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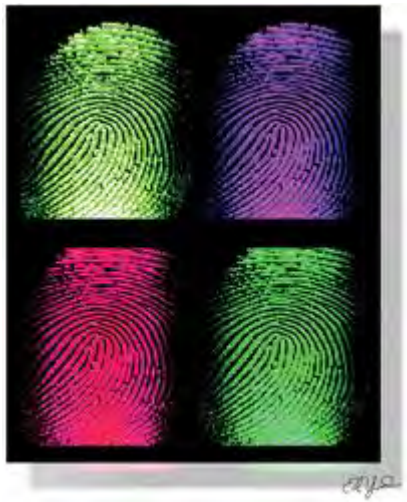

Source Evaluation for Per- and Polyfluoroalkyl Substances (PFAS)

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AEHS Conference,
San Diego, March 19, 2019

Innovative Solutions
Sound Science

Outline

- Understanding PFAS
- Sources / Uses
- Proven & Unproven Forensic Techniques
- Application Examples
- Strategic Approaches

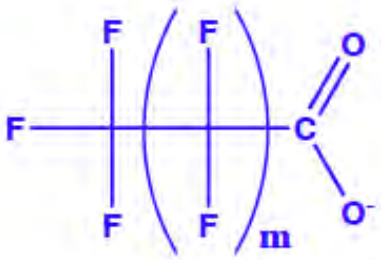
PFAS – At a Glance

- PFAS = **Per- and PolyFluoroAlkyl Substances**
- Polymers & **Non-Polymers**
- Organic aliphatic compounds with C-F bonds & a variety of chemical groups:
  - Common traits (stability, persistence, lipid & water repellants)
  - Variable traits (e.g., physical-chemical properties)
- Since 1950s, more than **4,000 individual PFAS** may be on the market, with all uses of each PFAS remaining unknown
- Modern, commercially available analytical techniques identify only up to about **25–30 individual PFAS compounds**

PFAS – Structure & Nomenclature Examples

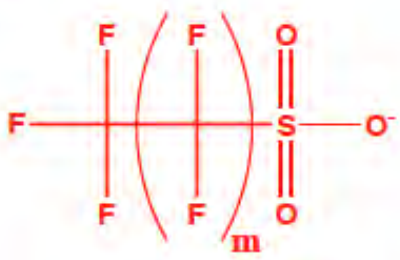
Per = fully fluorinated alkyl tail

Perfluoroalkyl carboxylates (PFCAs):



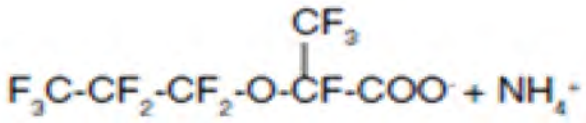
Examples:
m=2 PFBA
m=4 PFHxA
m=6 PFOA

Perfluoroalkane sulfonates (PFSAs):



Examples:
m=3 PFBS
m=5 PFHxS
m=7 PFOS

Perfluoroalkyl ether carboxylates (PFECAs):



GenX
(Perfluoro-2-propoxypropanoic acid)

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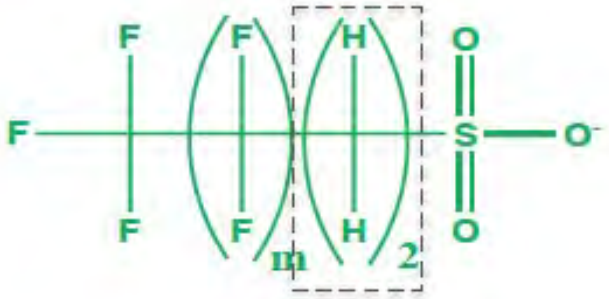
PFAS – Structure & Nomenclature Examples

