Sampling Considerations for PFAS Forensics: Beyond Method 1633

Presented by

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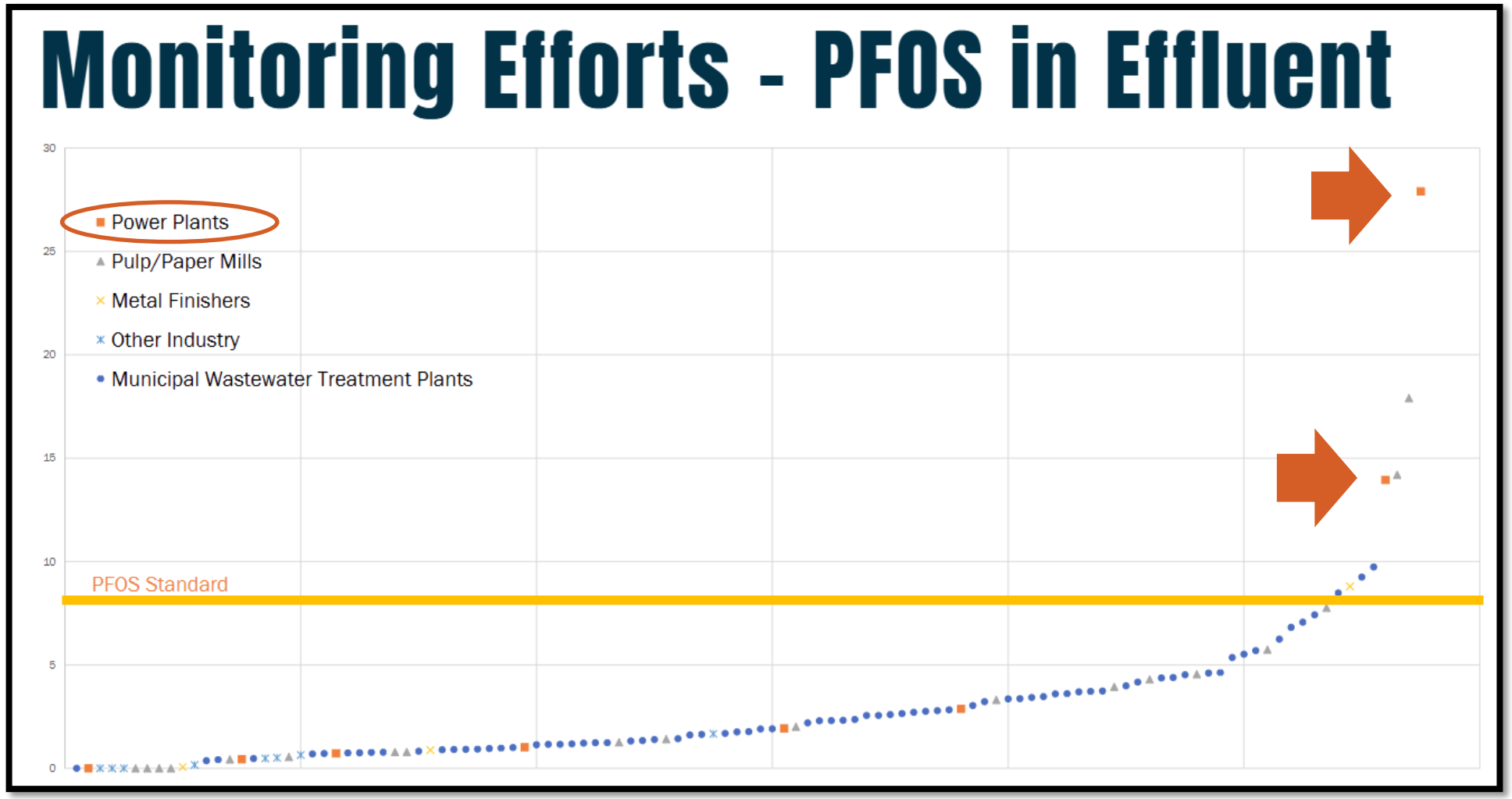
PIZZA, POPCORN AND PFCS: THE SICKENING TRUTH
PFAS found in drinking water wells in unexpected places
Paper mills as a significant source of PFAS contamination, but who's watching?
Mlive.com
Horsham Water and Sewer Authority Takes 2 Wells Out of Service Due to Detection of Perfluorooctane Sulfonate (PFOS) Above Provisional Health Advisory Level
WATER POLLUTION IN HOOSICK FALLS PROMPTS ACTION BY NY STATE
How Your Waterproof Jacket Might Be Making You Fat
Oscoda toxic PFC groundwater plumes approaching Lake Huron
FLINT RESIDENTS MAY HAVE BEEN DRINKING PFCs IN ADDITION TO LEAD
SECTIONS
HOME
SEARCH
The New York Times
BUSINESS DAY | INSIDE THE NEWS
Will Environmental Fear Stick to DuPont's Teflon?

Wisconsin Department of Natural Resources Data



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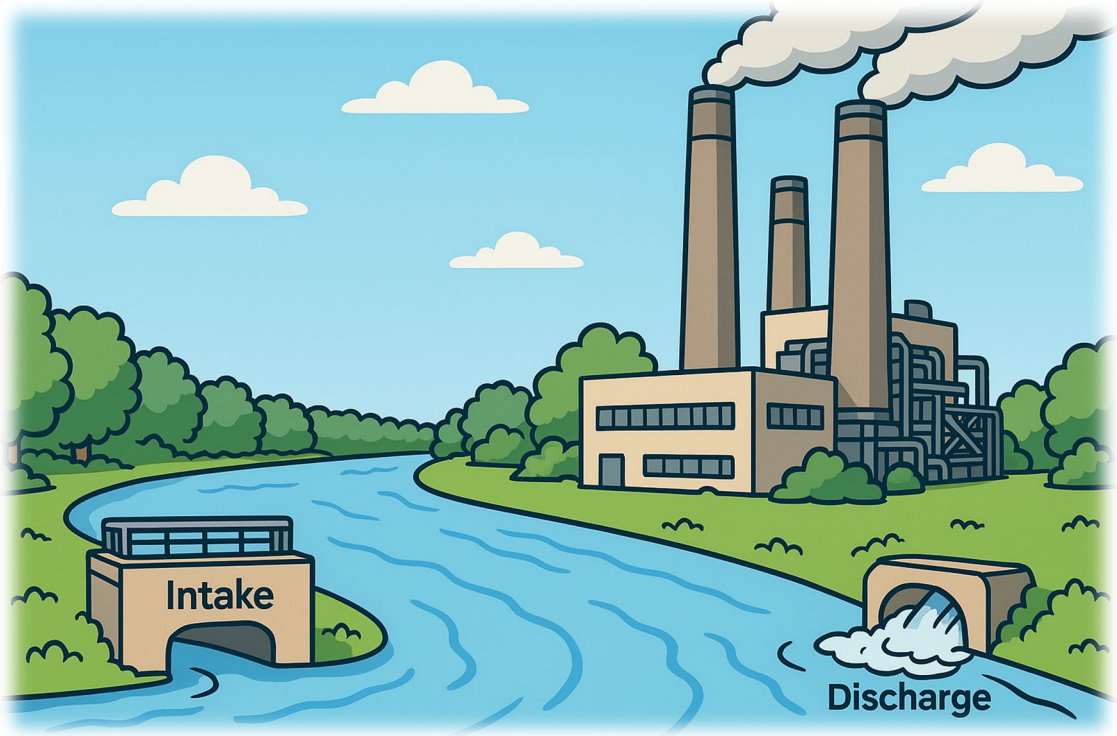
Potential PFAS Sources to Utility Plant Effluent

