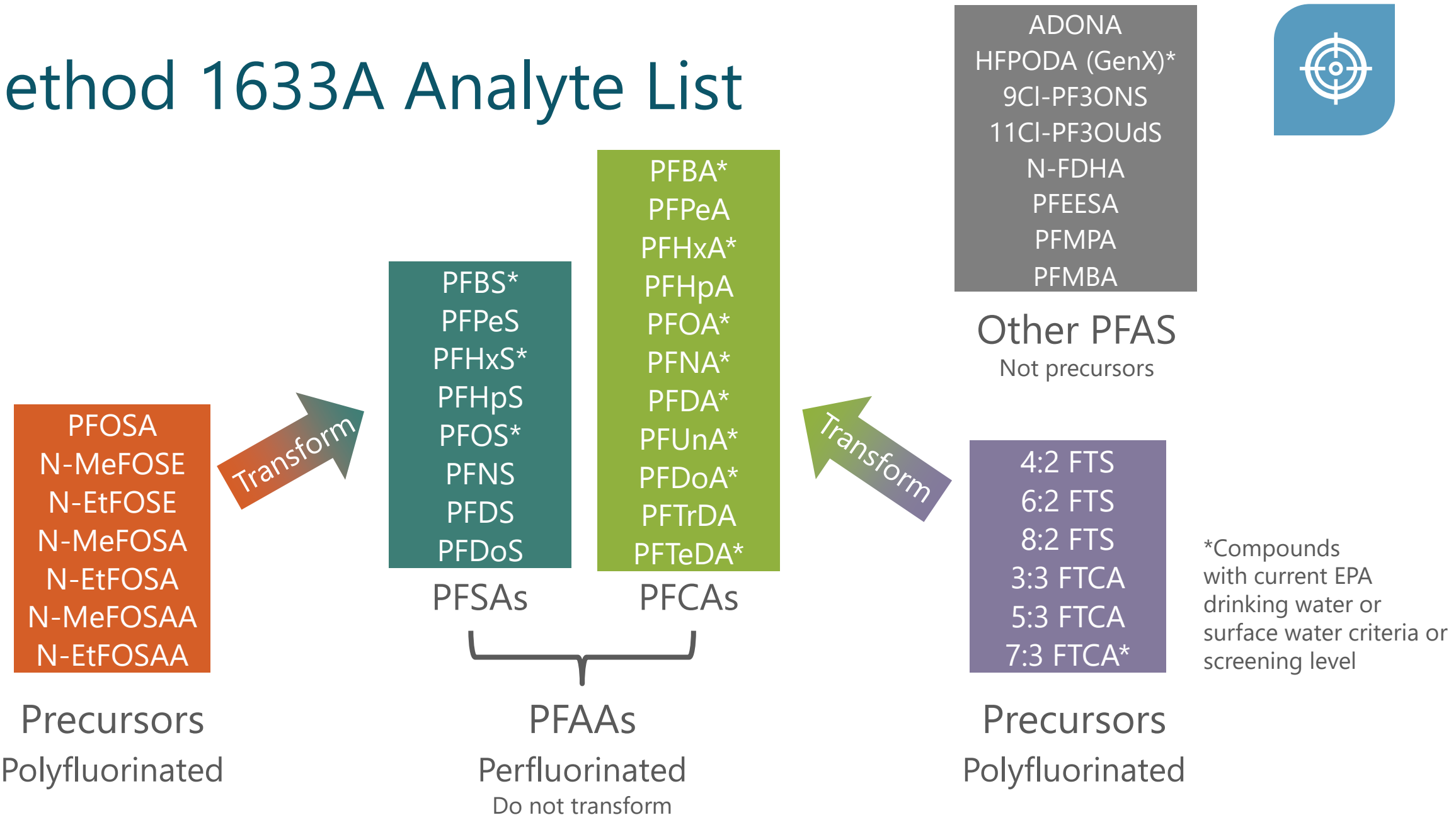
Total/Adsorbable Organic Fluorine (TOF)/(AOF)

Target Analysis

- Laboratory tests concentrations of a set list of analytes
- Selective and sensitive
- Limited by the number of analytical standards (comparison compounds)

Method	Number of PFAS
EPA 1633A	40
EPA 537/537.1	18
EPA 533	25
Alt. laboratory methods	Up to 100

Method 1633A Analyte List



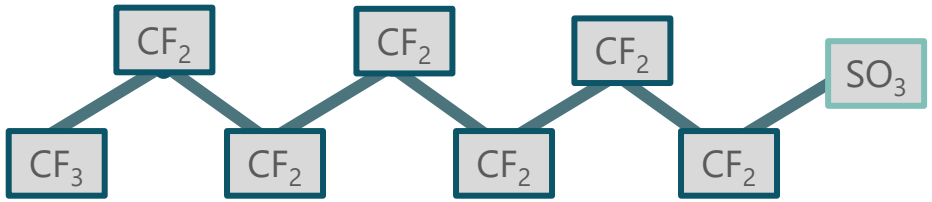
Types of Laboratory Analyses – Isomer Analysis

Target Analyses

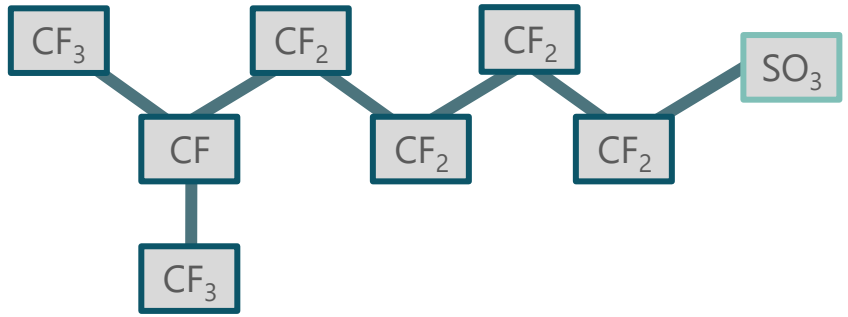
PFSAs: PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS