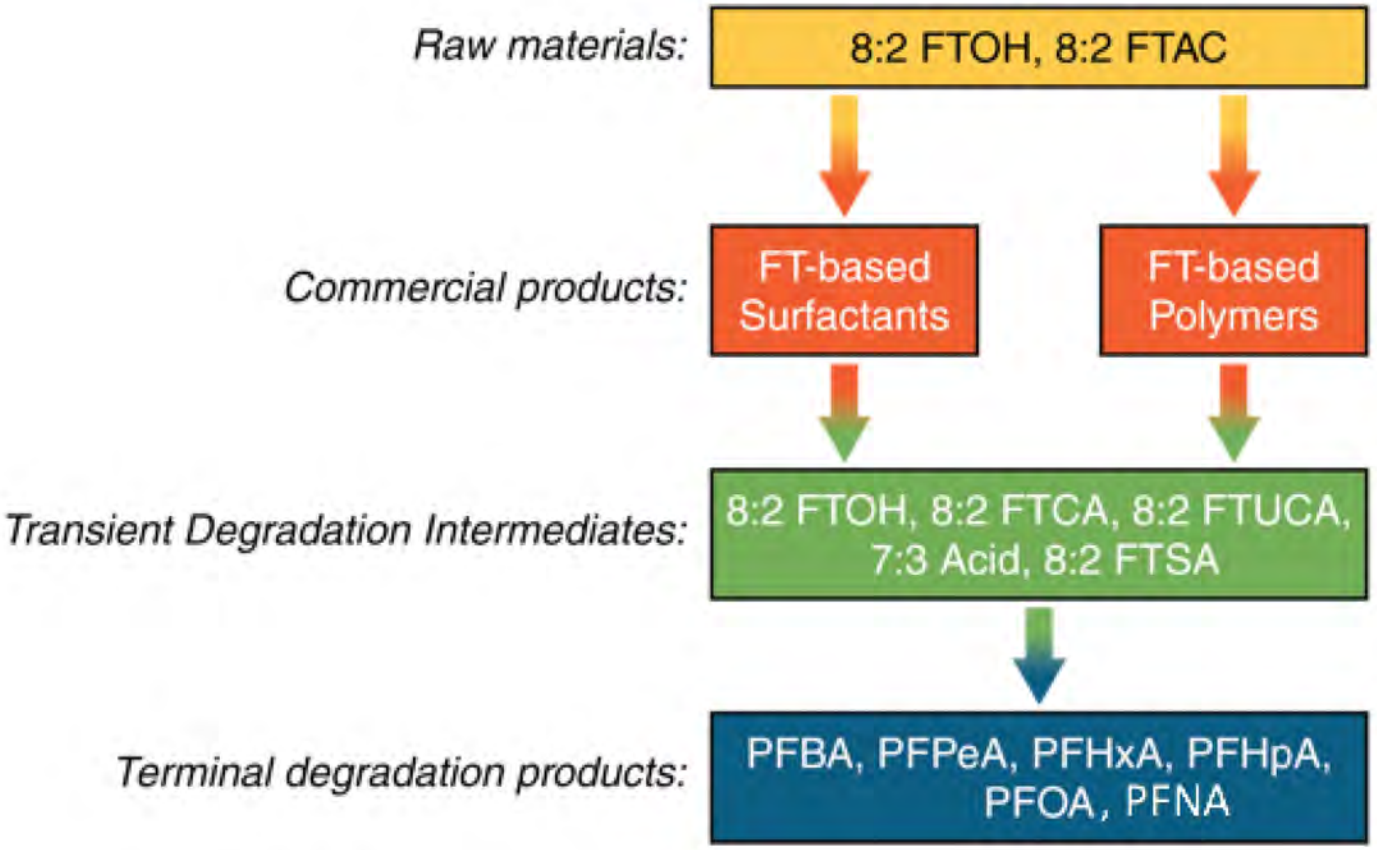
Poly = partially fluorinated alkyl tail

Polyfluoroalkyl substances: FluoroTelomer Sulfonates



m=5 6:2 FtS
m=7 8:2 FtS

PFAS – FluoroTelomer Degradation Pathway Overview



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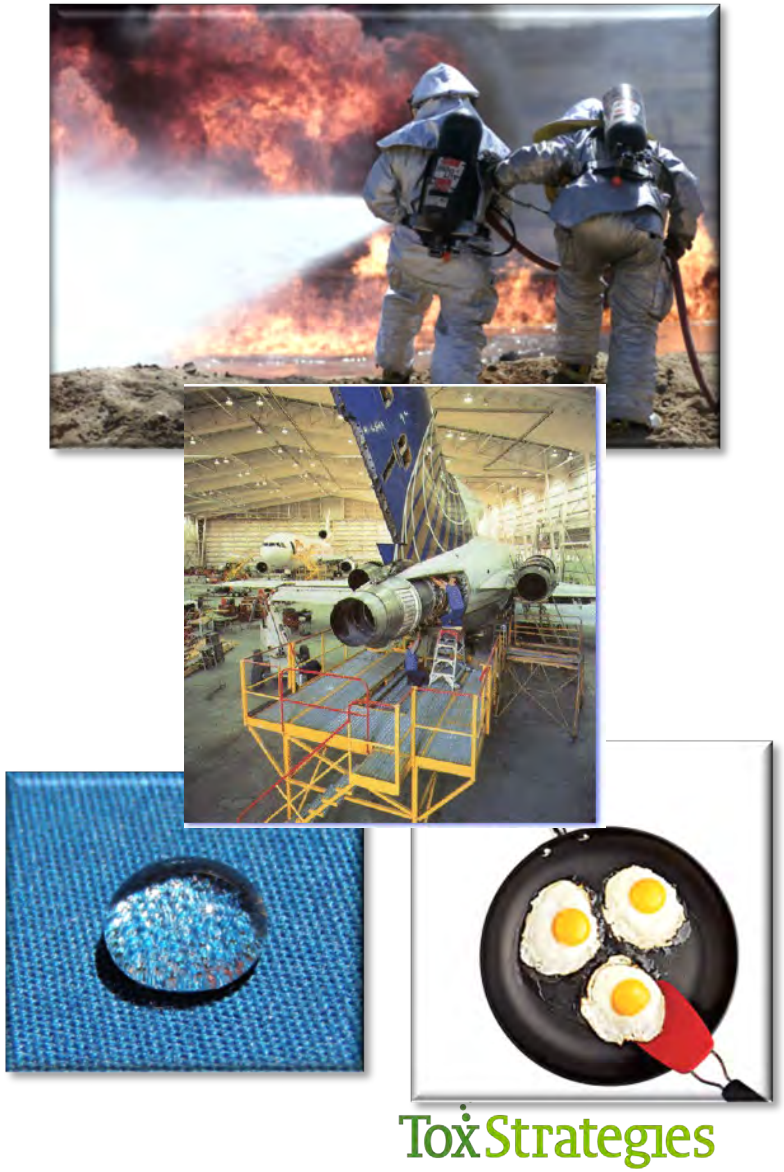
PFAS – Uses & Sources

- **AFFF (aqueous film-forming foam) used in fire training & response** – class B firefighting foam since late 1960s

- **Industrial sources**
  - Manufacturing (e.g., carpet, textile)
  - Chemical industry
  - Many others (aerospace, semiconductor, medical products, automotive, construction, electronics, metal plating, energy, oil & mining production, biocides, paper & packaging)

- **Consumer products**
  - Clothing
  - Food packaging
  - Furniture/household products
  - Outdoor equipment
  - Cosmetics/personal care products

- **Landfills & wastewater treatment plants**



PFAS – Environmental Behavior

→ Persistent organic pollutants (POPs)

→ Source zone – accumulation at air-water and air-product surfaces → slow migration

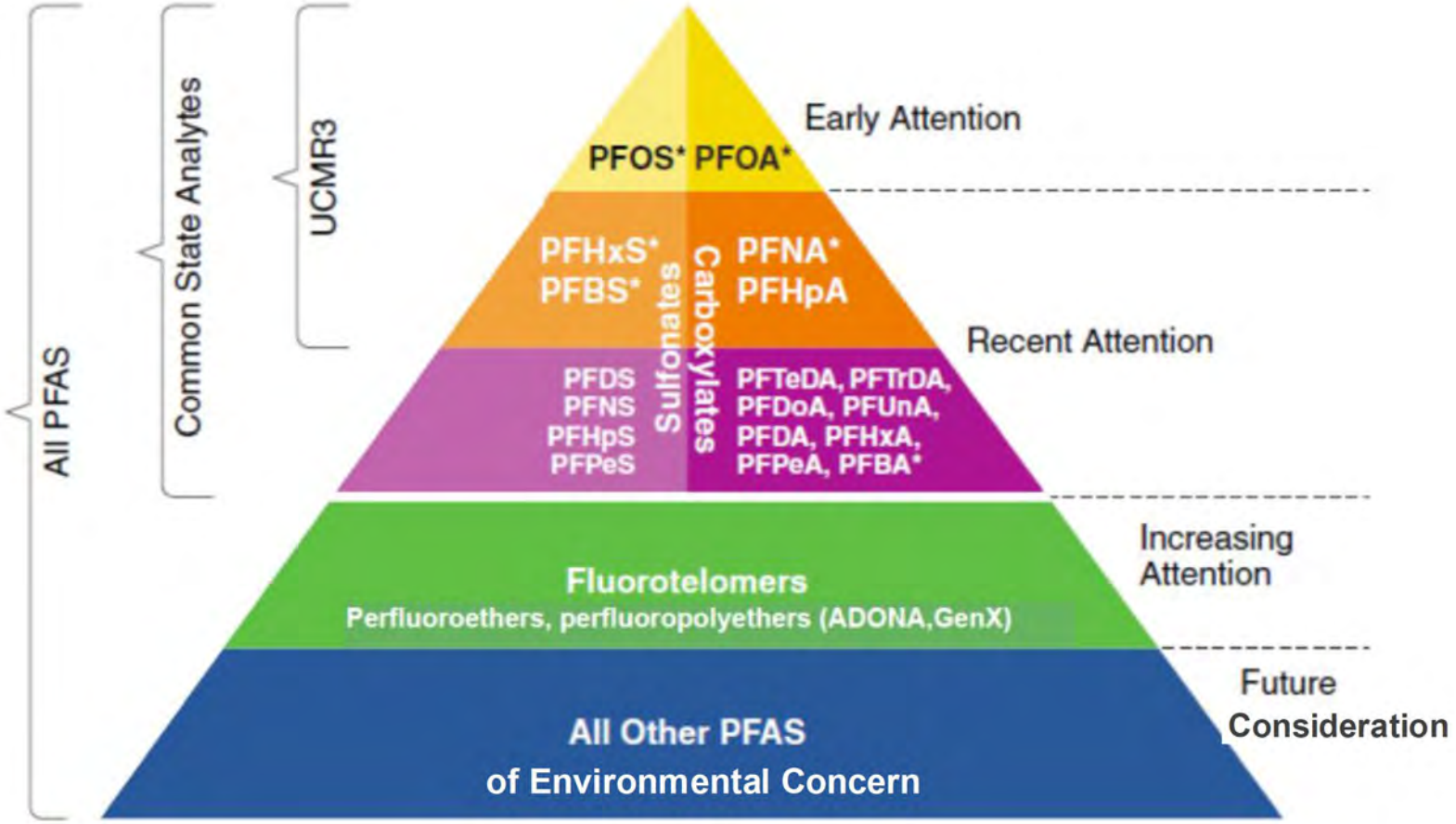
→ Microbial action can remove non-fluorinated functional groups