- On-site use of firefighting foam (aqueous film-forming foams [AFFF])
- Import of PFAS in cooling water
  - Depends on upstream sources
  - Potential concentration of PFAS by evaporation



Identifying and limiting sources is the best first step in addressing discharge concentrations

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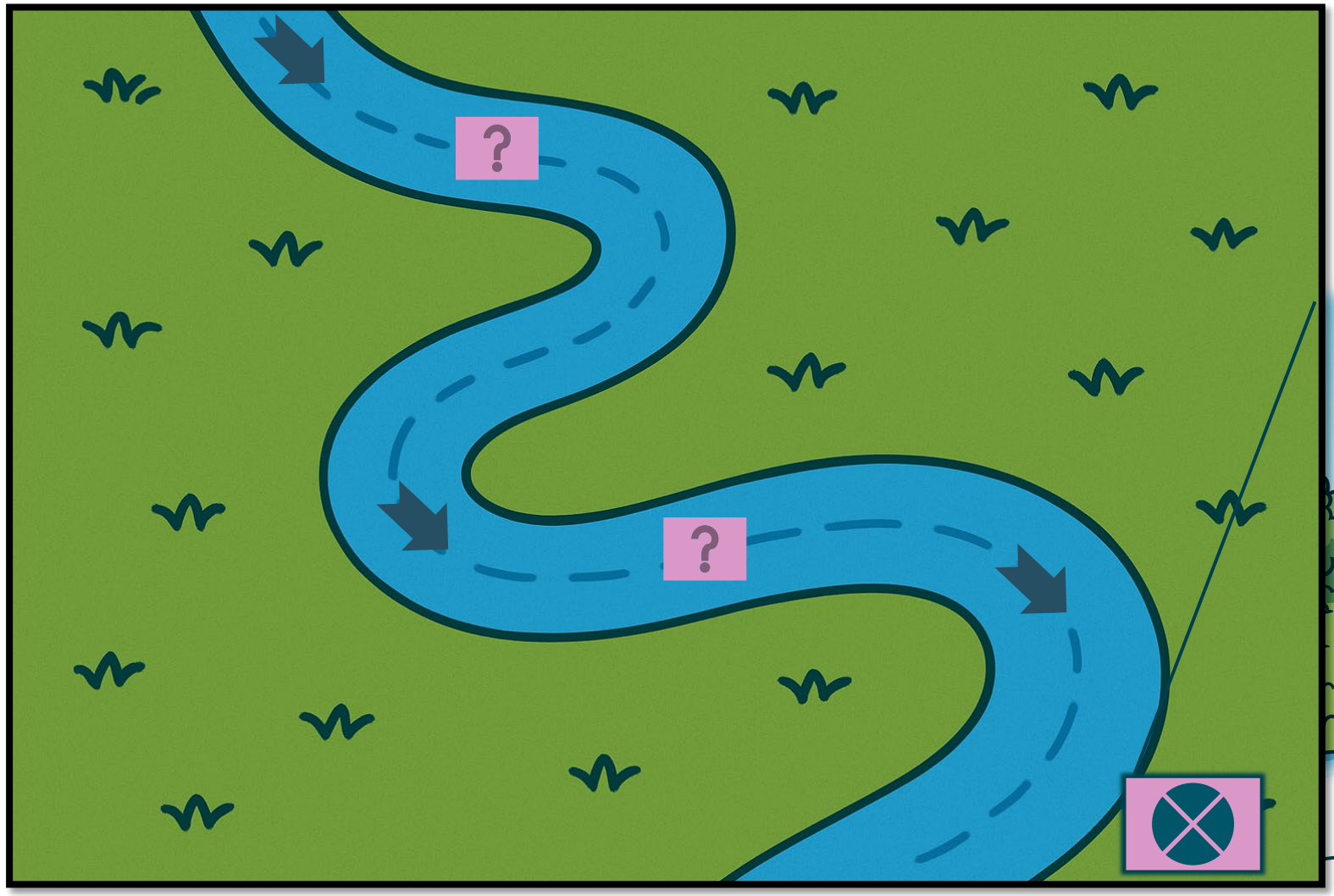
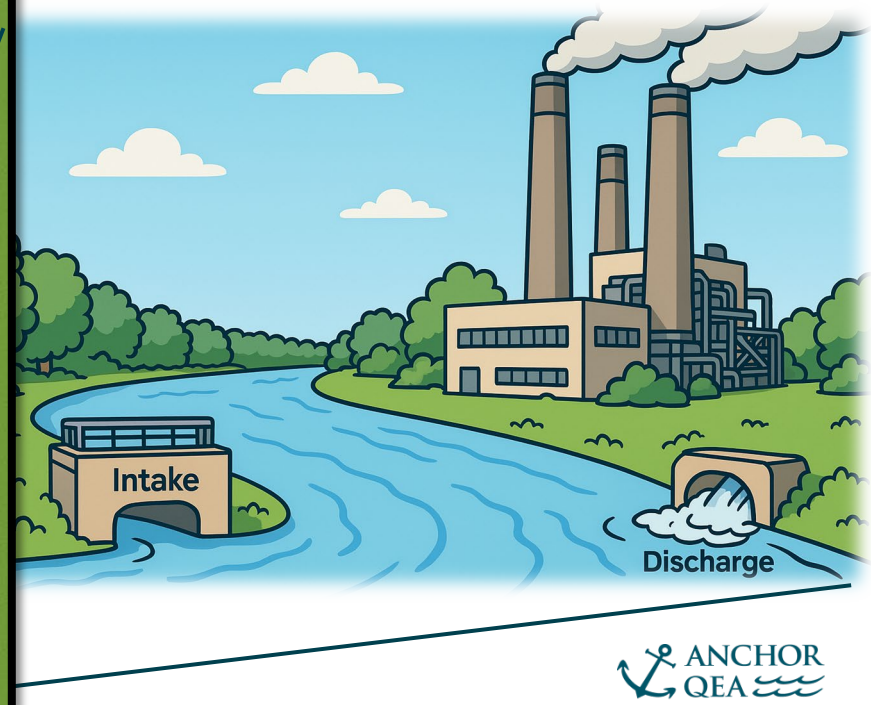
Initial Steps: Conceptual Site Model



Understand Upstream Sources

- *Historical Research*
- *Upstream/Intake Sampling*



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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