PFCAs: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFTeDA

PFAAs



Linear Arrangement



Branched Arrangement

Non-Target Analysis

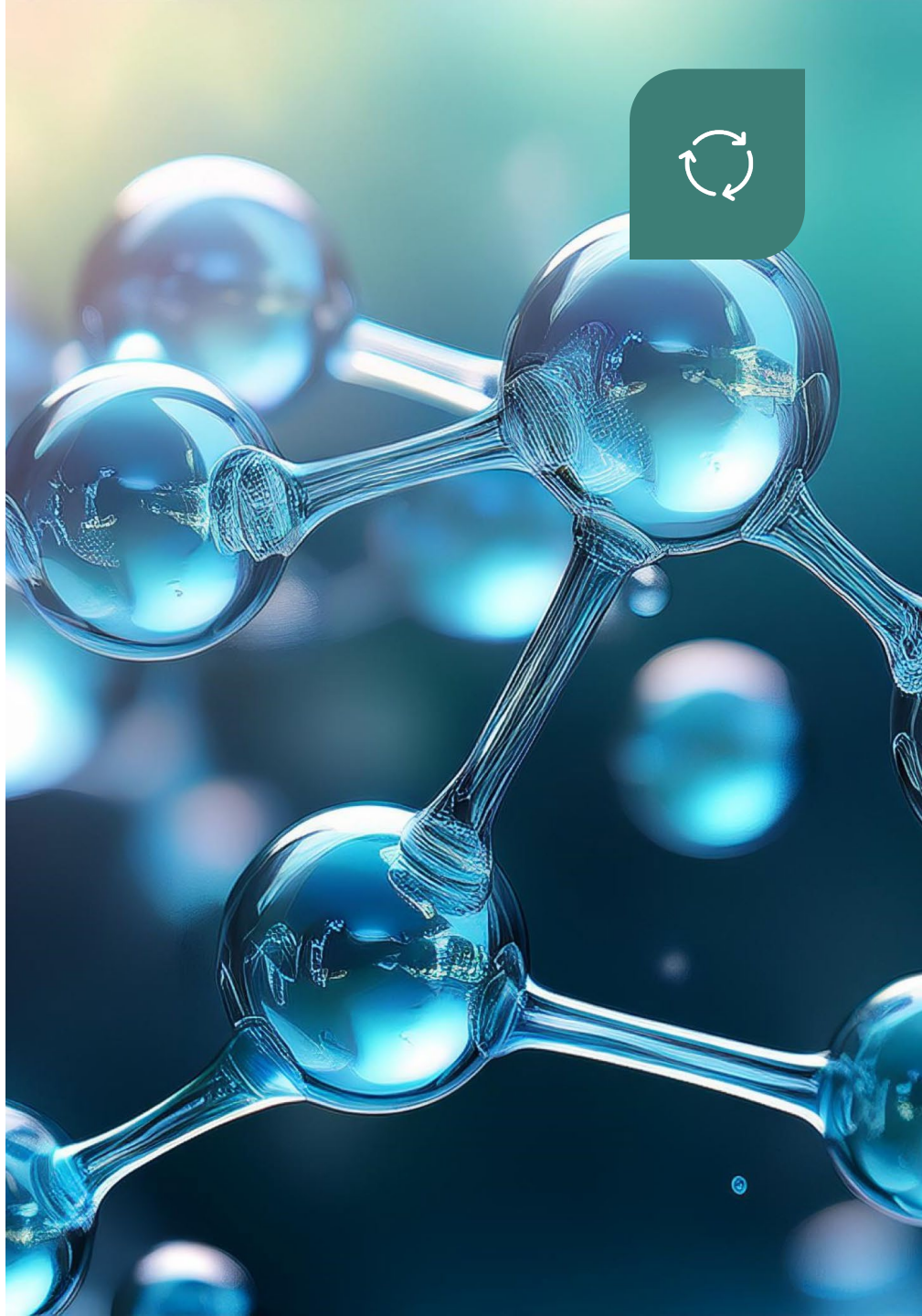
- Goal to identify all compounds
  - Not just pre-defined compounds
- No analytical standards for comparison
- More uncertainty with identifications
  - Relies on data analysis techniques
  - Qualitative and semiquantitative results
- May be able to determine presence or absence of unique compounds

Total Oxidizable Precursor Analysis

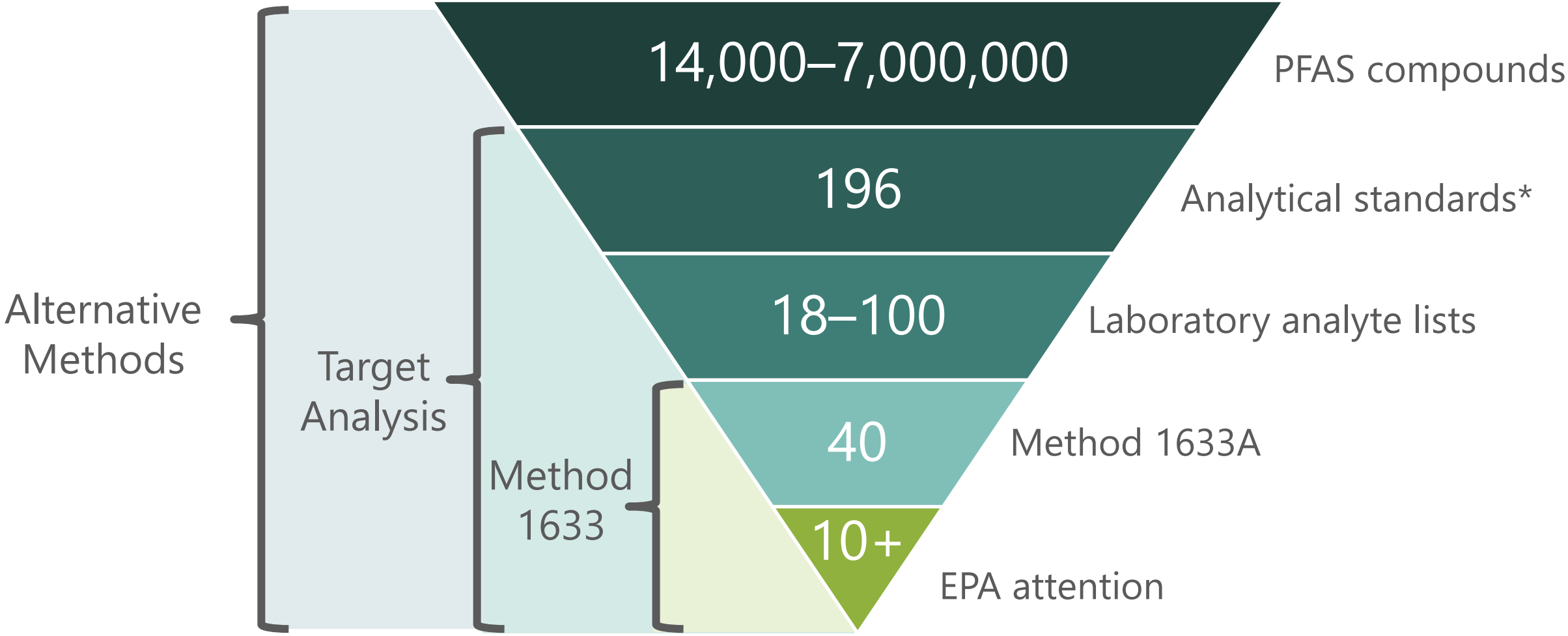
- Measures target analytes before and after a rigorous oxidation process
- Oxidation makes all precursors degrade to PFAAs
- “Before and after” approach gives information on magnitude of precursor compounds in the sample

TOF/AOF Analysis

- “Lump sum” measurement of organic compounds with fluorine
- EPA Method 1621: Adsorbable Organic Fluorine
- Can compare with total concentration of individually identified PFAS
- Multiple methods
  - Combustion Ion Chromatography (CIC)
  - Fluorine Nuclear Magnetic Resonance Spectroscopy (F-19 NMR)
  - Particle-Induced Gamma Ray Emission (PIGE) Spectroscopy