→ PFCAs & PFSAs accumulating in GW

→ Precursors may accumulate in soil and aquifer matrix more near point of release

→ Mobility in groundwater: anions>zwitterions>cations

PFAS – Targeted Compounds



Source: J. Hale, Kleinfelder

PFAS – Environmental Forensic Techniques

- Historical document review
- Chemical fingerprinting
  - Comprehensive chemical analysis
    - *Homologue groups*
    - *Precursor compounds – TOP*
    - *Fluorotelomers*
  - Branched vs. linear isomers
  - Chiral fingerprinting
- Multivariate statistics – Receptor models
- Other techniques ?
  - Signature chemicals
  - Isotopic fingerprinting
  - Atmospheric tracers
  - Tree-ring fingerprinting

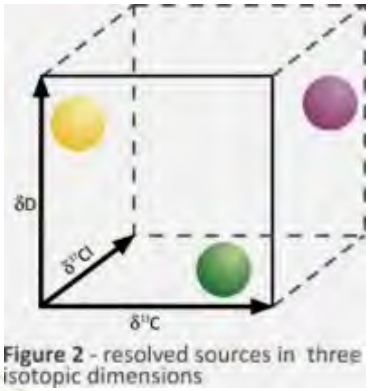
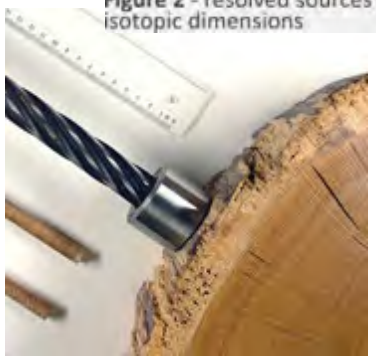


Figure 2 - resolved sources in three isotopic dimensions



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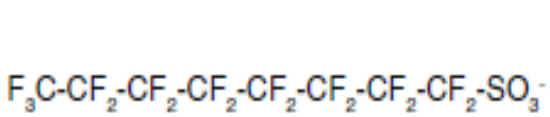
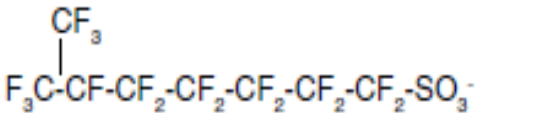
Historical Review Example – Manufacturing

- **Electrochemical fluorination (ECF)**
  - Licensed in 1945 by 3M → Commercial production started in 1951
  - Since early 2000s, no longer used for PFOS, PFOA ,& C8-based AFFF
  - Produces a **mixture of linear & branched perfluorinated isomers**



Linear Perfluorooctane sulfonate (PFOS)



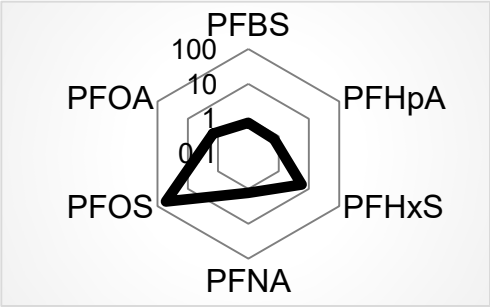
Branched Perfluorooctane sulfonate (PFOS)

- **Telomerization**
  - Produces fluorotelomer sulfonates that can be found at AFFF sites
  - Currently only for short-chain fluorotelomer-based products
  - Produces **mostly linear PFAS isomers with even number of C atoms**
  - Since early 2000s, fluorotelomer-AFFF formulations (<C6) are predominant

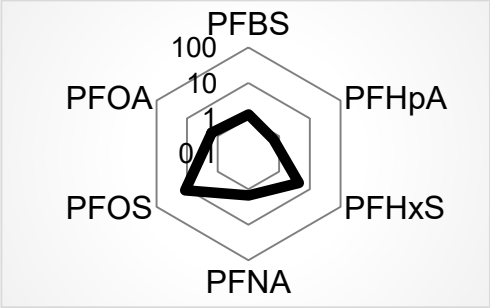
Chemical Fingerprinting – PFAS Distribution in Various Media

Distribution of UCMR3 Individual PFAS at Military Sites (AFFF Source)

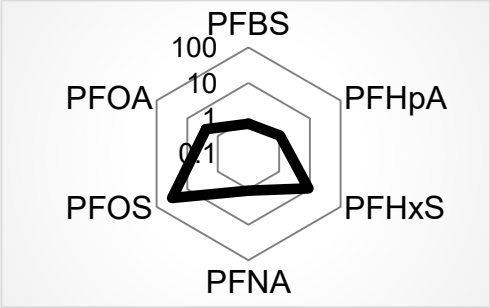
Surface Soil



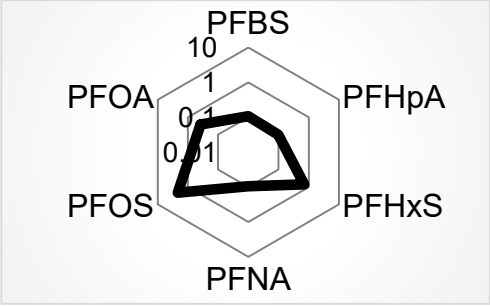
Subsurface Soil



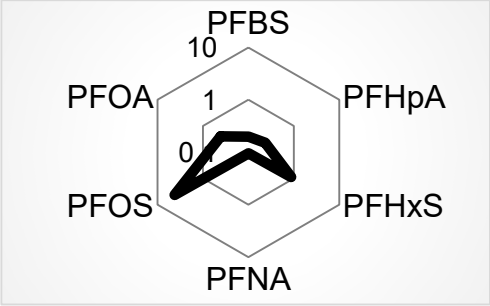
Sediment



Surface Water



Groundwater



Source: Hatton J, DiGuiseppi, B. 2018. PFAS Forensics. Presented at Battelle Conference on Chlorinated and Recalcitrant Compounds, 2018