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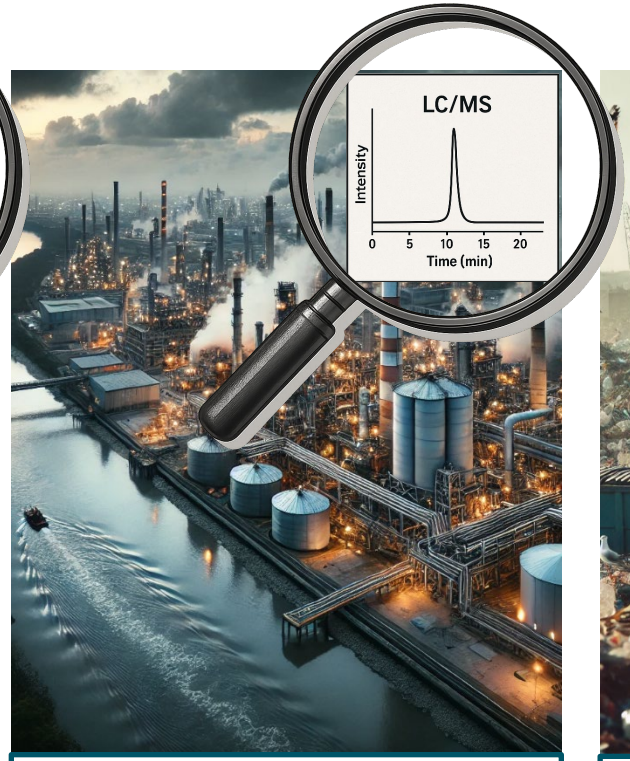
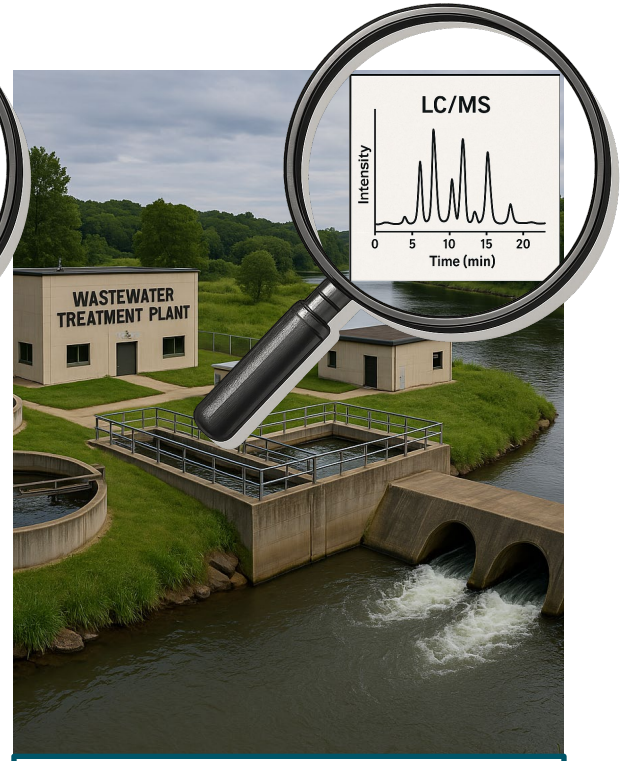


Industrial

Differs by application

Landfill

Contains markers determined by type of waste accepted



Wastewater

Contains markers determined by type of waste accepted

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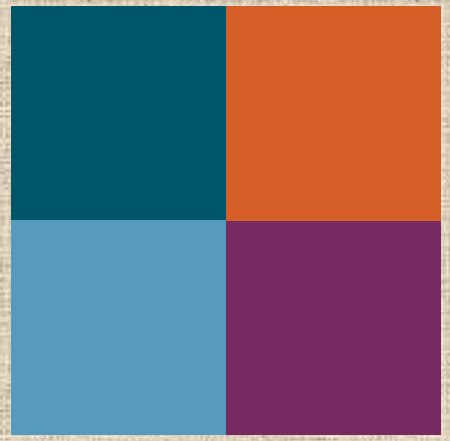
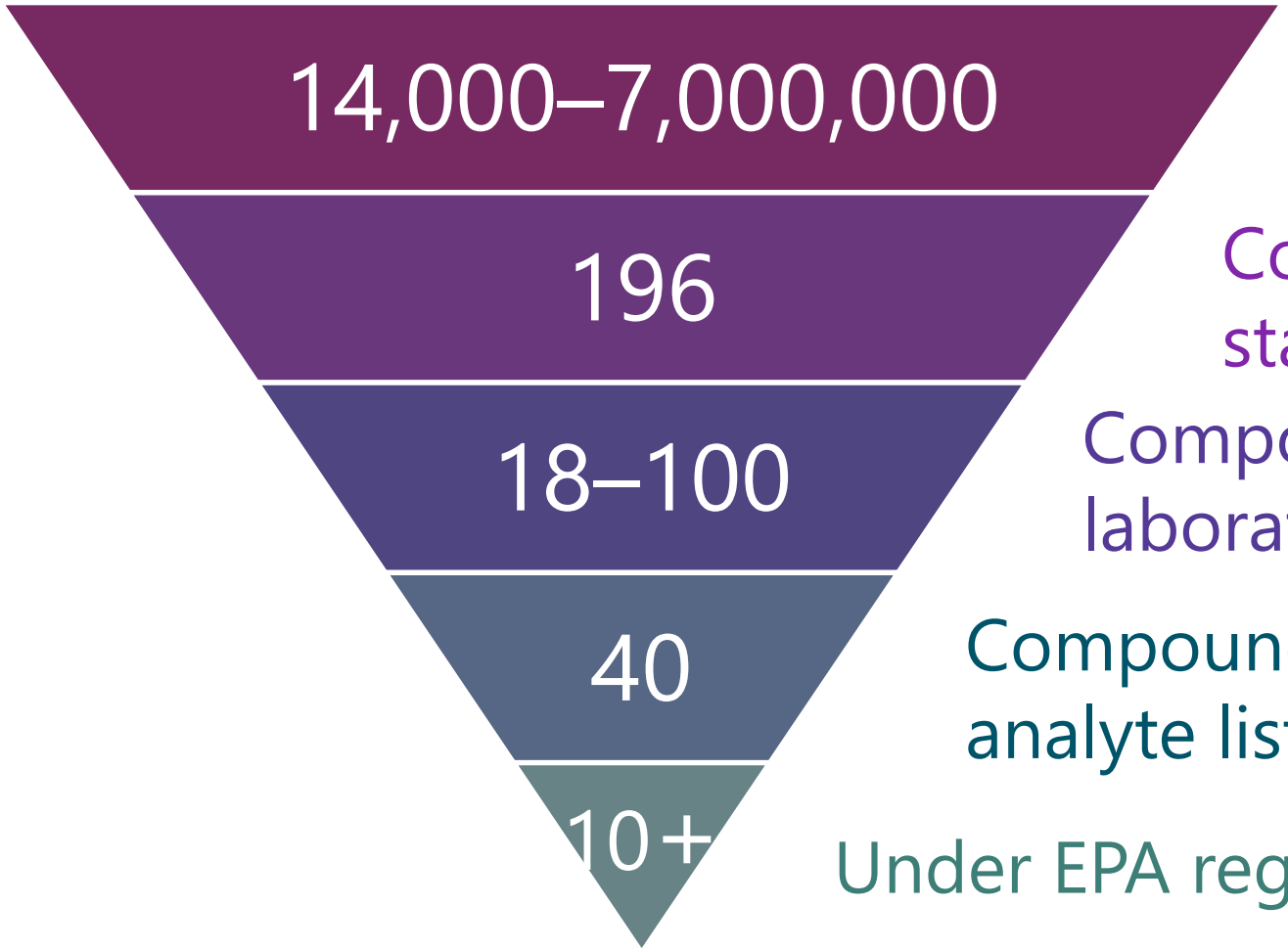
Forensics = Pattern Recognition



More Data = More Unique Patterns

PFAS



PFAS compounds

Commercially available analytical standards*

Compounds on commercial laboratory analyte lists

Compounds on EPA Method 1633 analyte list

Under EPA regulatory attention

*Estimated by Trier et al. 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).

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Types of Laboratory Analyses

Method 1633

TARGET ANALYSES

NON-TARGET ANALYSES

TOTAL ORGANIC FLUORINE (TOF)

TOTAL OXIDIZABLE PRECURSOR (TOP)

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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 1633	40
EPA 537/537.1	18
EPA 533	25
Alt. laboratory methods	Var.