PFAS



*Estimated by Trier et al. 2025

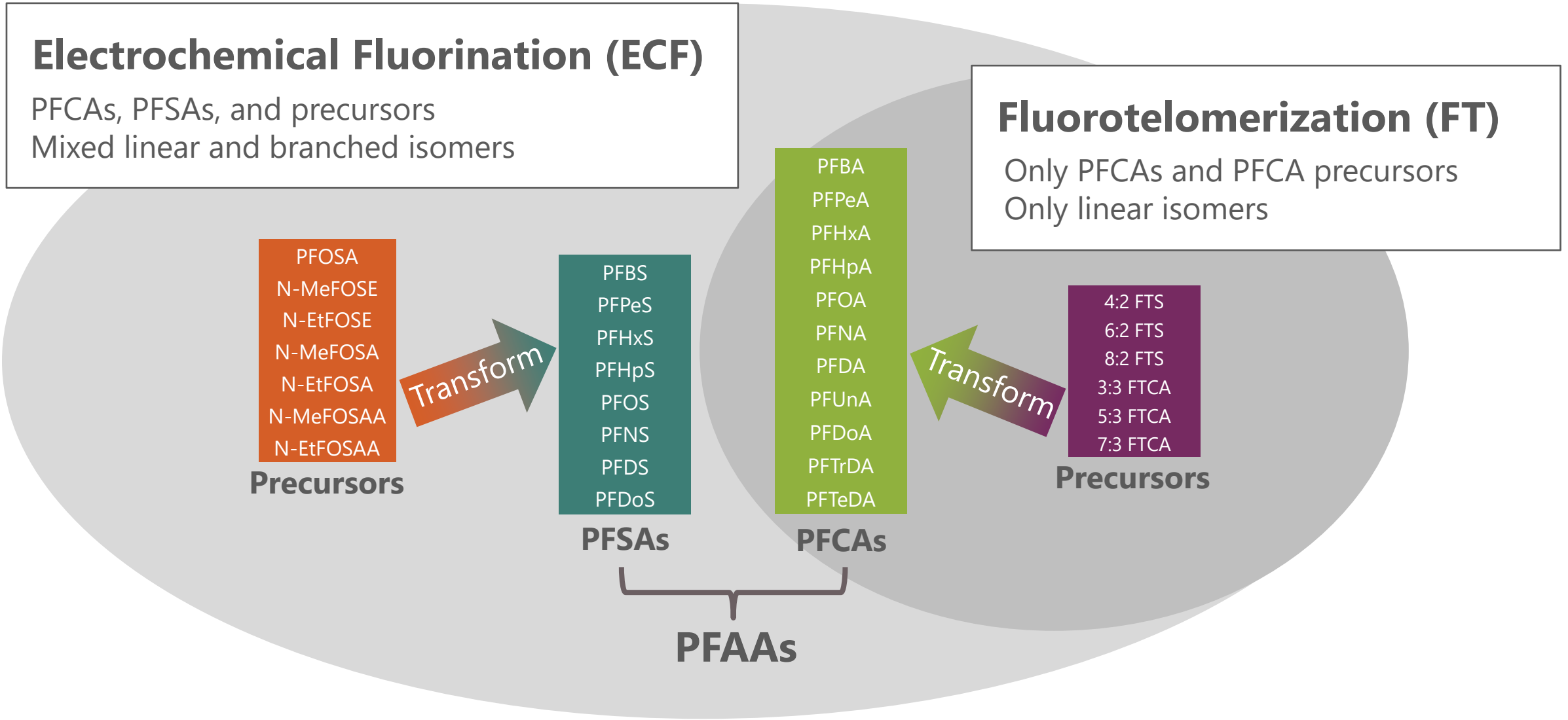
PFAS Formulations

Electrochemical Fluorination (ECF)

PFCAs, PFSAs, and precursors
Mixed linear and branched isomers

Fluorotelomerization (FT)

Only PFCAs and PFCA precursors
Only linear isomers



Types of PFAS Formulations/Source Signatures

AFFF
Two main types of formulations
All differ by maker and year

Industrial
Differs by application

Landfill
Contains markers determined by type of waste accepted

Wastewater
Contains markers determined by type of waste accepted

Images created with ChatGPT

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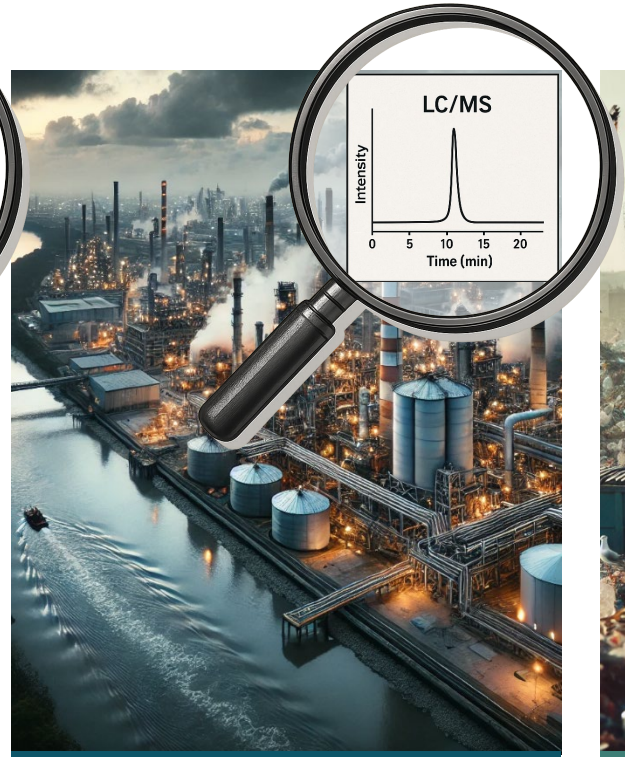
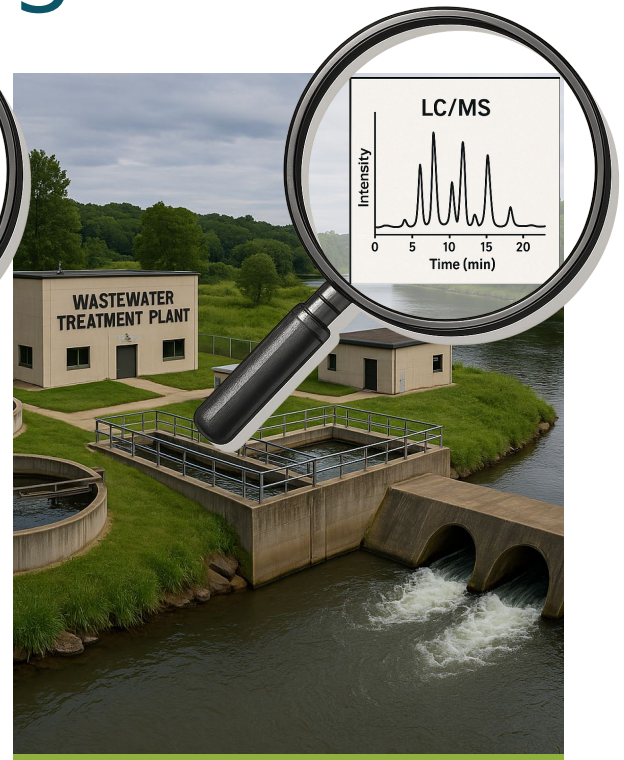


Industrial
Differs by application

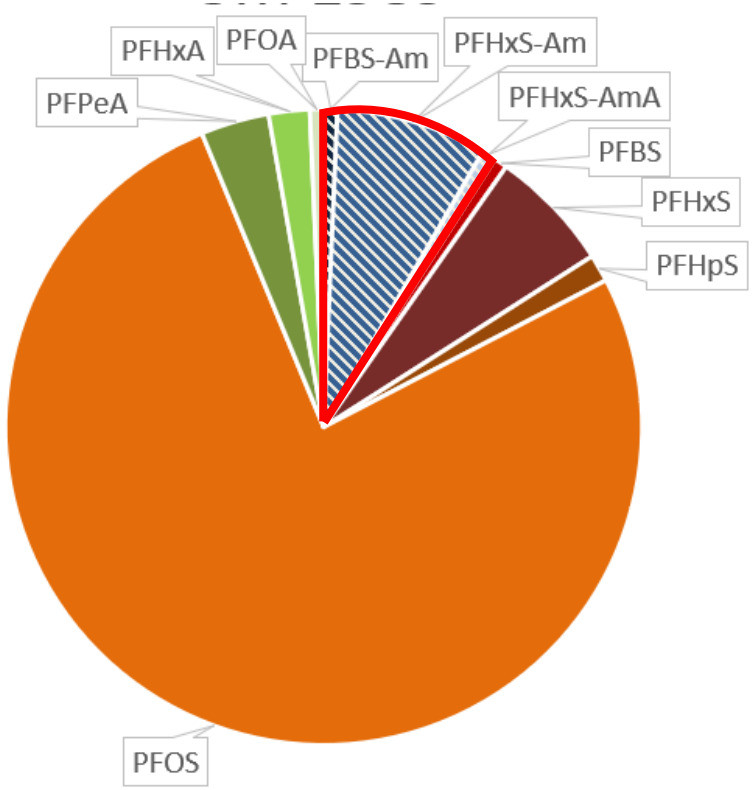
Landfill
Contains markers determined by type of waste accepted