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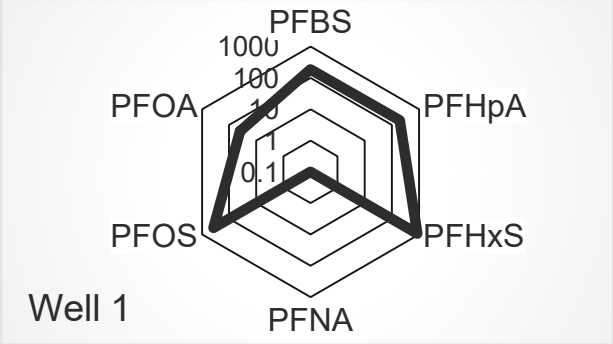
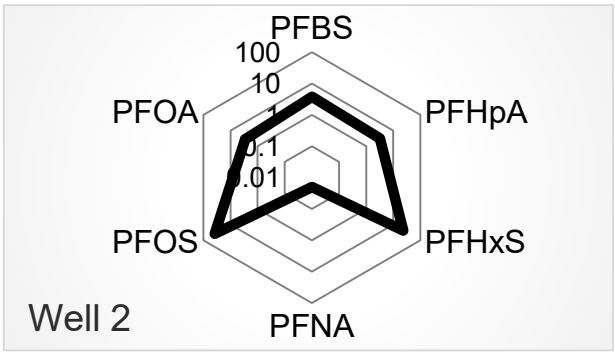
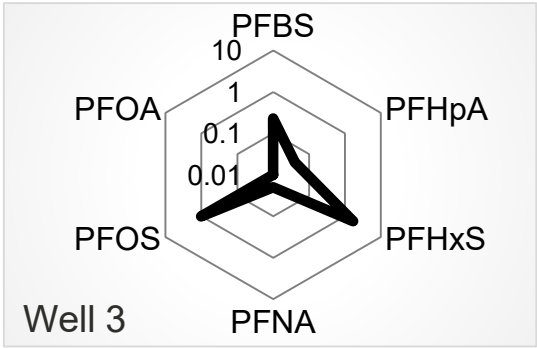
Chemical Fingerprinting – PFAS Transformation in GW

Near Source Zone





2.5 km Downgradient



Source: Hatton J, DiGuiseppi, B. 2018. PFAS Forensics. Presented at Battelle Conference on Chlorinated and Recalcitrant Compounds, 2018

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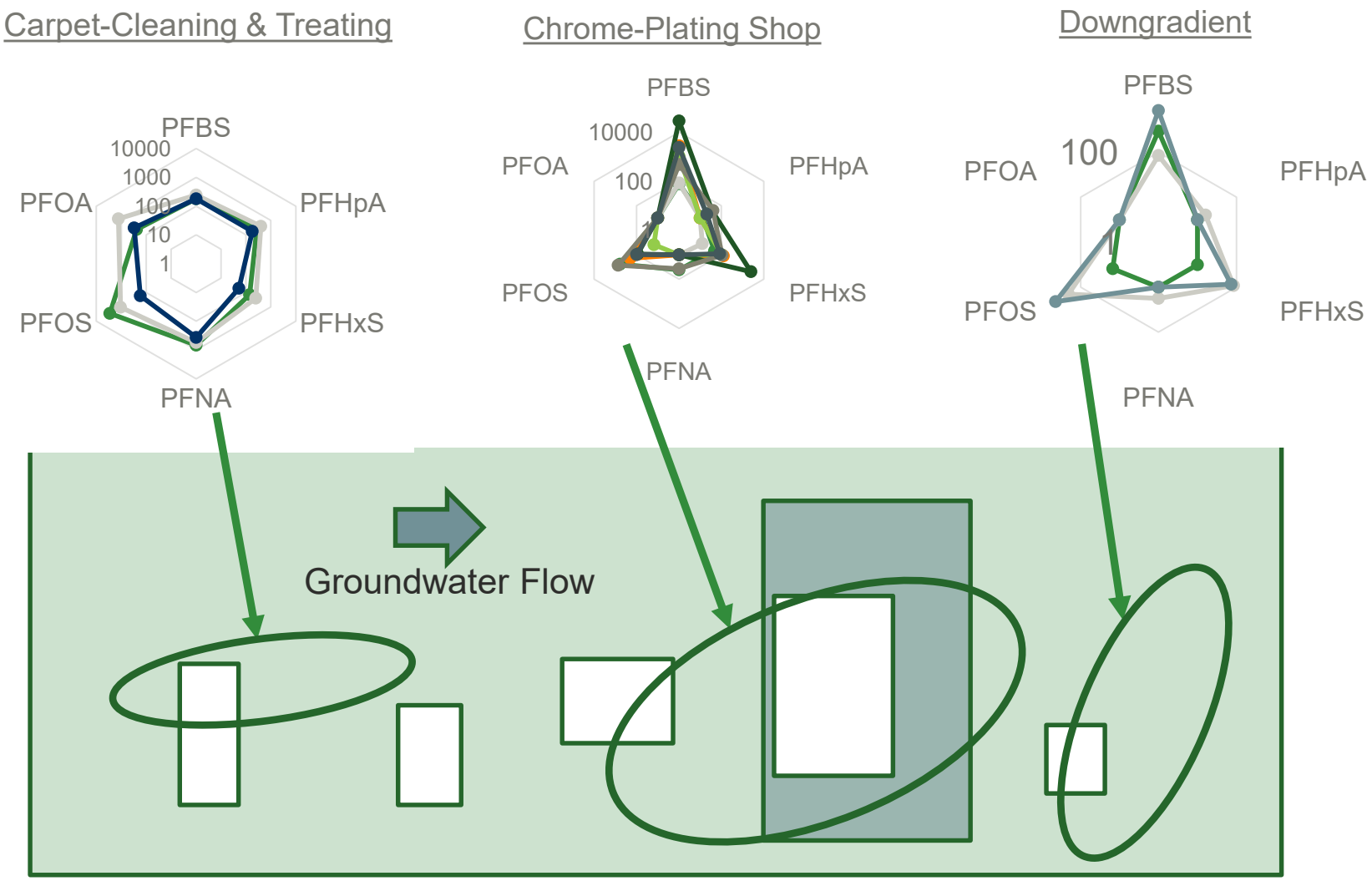
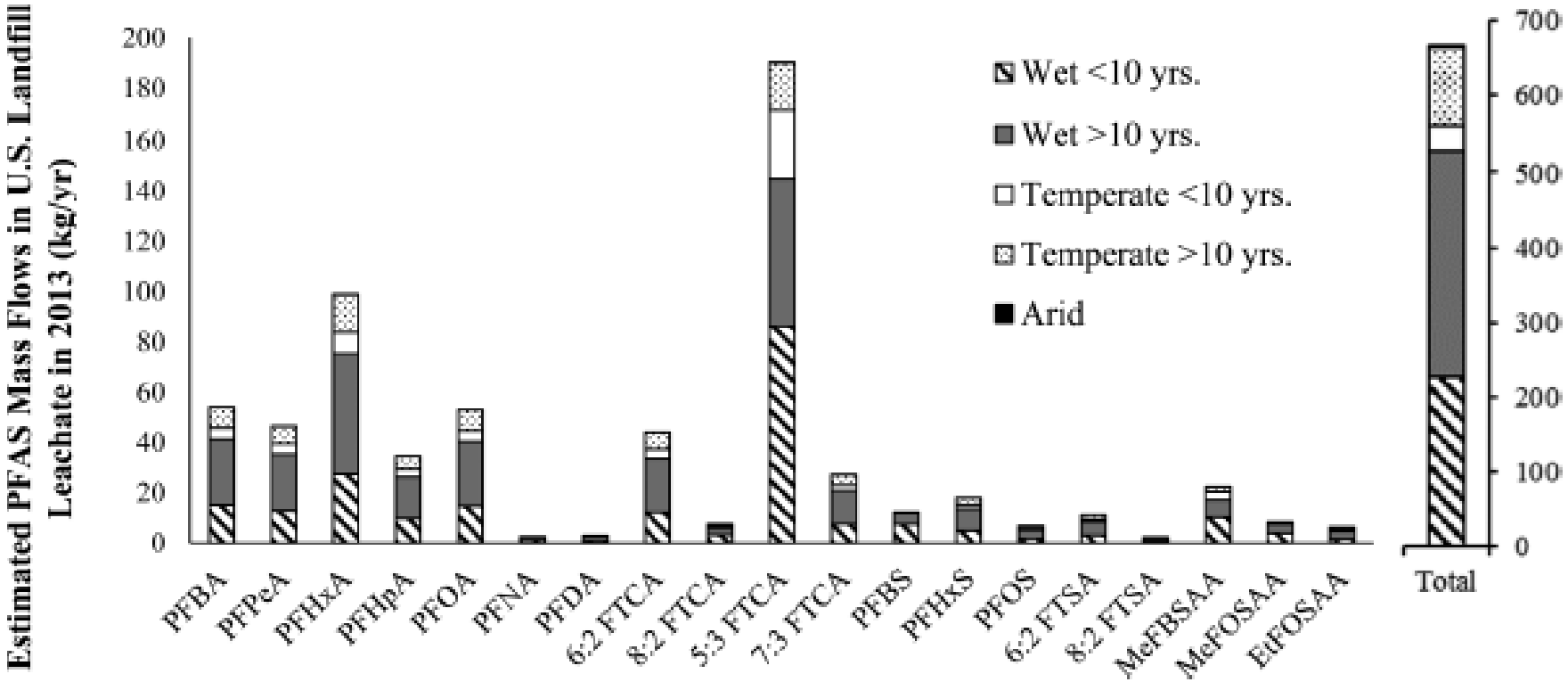
Chemical Fingerprinting – Forensic Case Study