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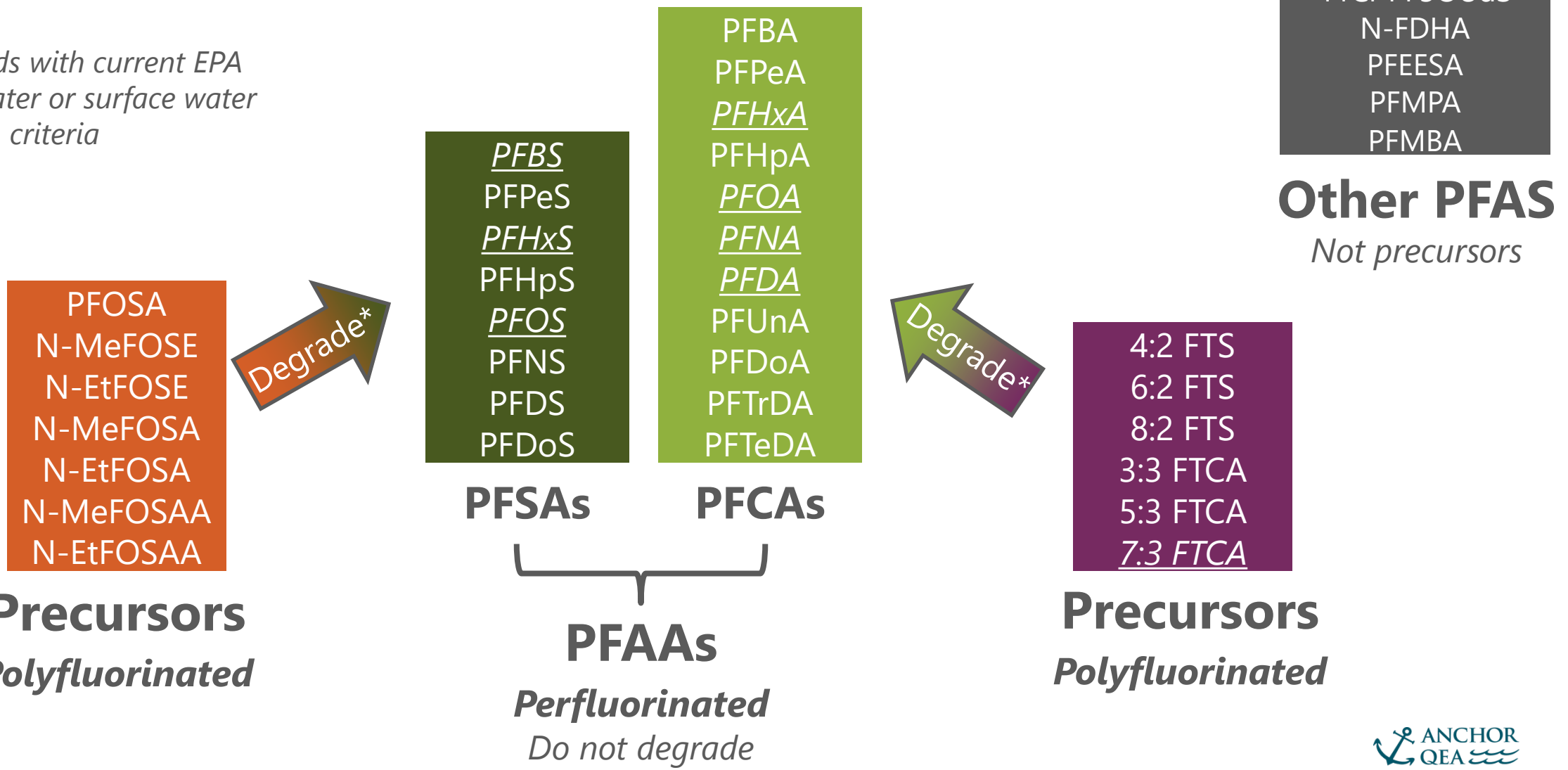
Method 1633 Analyte List

Compounds with current EPA drinking water or surface water criteria



Types of Laboratory Analyses – Isomer Analysis

TARGET ANALYSES

NON-TARGET ANALYSES

TOF

TOP

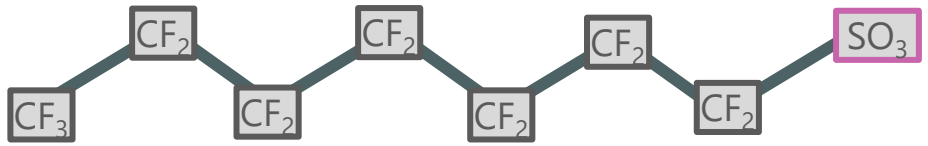
PFBS
PFPeS
PFHxS
PFHpS
PFOS
PFNS
PFDS
PFDoS

PFSAs

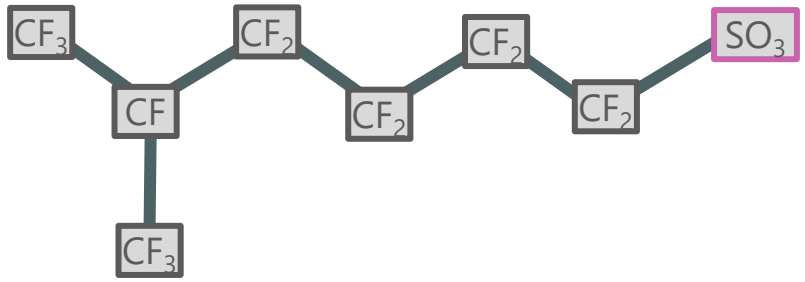
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnA
PFDoA
PFTrDA
PFTeDA