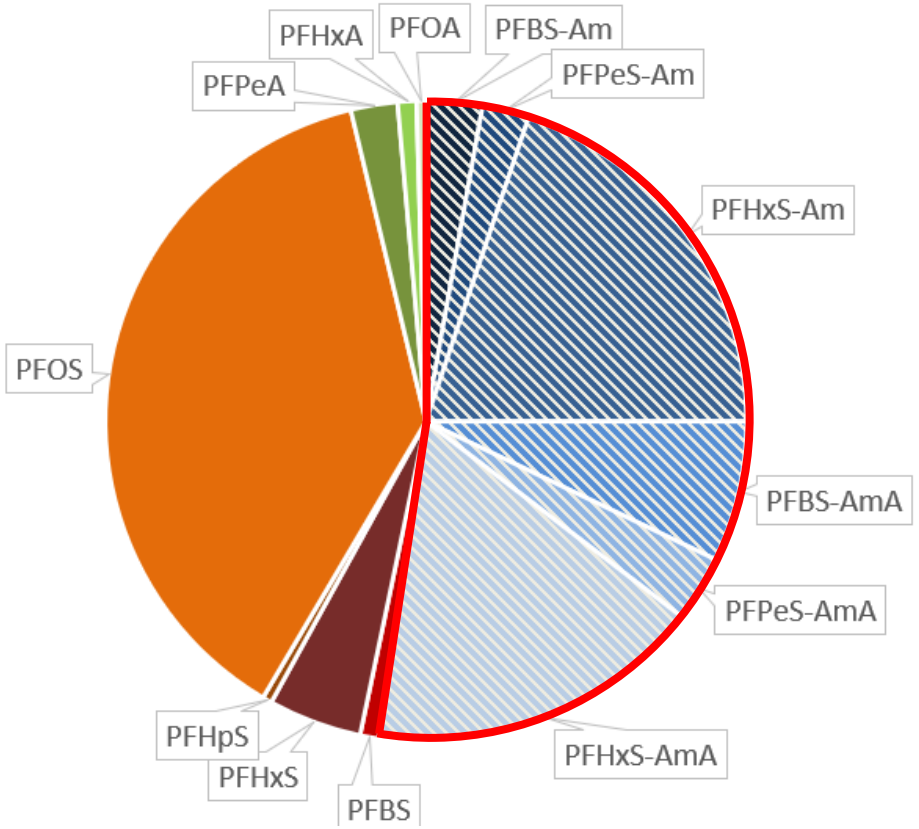
Wastewater
Contains markers determined by type of waste accepted

Images created with ChatGPT

AFFF: ECF-Based Formulations



3M (1989)



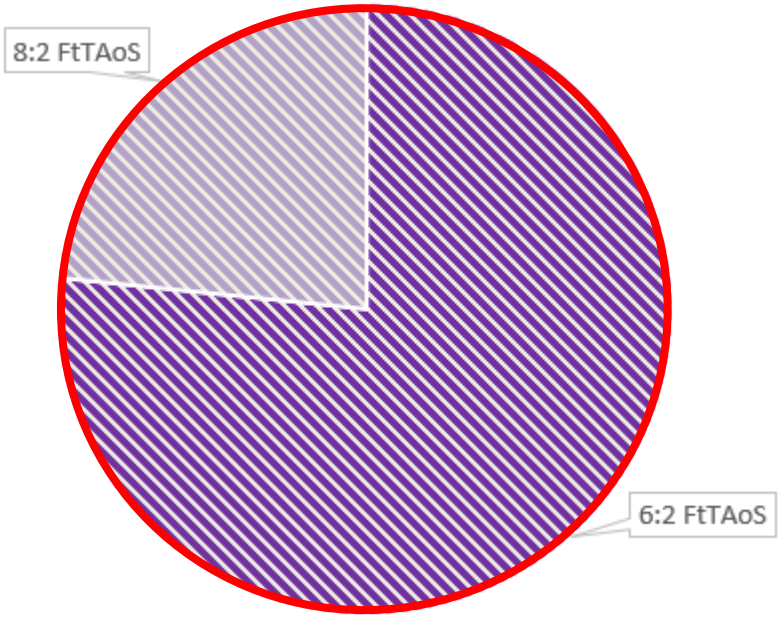
3M (2001)

Notes:
Solid shading: target analytes (Method 1633A)
Hatched shading: non-target analytes

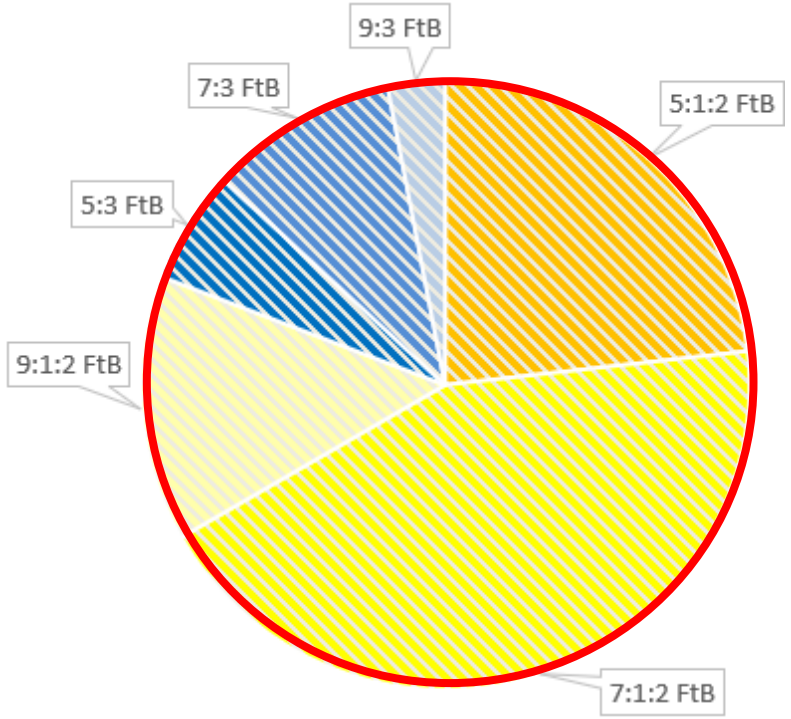
Formulations shown are as produced. Proportions will change due to environmental degradation.

Data from: Houtz, E.F., C.P. Higgins, J.A. Field, and D.L. Sedlak, 2013. "Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil." *Environmental Science & Technology* 47(15):8187–8195.

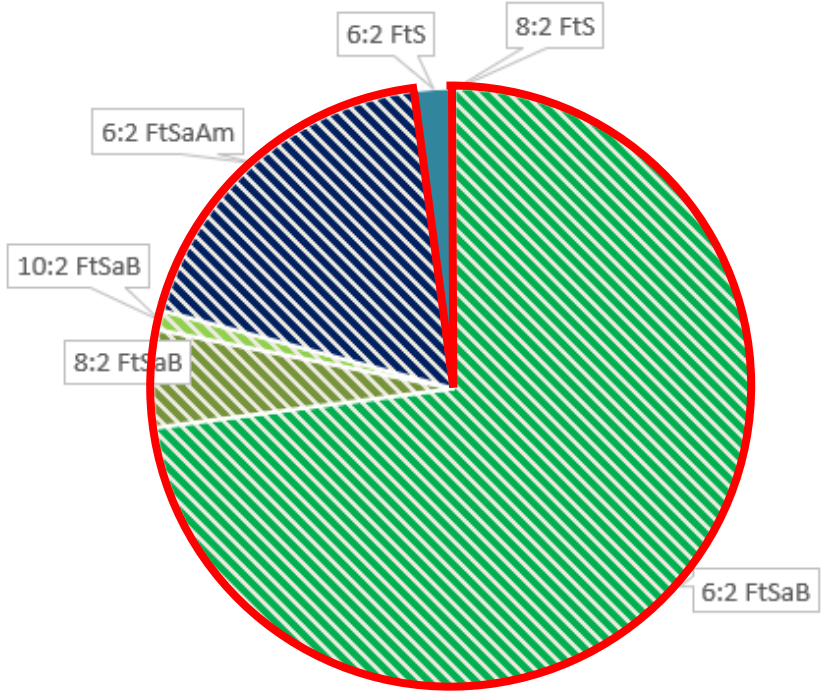
AFFF: FT-Based Formulations



Ansul (1986/1987)



Buckeye (2009)



National Foam (2005)

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Solid shading: target analytes (Method 1633A)
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Data from Houtz et al. 2013

PFAS Source Signatures: Industrial

- Industrial PFAS are manufactured through the same ECF and FT processes
- Composition depends on type of industry