Source: Hatton J, DiGuiseppi, B. 2018. PFAS Forensics. Presented at Battelle Conference on Chlorinated and Recalcitrant Compounds, 2018

Chemical Fingerprint of PFAS from Landfills – Case Studies Across the U.S.



Data based on 95 leachate samples from 18 landfills (mostly MSW) of different ages and climates, analyzed for 70 PFAS between Feb. 2013-Dec. 2014

Source: Lang JR, Allred BM, Field JA, Lewis JW, Barlaz MA. 2017. National estimate of per- and polyfluoroalkyl substance (PFAS) release to U.S. municipal landfill leachate. Environ Sci Technol 51:2197-2205.

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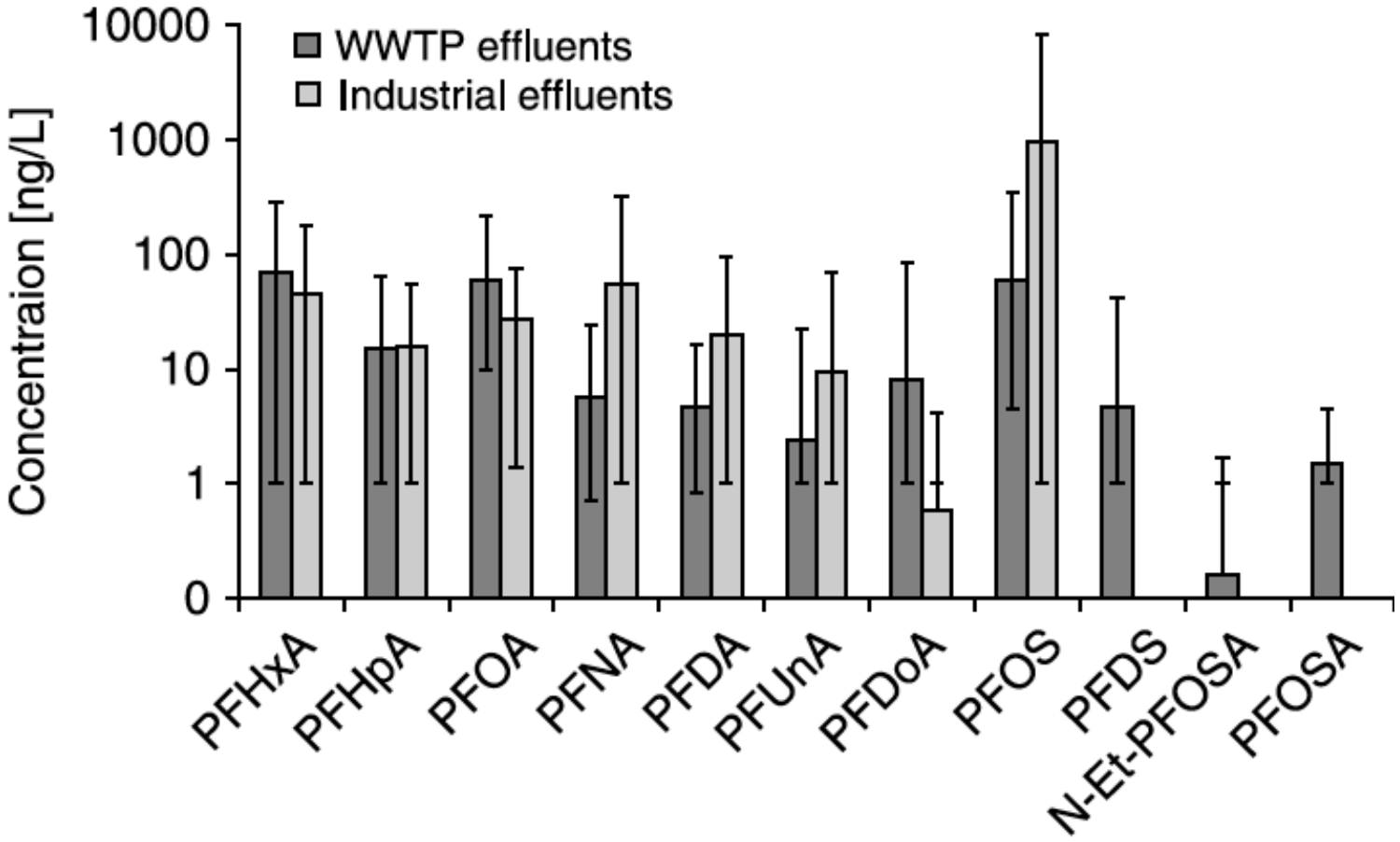
Chemical Fingerprinting – PFAS in Wastewater Treatment Plant and Industrial Effluents

Overview

- 11 individual PFAS were measured in:
  - 21 municipal wastewater treatment plant effluents (including domestic and industrial influents) – daily composite samples
  - 9 industrial point sources – grab samples from:
    - Paper industry
    - Electrical industry
    - Metal industry
    - Printing industry
    - Laundry and dry cleaning

Source: Clara M, et al. 2008. Point source emissions of perfluorinated alkylated substances. Water Sci Technol 58(1):59-66.

Chemical Fingerprints of PFAS in Wastewater Treatment Plant and Industrial Effluents



Source: Clara M, et al. 2008. Point source emissions of perfluorinated alkylated substances. Water Sci Technol 58(1):59-66.