PFCAs

PFAAs



Linear Arrangement



Branched Arrangement

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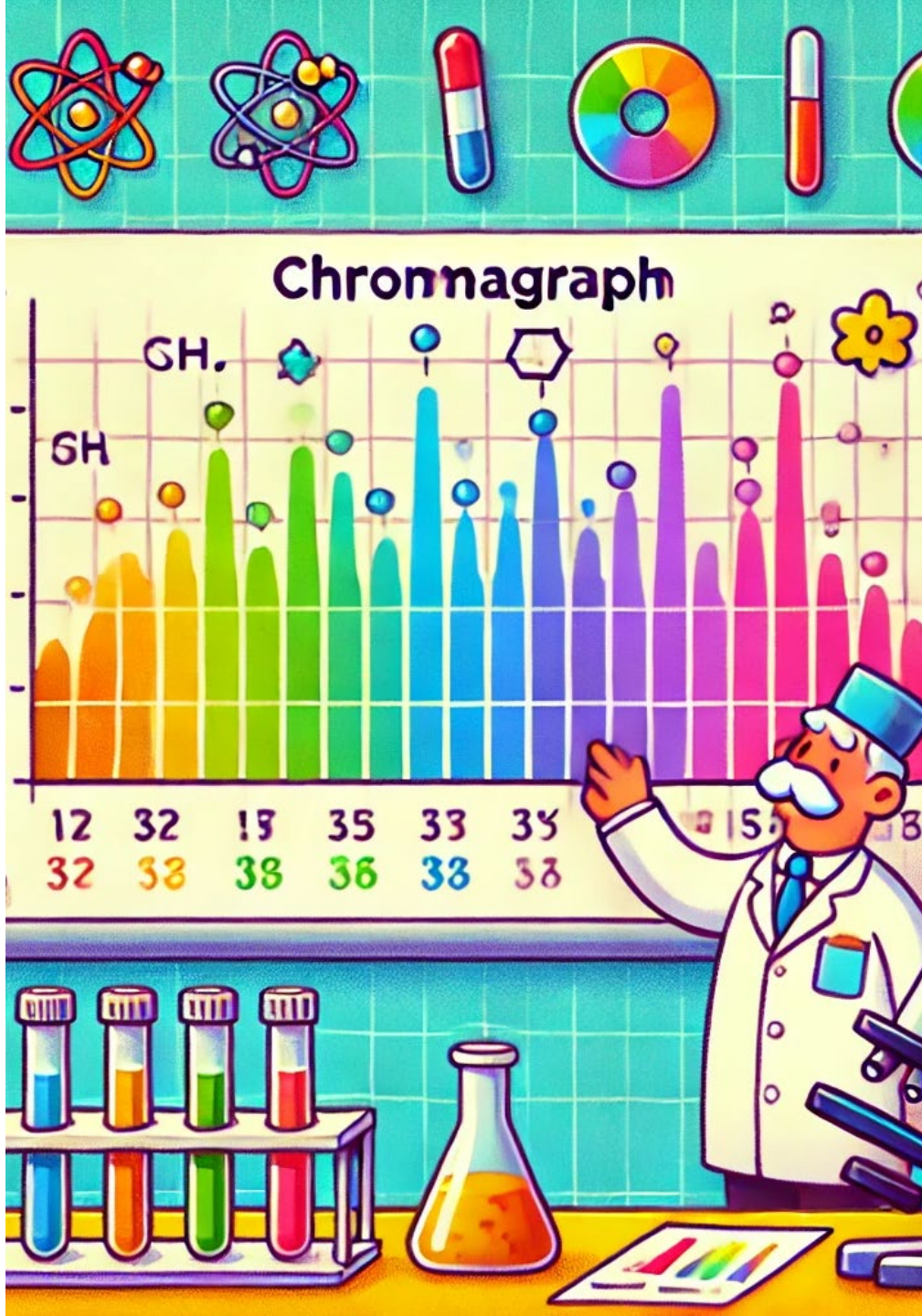
Non-Target Analysis

- 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



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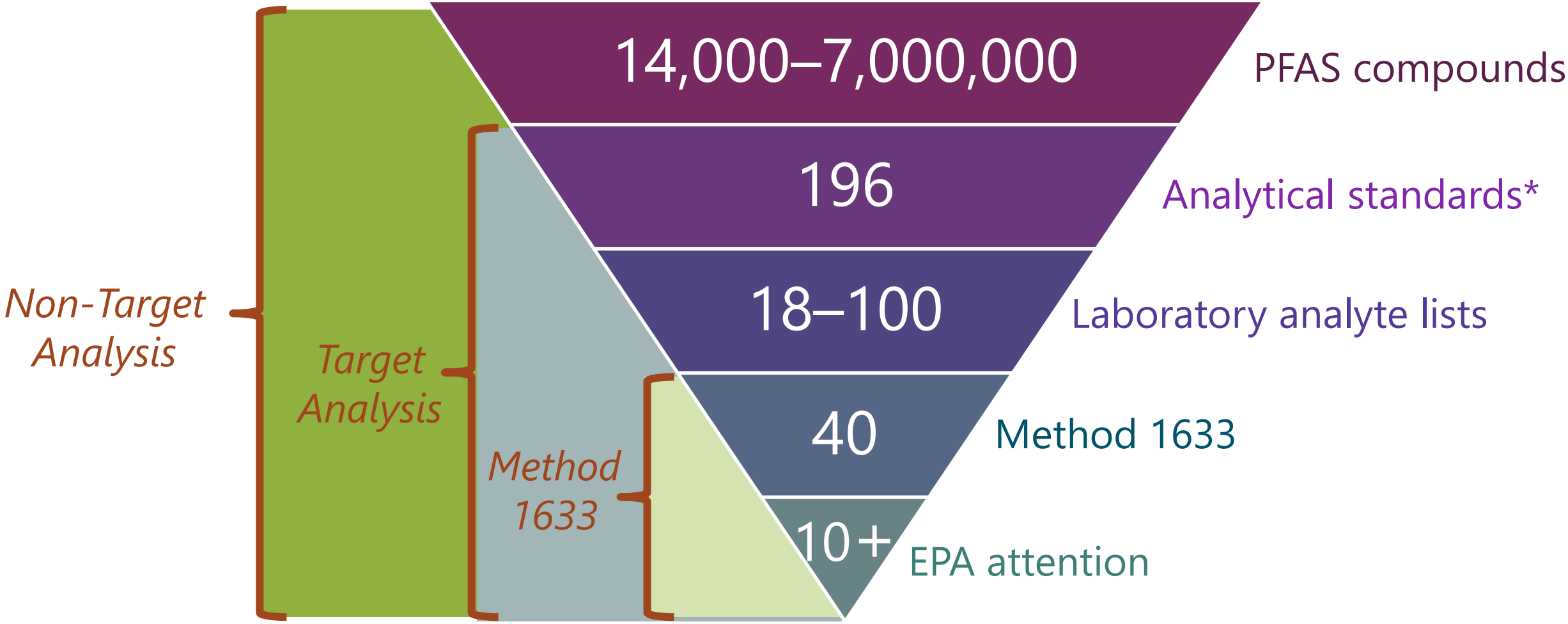
PFAS



*Estimated by Trier et al. 2025.

PFAS Source Signatures: AFFF

Two Main Formulations

Used 1964 to 2010

PFCAs, PFSAs, and precursors

Mixed linear and branched isomers

Electrochemical Fluorination (ECF)

PFOSA
N-MeFOSE
N-EtFOSE
N-MeFOSA
N-EtFOSA
N-MeFOSAA
N-EtFOSAA

Precursors

Degrade*

PFBS
PFPeS
PFHxS
PFHpS
PFOS
PFNS
PFDS
PFDoS

PFSAs

PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnA
PFDoA
PFTrDA
PFTeDA

PFCAs

Degrade*

Fluorotelomerization (FT)