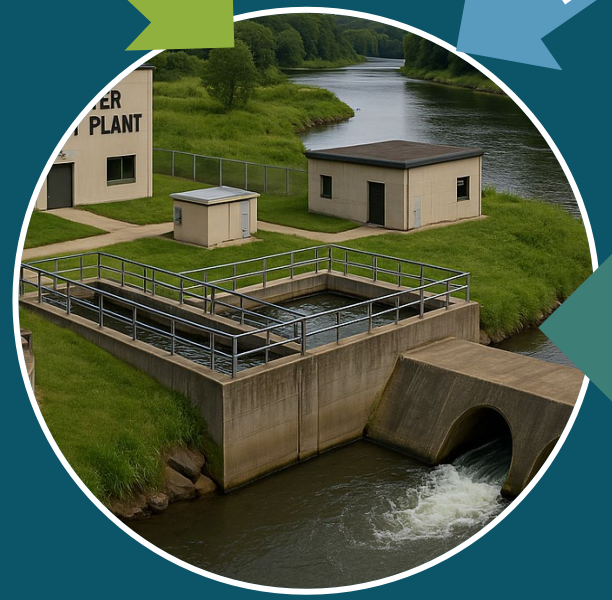
Industrial Use	Method 1633A Target Analytes	Alt. Target/Non-Target Analytes
Metal plating	PFBS, PFOS, 6:2 FTS	6:4 FTS, PFECHS
Waterproof textile coatings	PFBS, PFOS, PFOA	
Nonstick coatings	PFOA, PFNA, GenX, ADONA	PFECAs, ClPFPECAs
Paper manufacturing	6:2 FTS, PFHxA, MeFOSA	PAPs, PFECHS
Electronics	PFOS, PFOA, PFBS	

PFAS Source Signatures: Landfill and Wastewater

- "Pass-through" facilities
  - Effluent composition depends on inputs
- Some standard chemical markers
  - Landfill (changes with climate/age of landfill)
    - 5:3 FTCA (1633A compound)
  - Wastewater treatment plants
    - Pharmaceuticals (e.g., acetaminophen)
    - Caffeine
    - Artificial sweeteners

Understand Source Interactions

Runoff



Effluent

Waste

Leachate

Initial Steps: Historical Research

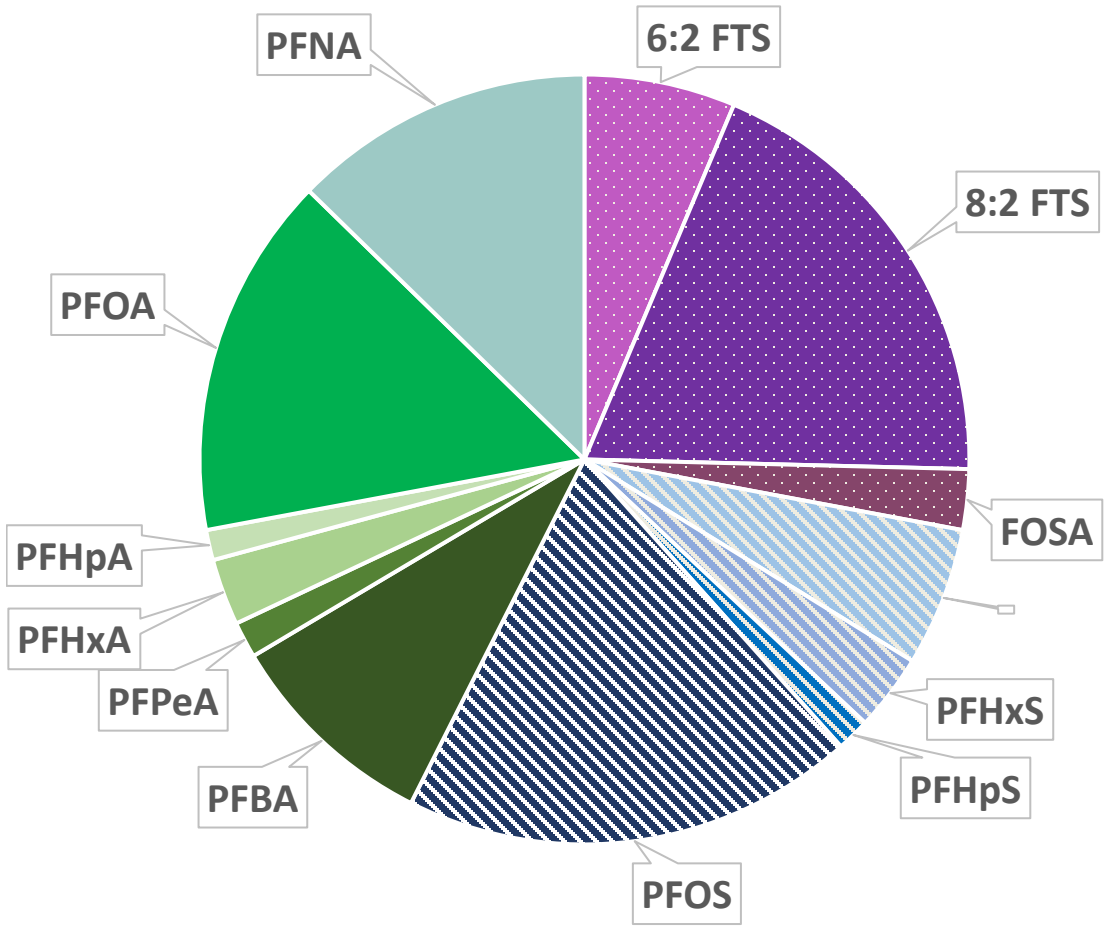
- Research site histories
  - Local point sources
  - Non-point/background levels
- Product use history
- Potential discharge pathways

Initial Steps: Data Management

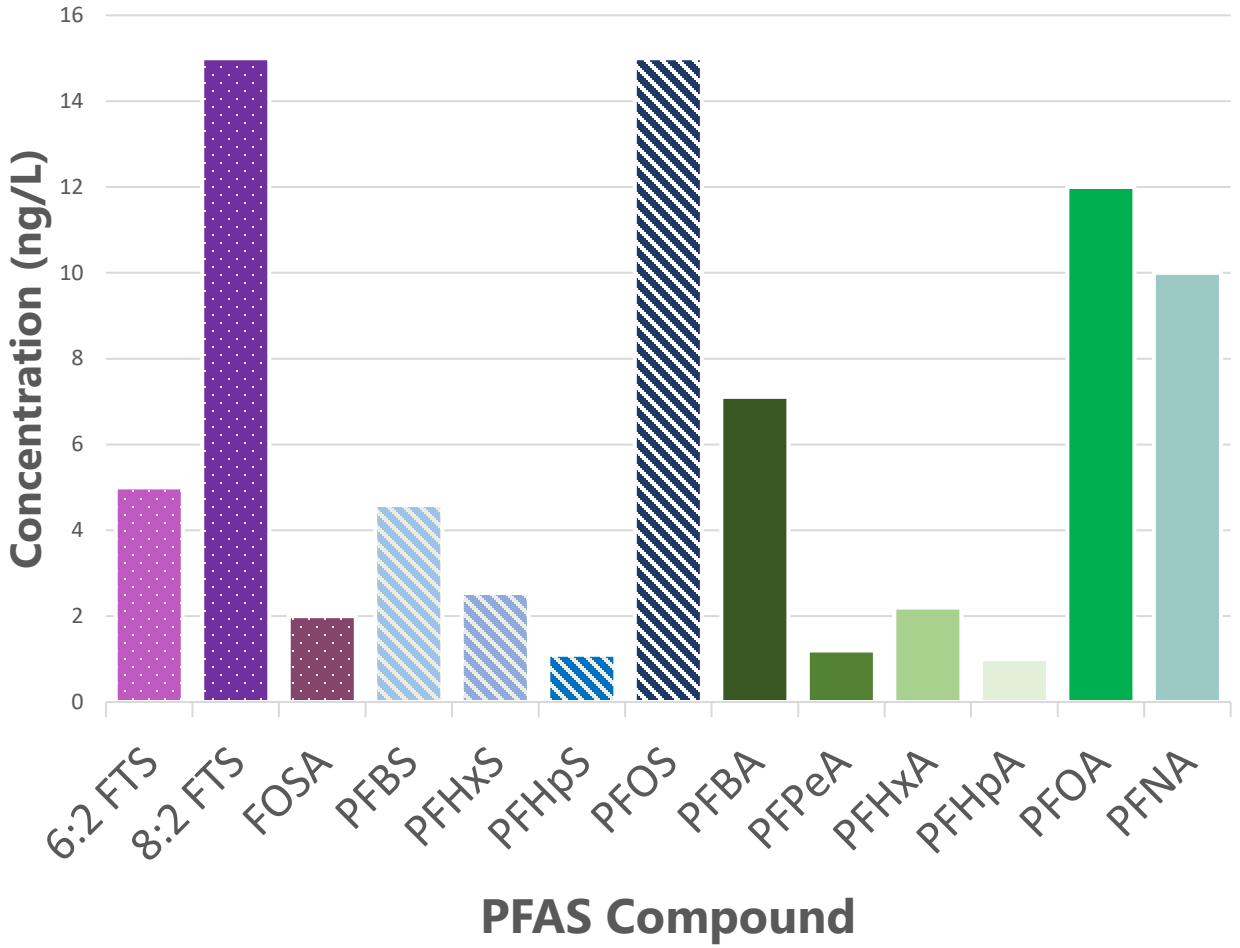
- Understand age and suitability of data
  - Detection limits and compound lists have changed over time
- Make data treatment decisions
  - Non-detect values