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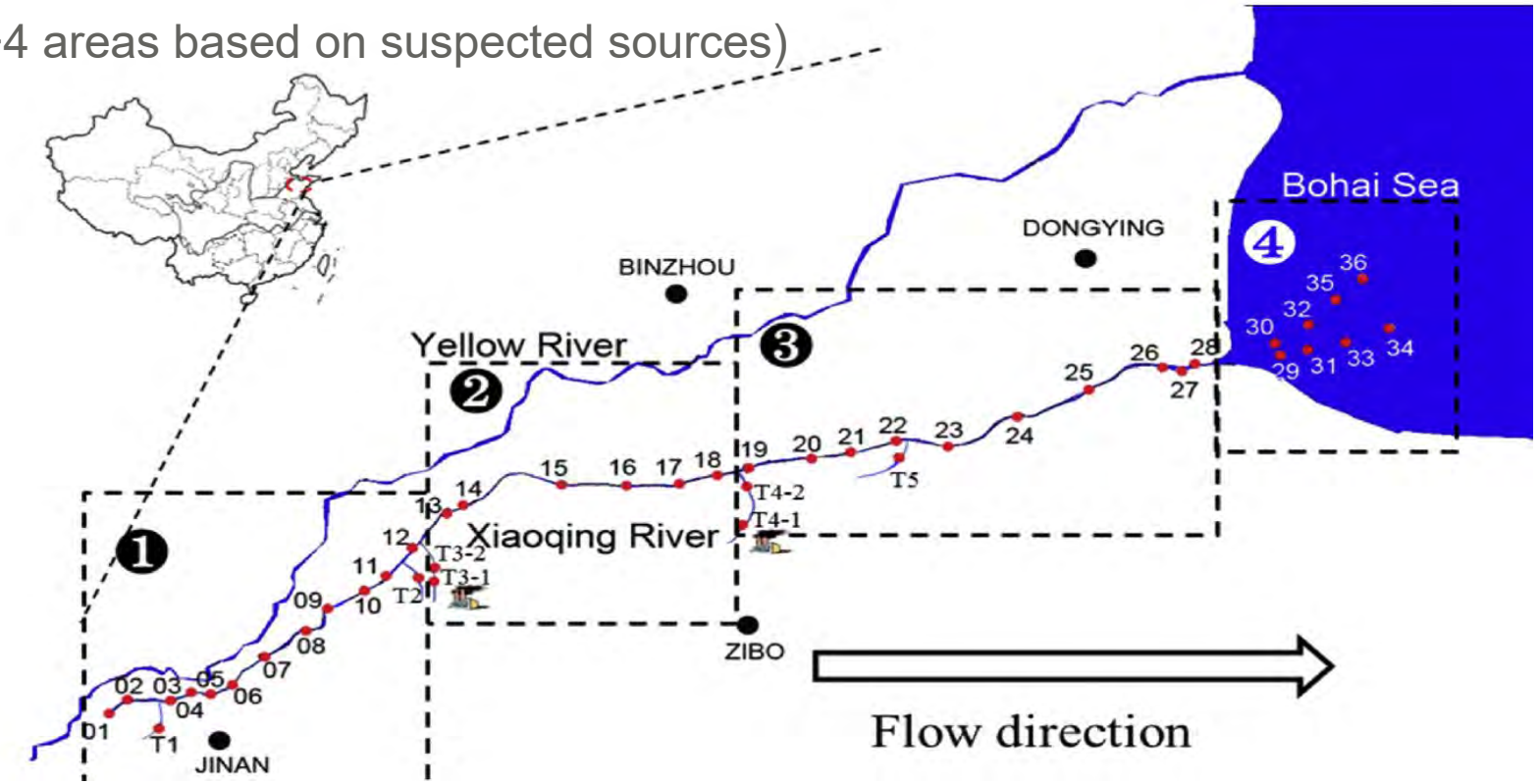
Chemical Fingerprinting – Forensic Study along Xiaoqing River, China

Sample Locations (Water & Sediment)

(1–4 areas based on suspected sources)



1. *Urban & wastewater effluent sources*
2. *Minor point source*
3. *Major point source (FP Manufacturer)*
4. *Marine estuary*

Source: Shi Y. et al. 2015. Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environmental Pollution 206: 104-112.

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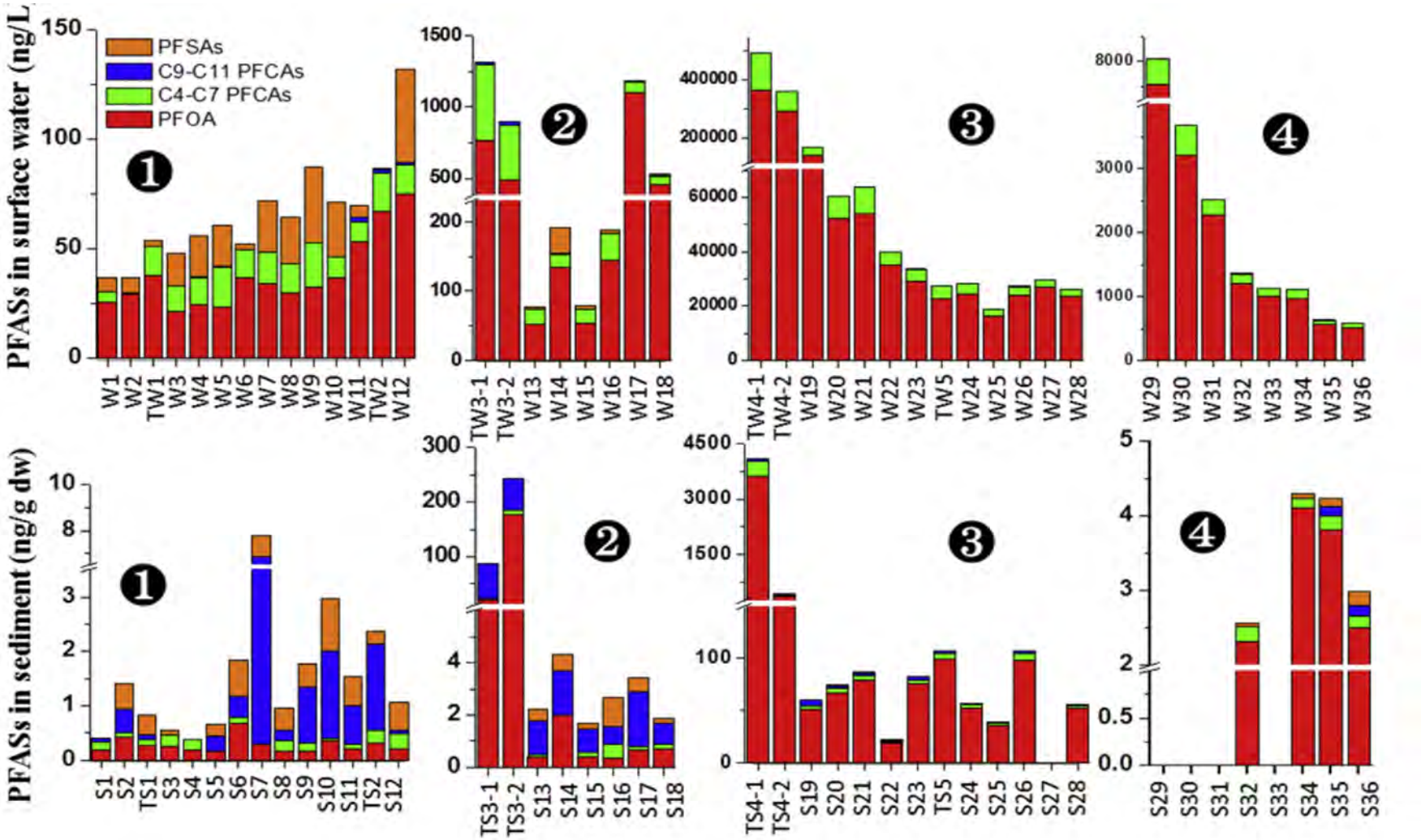
Chemical Fingerprinting – PFAS Distribution along Xiaoqing River, China