4:2 FTS
6:2 FTS
8:2 FTS
3:3 FTCA
5:3 FTCA
7:3 FTCA

Precursors

Used 1973 to present

Only PFCAs and PFCA precursors

Only linear isomers

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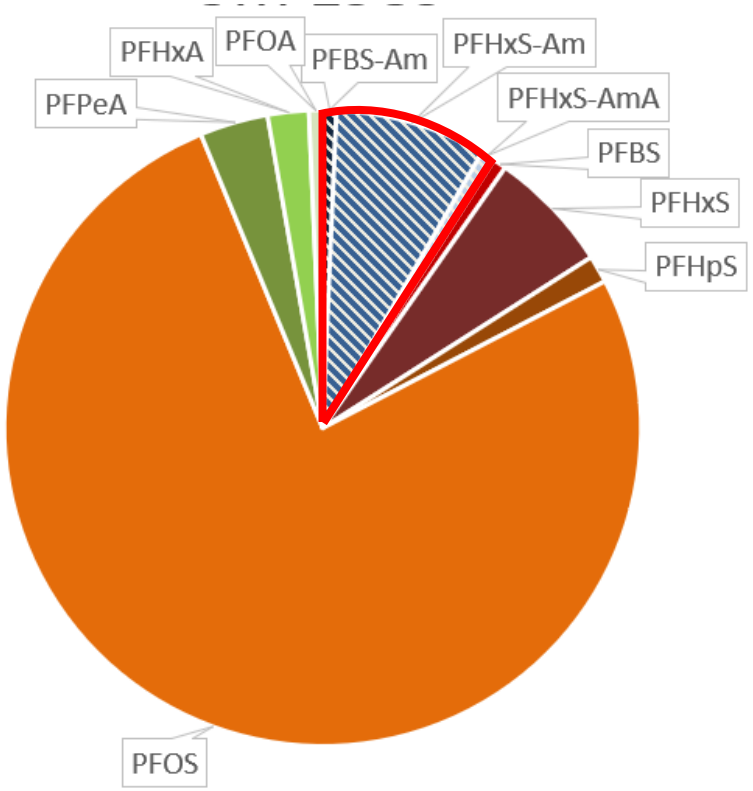
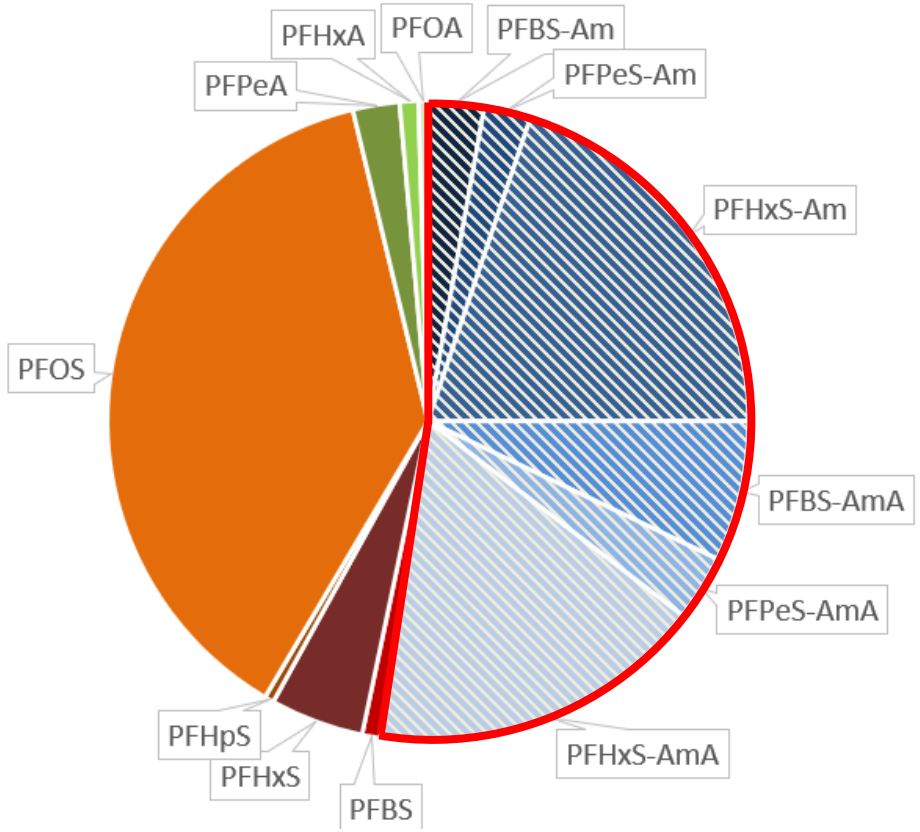
AFFF: ECF-Based Formulations

Solid: Target Analytes (Method 1633)
Hatched: Non-Target Analytes



3M (1989)



3M (2001)

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

Data from Houtz et al., 2013. Environmental Science & Technology 47: 8187-8195

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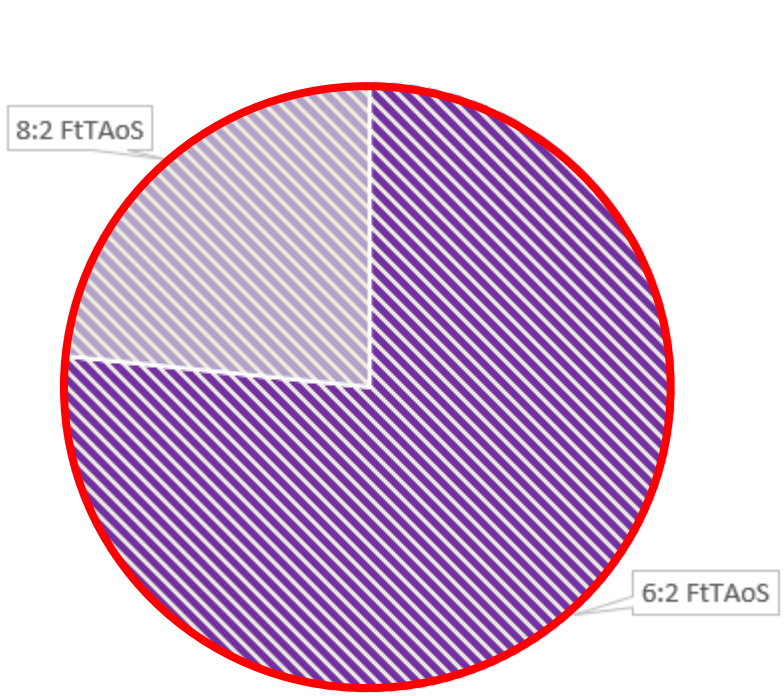
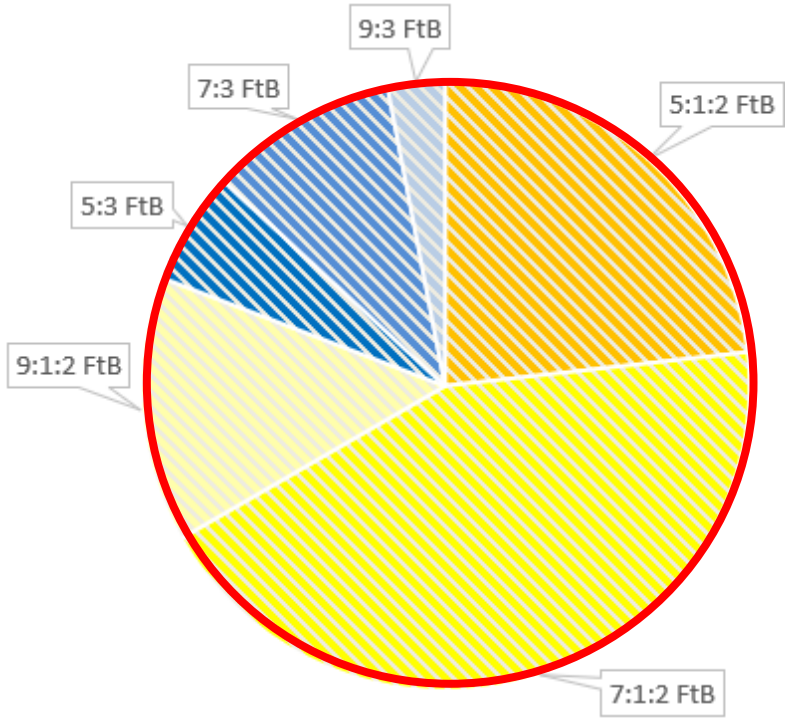
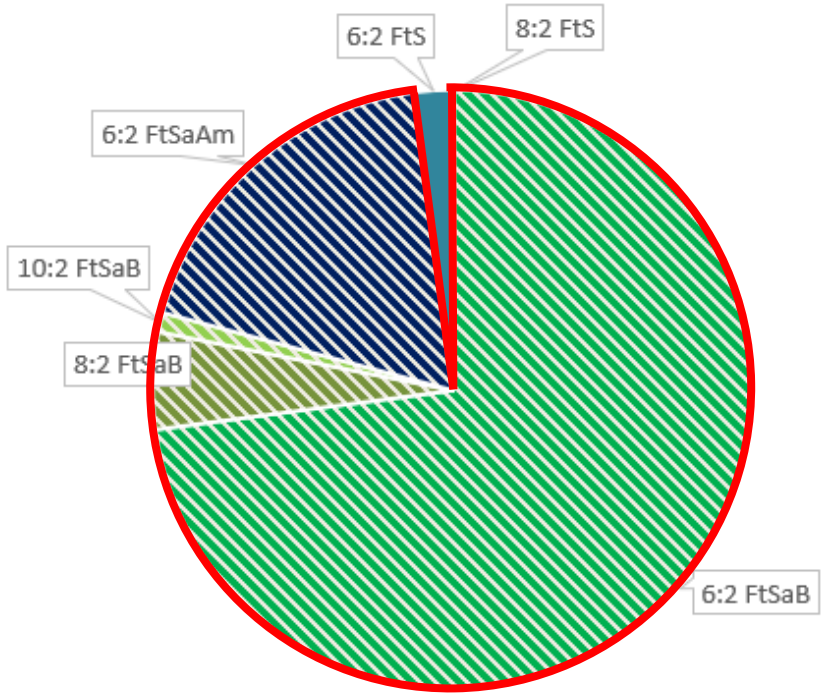
AFFF: FT-Based Formulations