Forensic Techniques: Data Visualization

Pie Chart

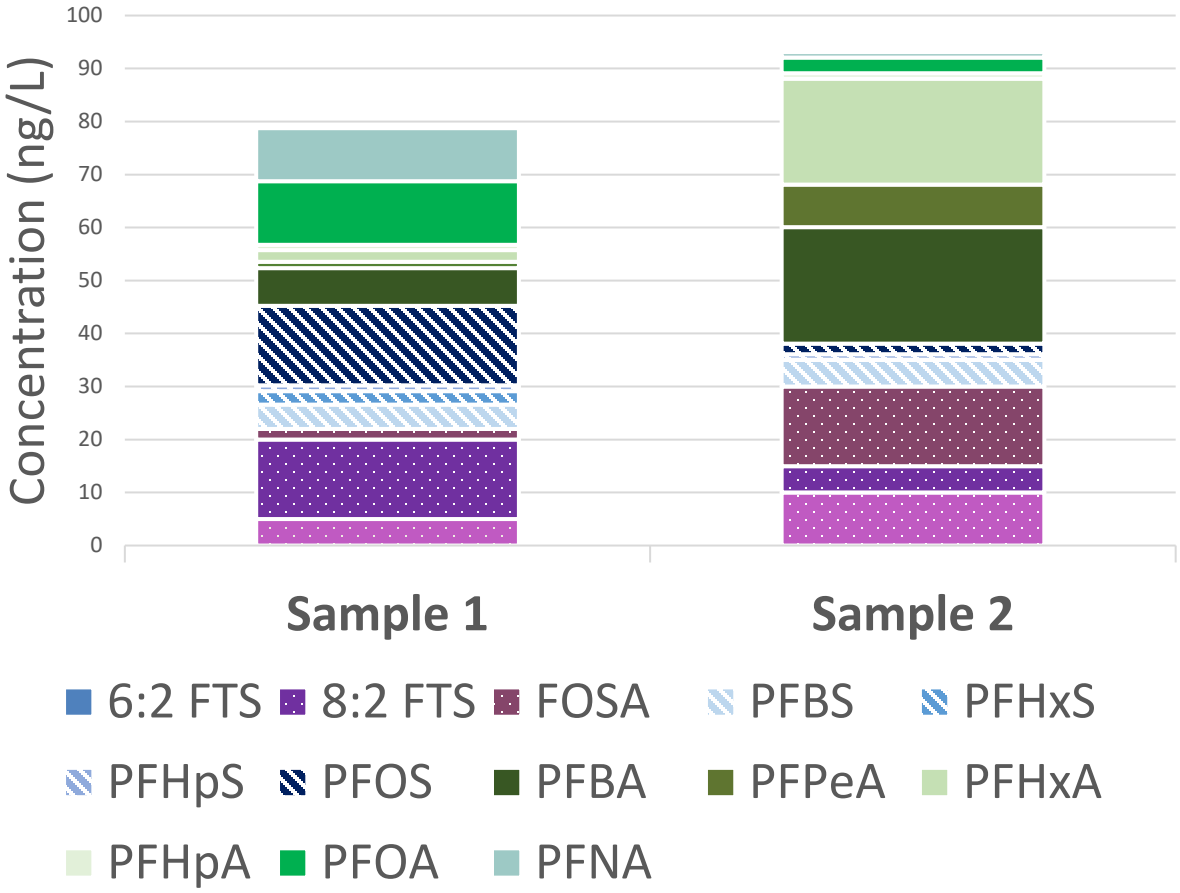


Bar Chart

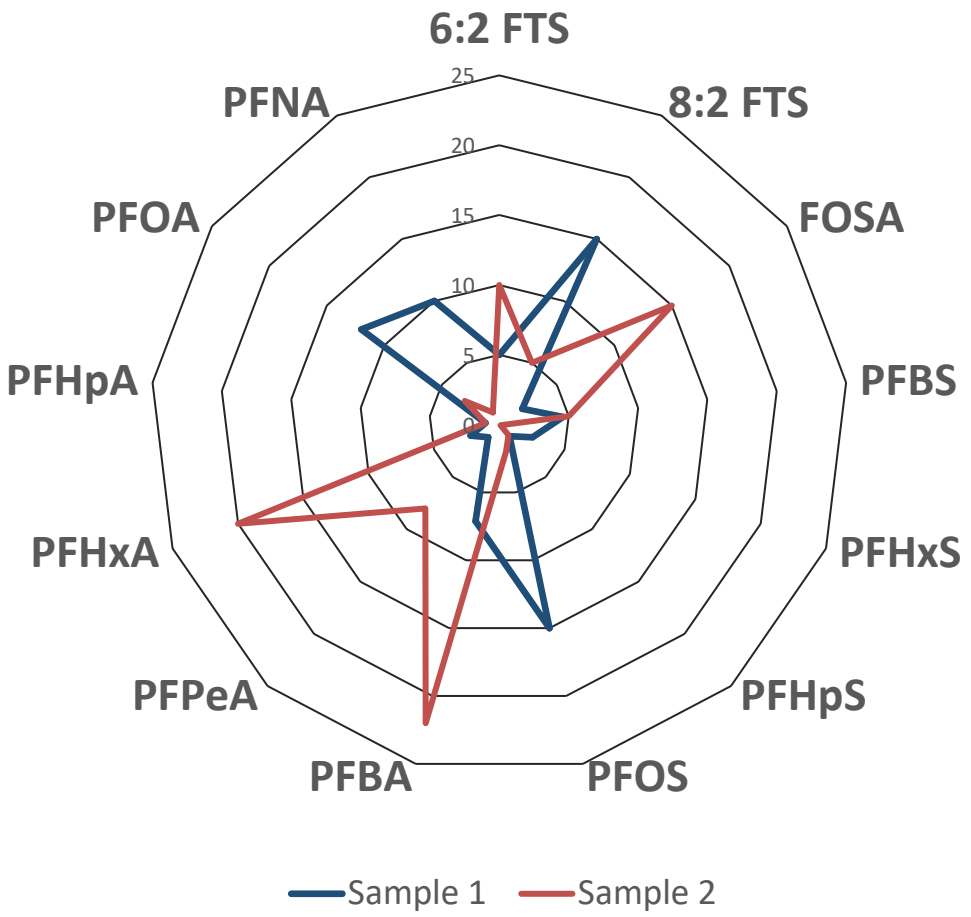


Forensic Techniques: Data Visualization (cont.)