Source: *Shi Y. et al. 2015. Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environmental Pollution 206: 104-112.*

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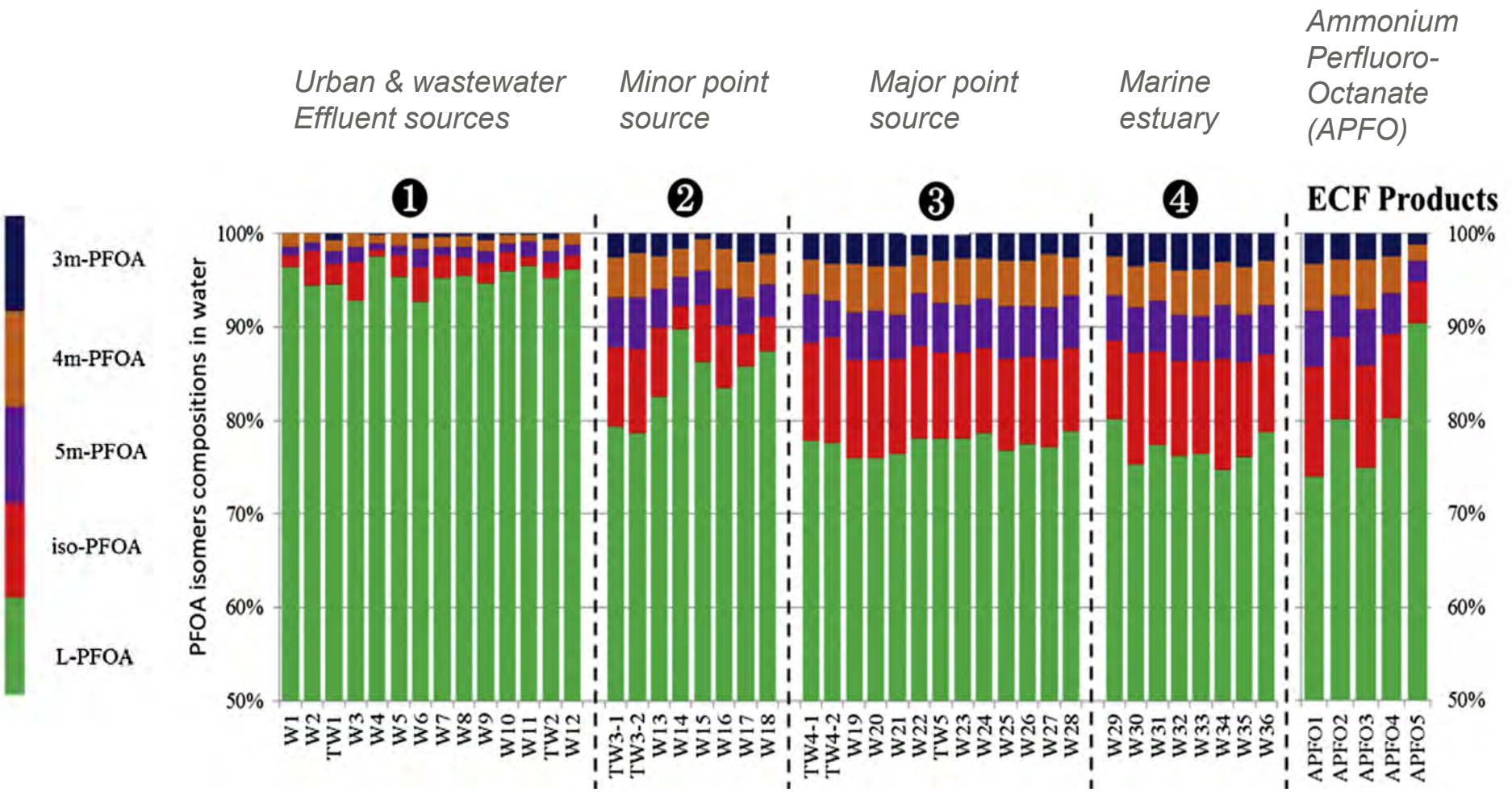
Chemical Fingerprinting – Linear Vs. Branched PFOA Isomers along Xiaoqing River, China



Source: *Shi Y. et al. 2015. Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environmental Pollution 206: 104-112.*

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Chemical Fingerprinting Study along Xiaoqing River, China

Findings

- Isomer profiles are well conserved in surface water over a large range of concentrations, organic carbon & salinities
- C4-C8 PFCAs homologue patterns were also well conserved in surface water

→ **Isomer profiles provide useful forensic tools in surface-water investigations**

Source: Shi Y. et al. 2015. Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environmental Pollution 206: 104-112.

Chemical Fingerprinting – Chiral Signatures for Source Differentiation

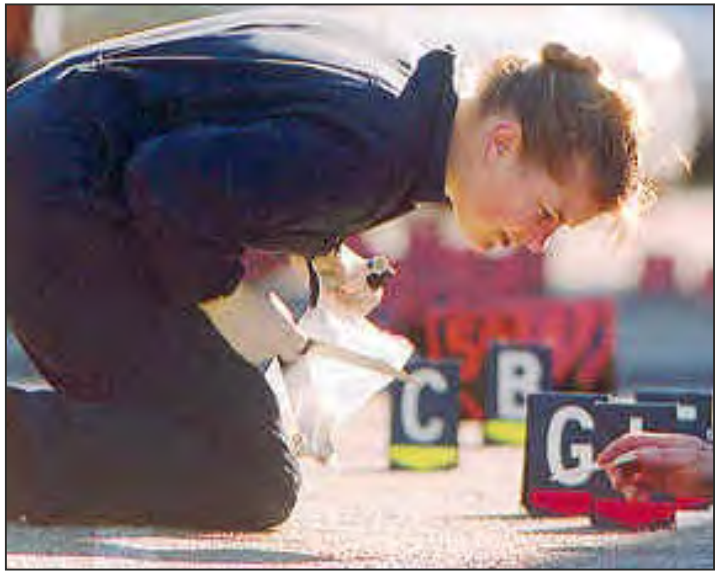
- Branched isomers in living organisms have two main sources:
  - Direct ingestion
  - Precursor transformation
- Chiral analysis provides the proportion between enantiomers (chiral isomers)
- Enantiomer fraction (EF) of branched PFAS:
  - Around 0.5 → direct ingestion
  - Distinct from 0.5 → produced by precursor metabolization

Source: Miralles-Marco A, Harrad S. 2015. Perfluorooctane sulfonate. A review of human exposure, biomonitoring and the environmental forensics utility of its chirality and isomer distribution. Environ Int 77:148-159.