Solid: Target Analytes (Method 1633)
Hatched: Non-Target Analytes







Ansul (1986/1987)

Buckeye (2009)

National Foam (2005)

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

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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

Manufacturing Type	Method 1633 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 (1633 compound)
  - Wastewater treatment plants
    - Pharmaceuticals (e.g., acetaminophen)
    - Caffeine
    - Artificial sweeteners

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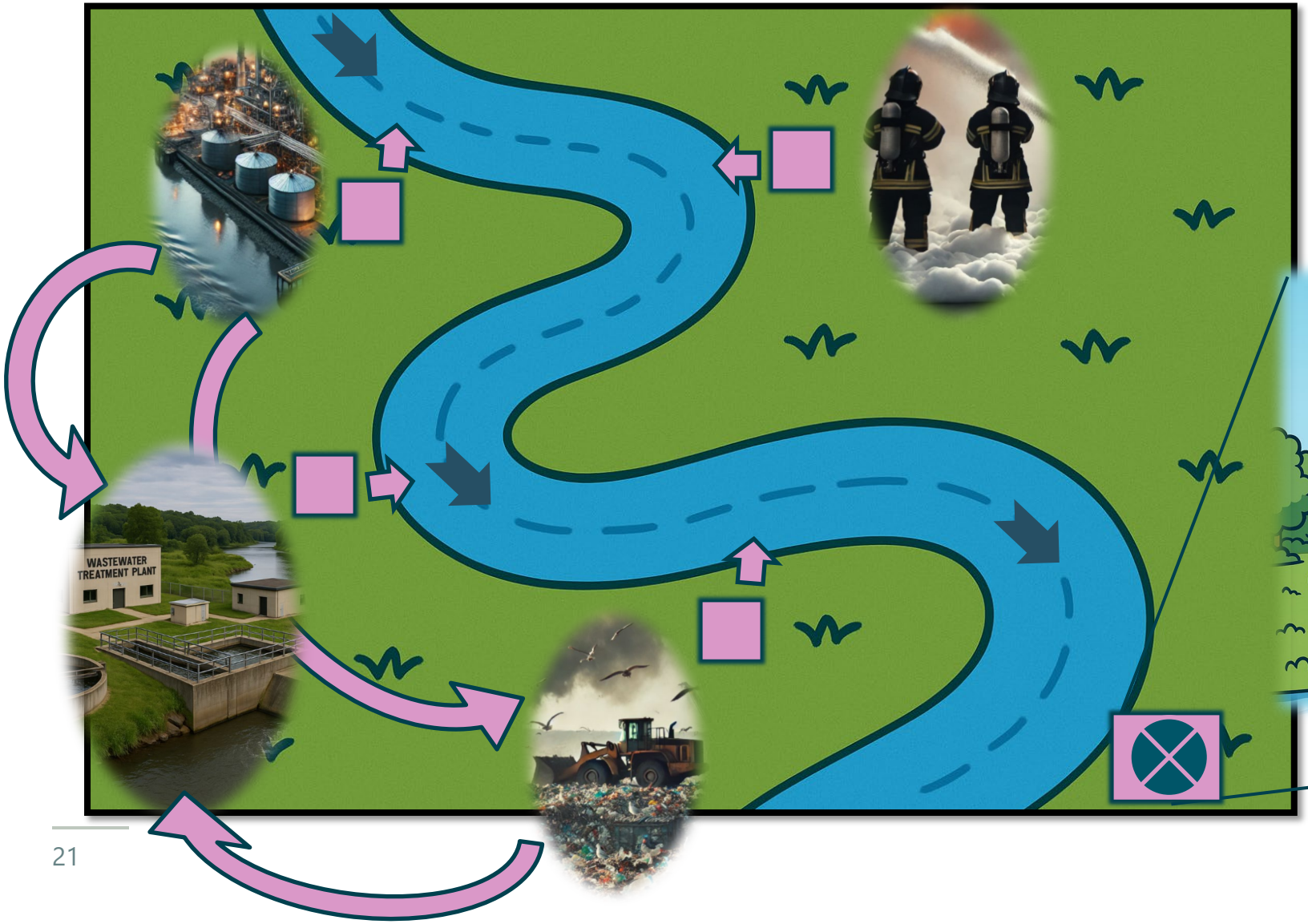
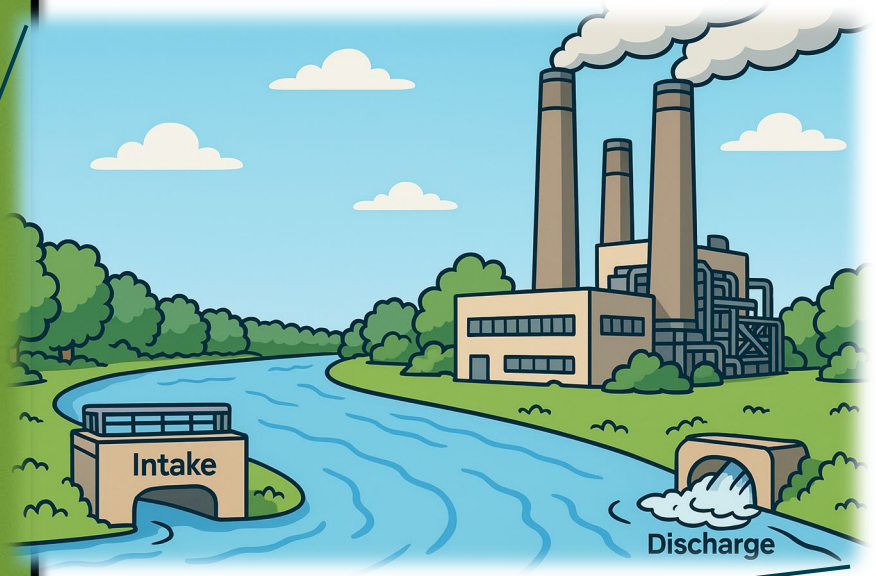
Understand Source Interactions