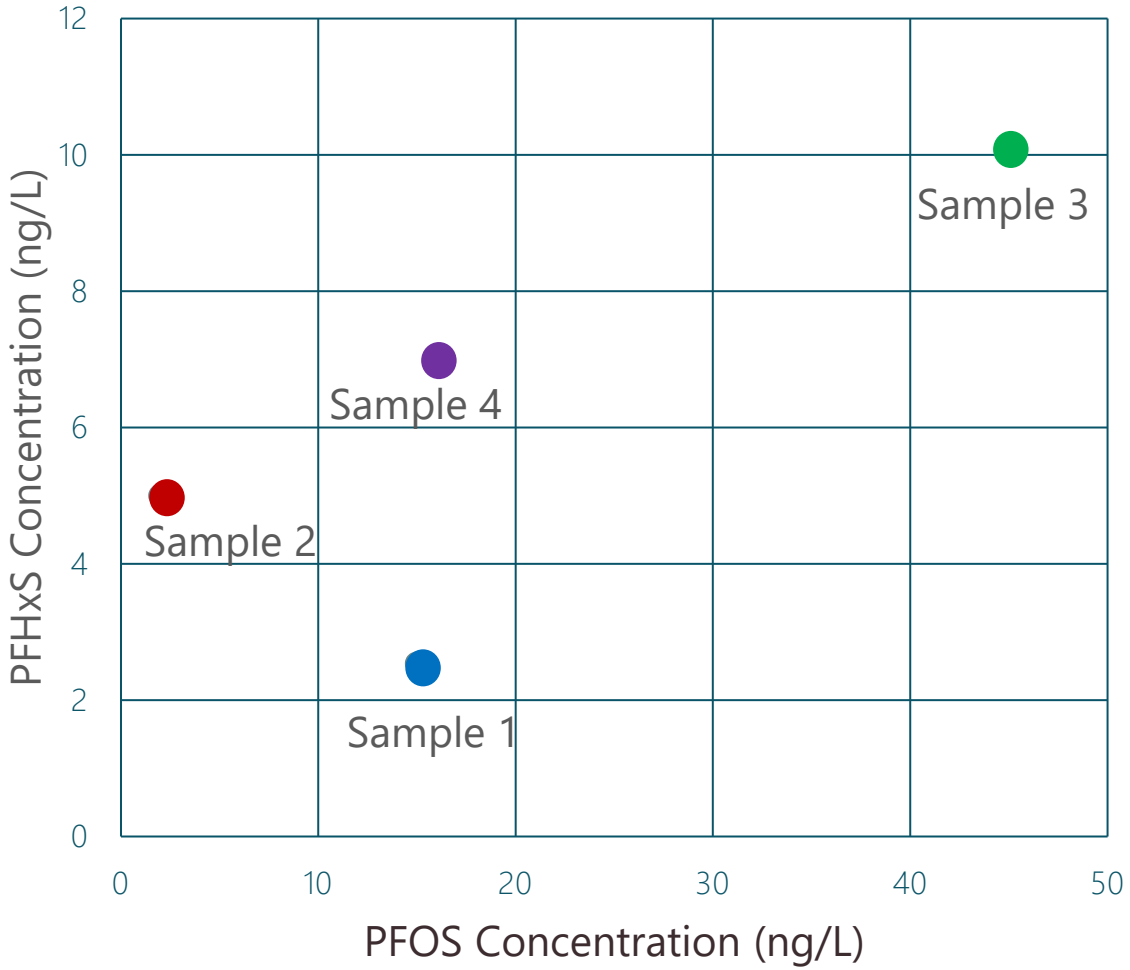
Stacked Bar Chart



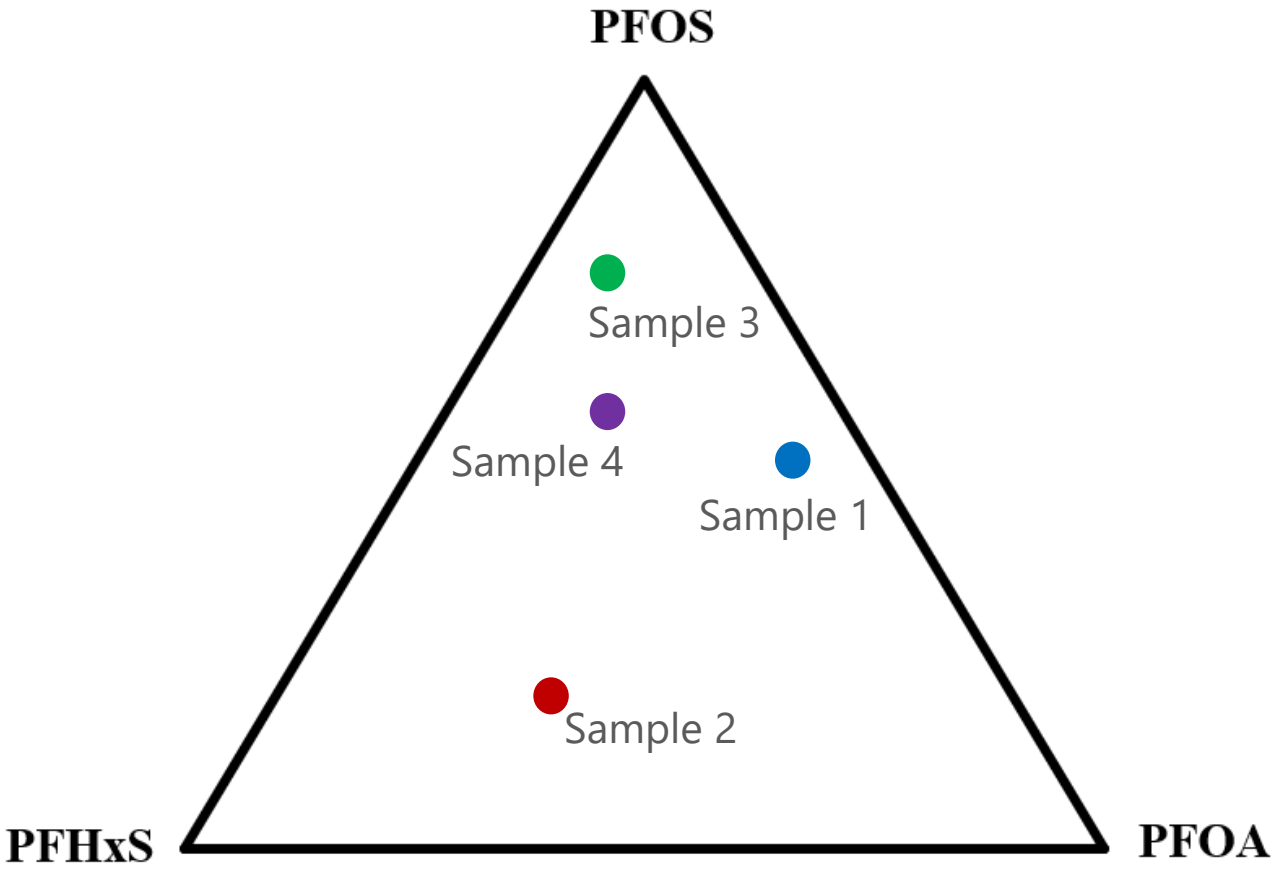
Radar Plot



Forensic Techniques: Data Visualization (cont.)