PFAS – Limitations of Applied Techniques

Forensic Technique	Limitations
Chemical fingerprinting	Precursor transformations □ hard to predict effects on spilled PFAS fingerprints
	Distribution of precursors along a contaminated plume may not be uniform
	Degradation processes are poorly understood
	Environmental fractionation of individual PFAS
	Inconsistent list of target compounds from reported studies that provide fingerprints
Multivariate statistics (e.g., receptor models)	Assume no change in PFAS composition as they migrate from source to receptors
	Assign sources based on resulting PFAS patterns/groupings, rather than testing specific source signatures

Other Forensic Techniques
Potentially Applicable to PFAS



Signature Chemicals – Potential for Tracking AFFF

AFFF composition:

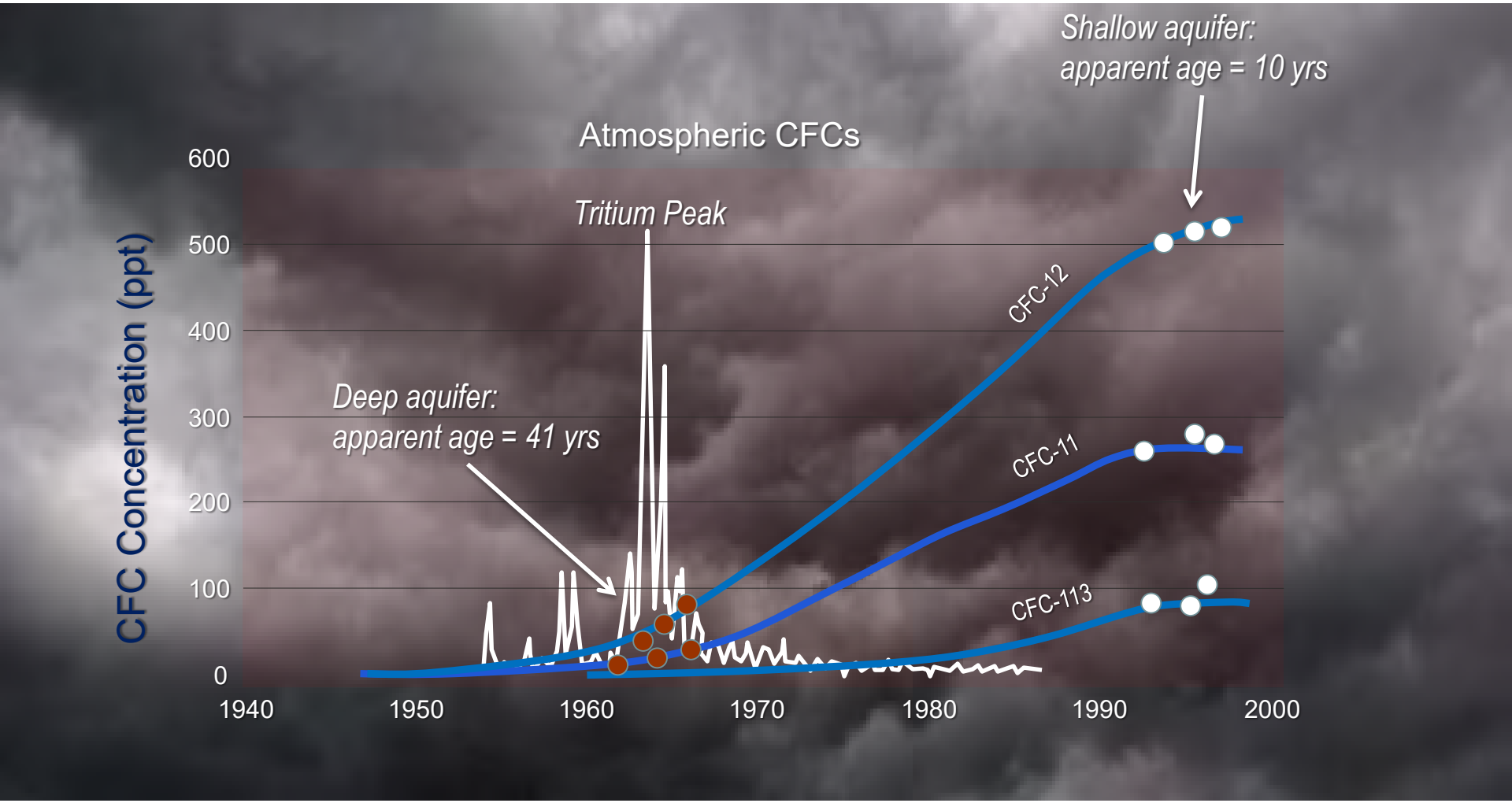
- Fluorinated Surfactants
- Hydrocarbon Surfactants
- Organic Solvents
- Water
- Minor Ingredients Include:
  - Corrosion Inhibitors
  - Inorganic Salts
  - Biocide
- Polymer (Polysaccharide) in Alcohol Resistant AR-AFFF

Source: Cortina T, Korzeniowski S. 2018. Update on fire fighting foams for ITRC PFAS Team. Presented on July 24, 2018.

Isotopic Fingerprinting – Overview

Principles	Applications
I. There is a **measurable variability in stable isotopic composition** of many natural geologic materials and manufactured products	**Isotopic ratios may be linked to sources and used to allocate contributions**
II. Contaminant degradation changes the isotopic composition by increasing the amount of heavier isotope in the remaining contaminant (thus increasing the delta value)	**Changes in isotopic ratios (in time and space away from source) help confirm and measure degradation processes and evaluate degradation pathways** as part of MNA and fate & transport evaluation

Atmospheric Tracers – Overview & Example



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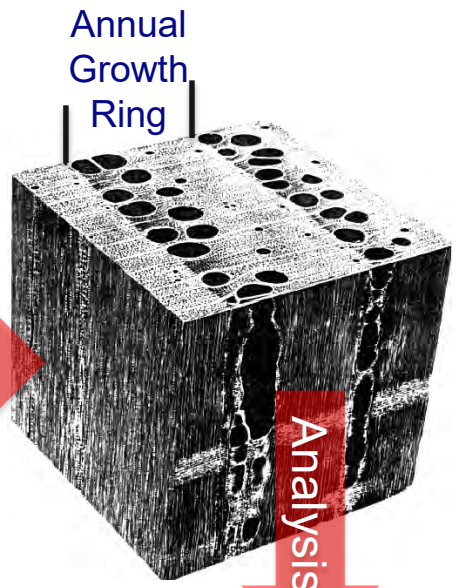
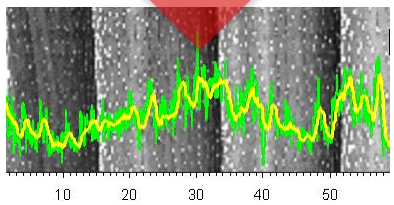
Tree-Ring Fingerprinting – Overview

Contamination in root zone can affect both ring width and chemical composition

Fixation



Analysis



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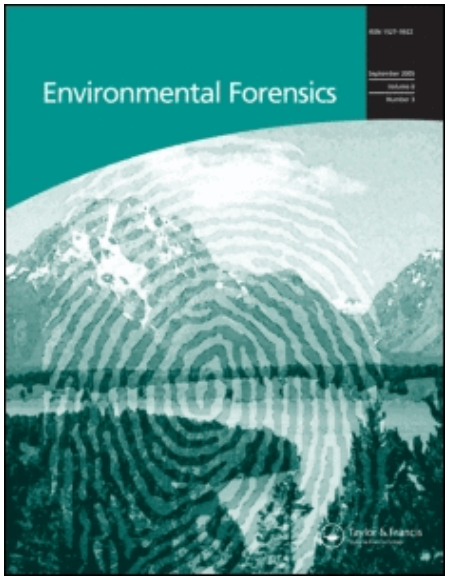
PFAS – Building Strategic Approaches

"***More Is Better!***"

- Use multiple, independent lines of evidence
- Target more individual PFAS, including Fts
- Evaluate TOP
- Take advantage of published fingerprints
- Consider all possible sources
- Obtain source-representative samples
- Evaluate PFAS distribution in time & space
- Evaluate potential degradation
- Consider forensic techniques not yet applied to PFAS



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Questions and Discussion

- Other Types of Challenges
- Case Studies
- Lessons Learned