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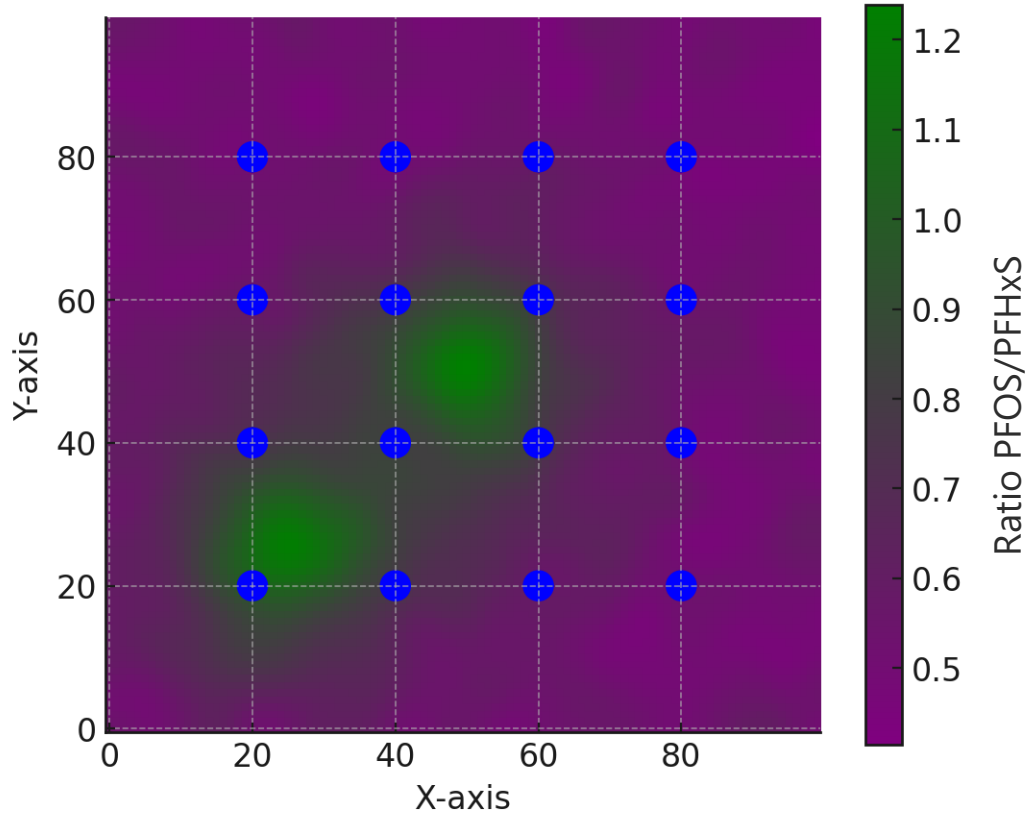
Forensic Techniques: Spatial Analyses

- Patterns across space can indicate source areas
  - Concentrations of single unique indicator compounds
  - Ratios (e.g., PFOS:PFHxS)
    - One moves faster, which changes the ratio with distance
  - Percent composition of precursors
  - Percent composition of linear versus branched isomers
  - Advanced statistical analyses



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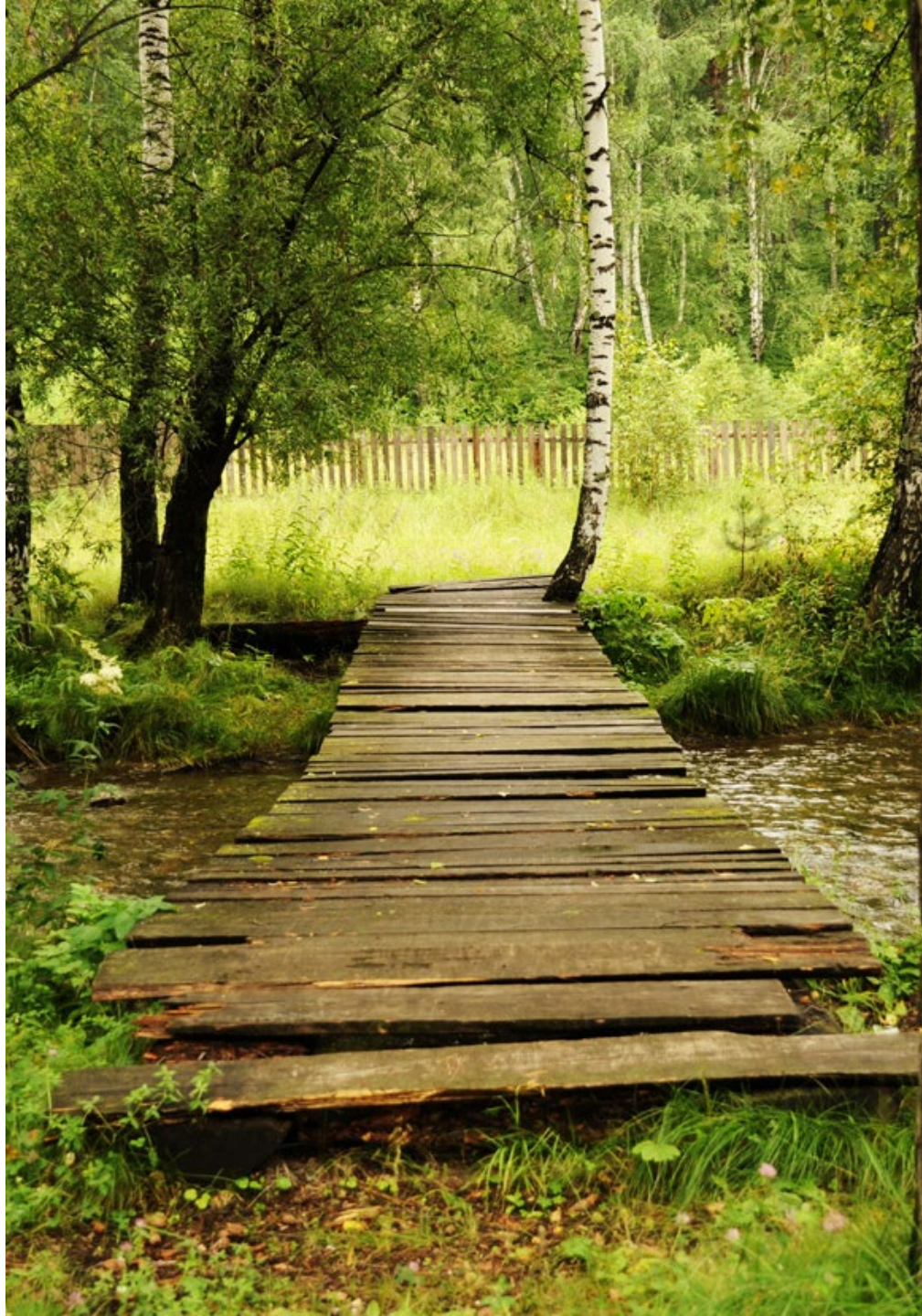
Conclusions

- Identifying and reducing PFAS sources is the best first step to reducing effluent concentrations
- Start by comparing intake and effluent concentrations
  - Follow up with historical research for on- and off-site potential sources
- Develop a testing strategy based on most likely source profiles
  - Method 1633 may not tell you everything
  - Weigh pros and cons of additional laboratory testing methods to understand forensic marker compounds
- Use PFAS and spatial data together to determine source areas



What questions do you have?