Crossplot



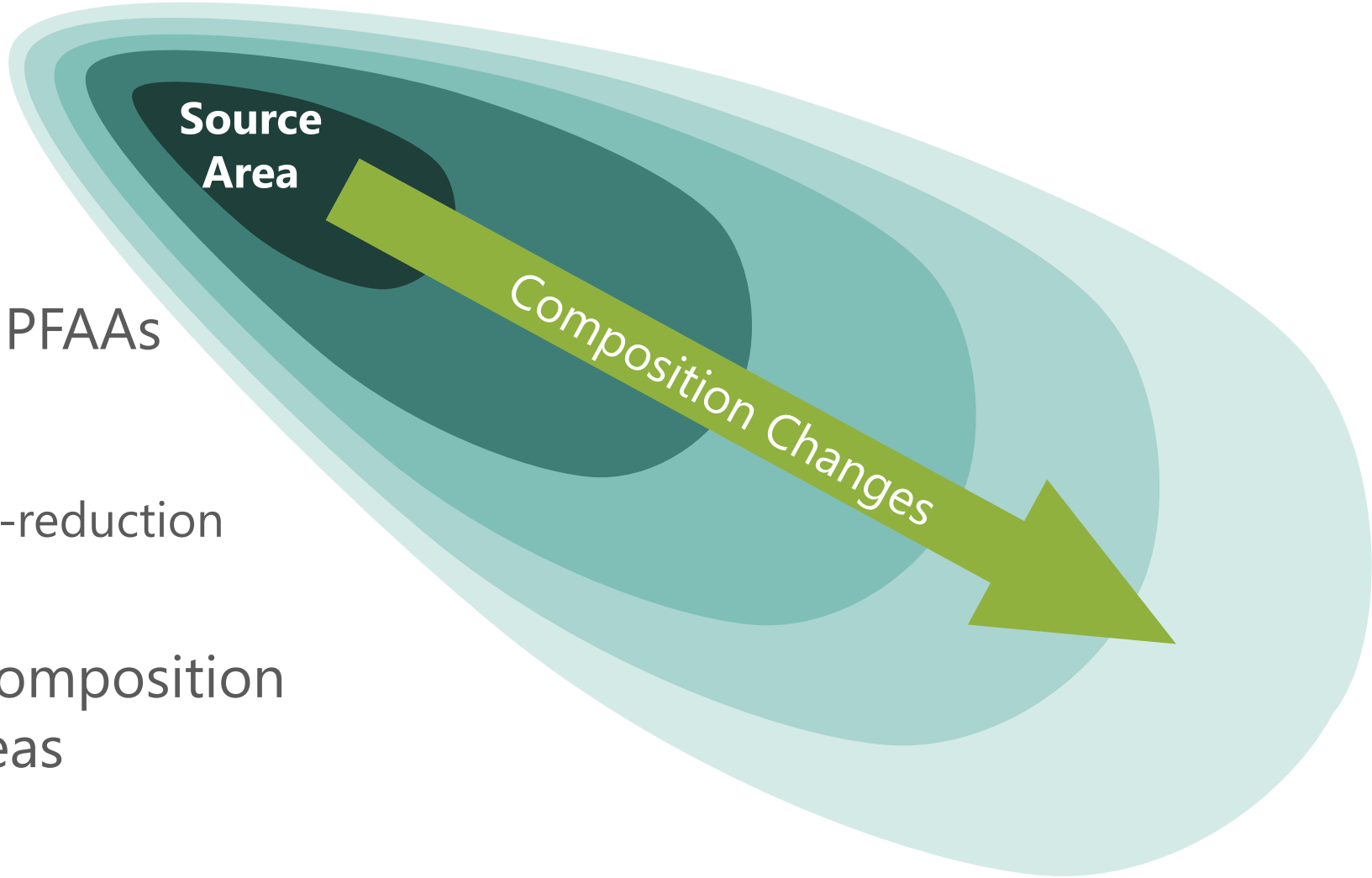
Ternary Plot

Forensic Techniques: Diagnostic Ratios

Ratio	Sample 1	Sample 2
PFOS/PFOA	1.25	0.67
PFCAs/PFSAs	5.9	20
% PFSA	29%	9%
% precursors	27%	32%
Linear/branched isomers (PFOA)	300	0.2

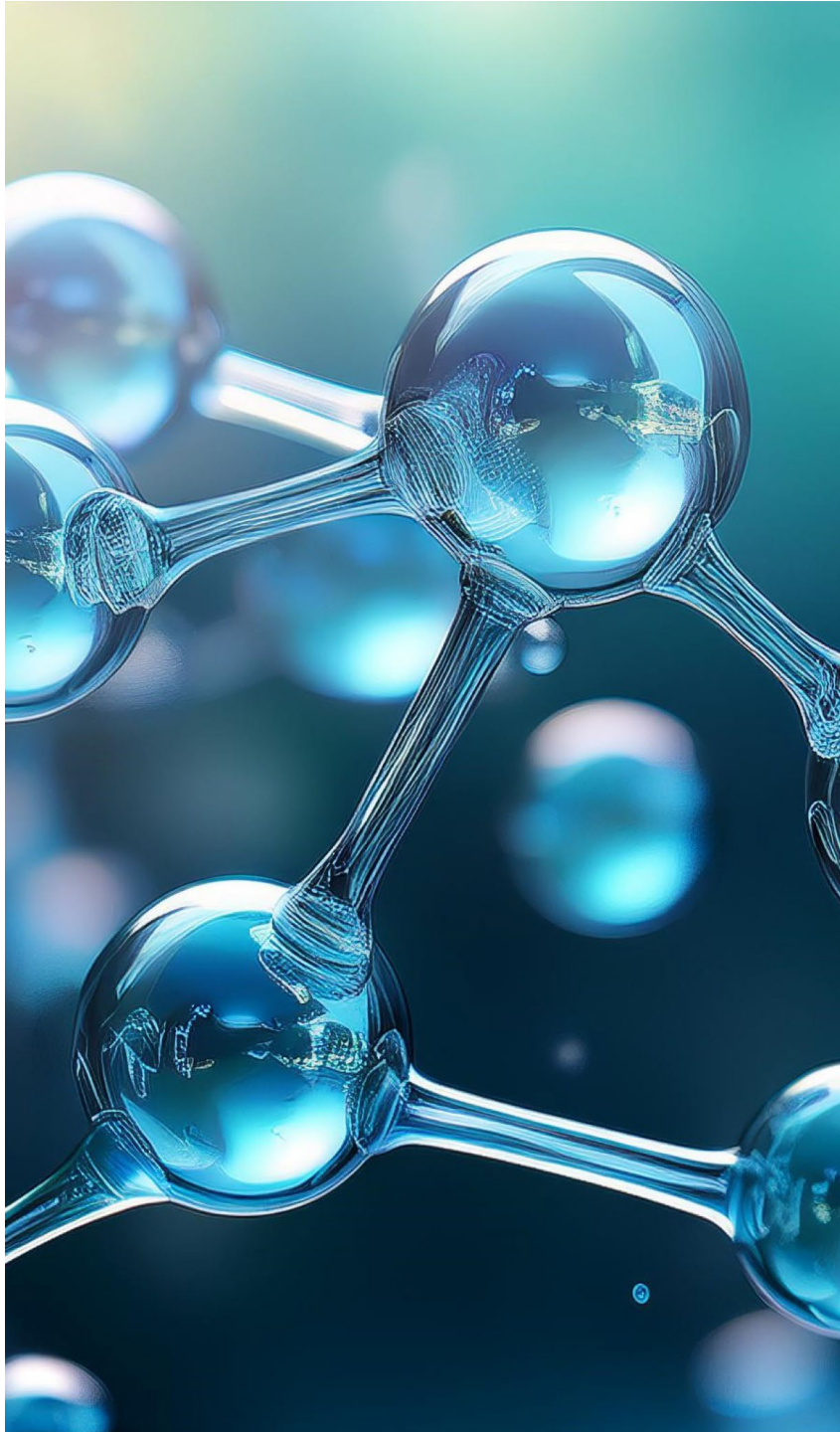
Spatial Components to PFAS Composition

- Some PFAS move faster than others
  - Ratios change
- Precursors degrade to PFAAs
  - With time
  - With changing oxidation-reduction potential
- Analysis of changing composition can indicate source areas



Conclusions

- There are several laboratory analytical methods
  - Each give different information about PFAS composition
- There are several PFAS source types
  - Each have unique characteristics
- Historical research for on- and off-site potential sources is the best first step
- Many data visualization techniques are available for initial review of data
- PFAS composition changes with movement in the subsurface




Questions?
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