Utility of historic data sets in forensic PFAS evaluations

Moderator: Rick Wice, PG, F.SAME, Battelle

Speaker: Tiffany Thomas, Ph.D., Principal Chemist, Haley & Aldrich

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MAY 14-16, 2024
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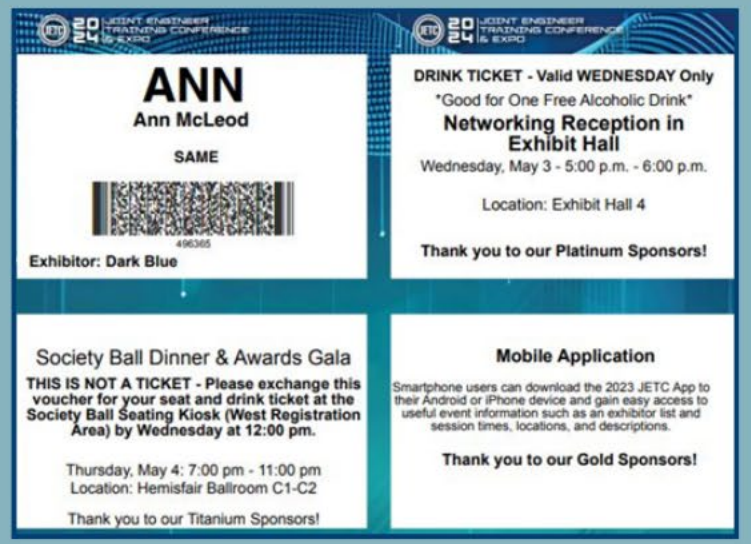

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  - Call currently third Wednesday of the month 1500-1600 hrs. May Change in Future
- For more information contact ECOI Chair Ann Ewy annewysame@gmail.com

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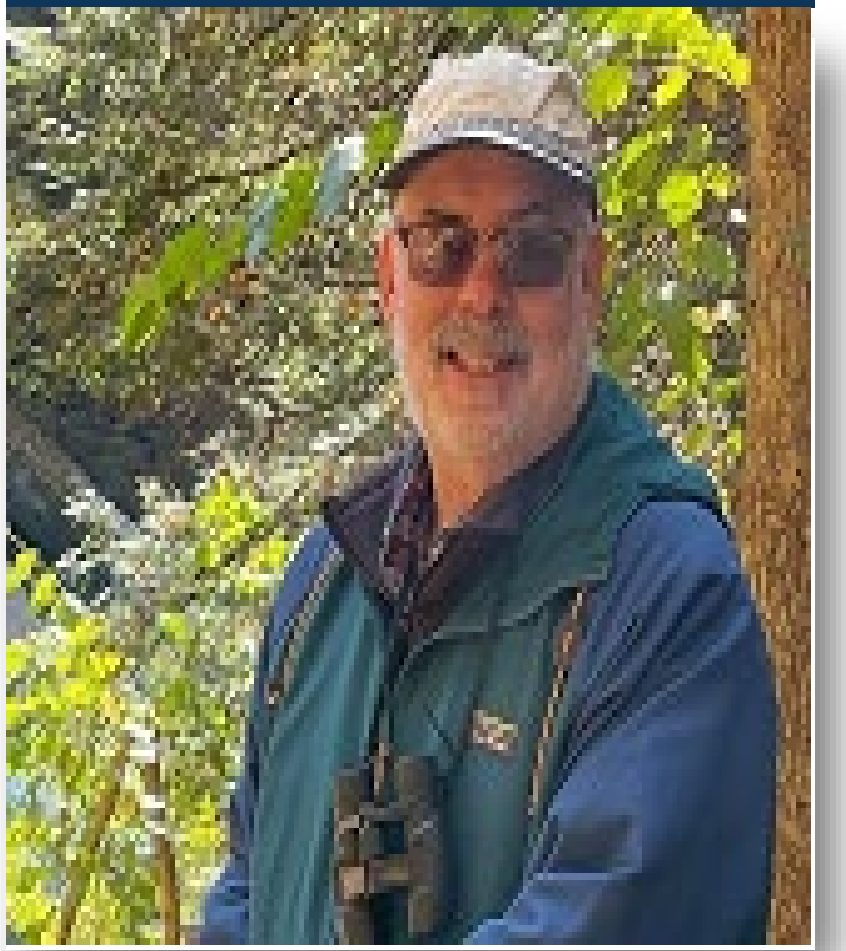

Rick Wice, PG. F.SAME

Battelle

Senior Geologist

Fun Facts

- Yankees, Celtics, Steelers, Navy Football
- Australia, Israel, Italy, Pac NW
- Did you know I really like the KY Bourbon Trail!
- Cycling, Hiking, Kayaking

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SPEAKER

Tiffany Thomas, PhD

Haley & Aldrich
Principal Chemist

HALEY ALDRICH

Fun Facts

- Favorite places: Oregon Coast, Southwestern Colorado, Banff
- Did you know I'm kind of a Star Wars nerd?
- Hobbies: Home renovations, painting, dancing, and baking

Live Content Slide

Poll: What is your level of understanding regarding PFAS?

Overview

1. Latest forensic research summary
2. General trends in PFAS datasets
3. Historical data and lines of evidence
4. Forensic chemistry of PFAS
5. Example case study

Latest forensic research and limitations

Latest forensic research on PFAS source identification

- Use of Total Oxidizable Precursor (TOP) assay to determine source signatures – includes analysis using multivariate statistical tools (ESTCP ER20-1330; Sedlak et al.)
- Development of PFAS source materials forensic library (ESTCP ER20-1121; Benotti et al.)
- Development of PFAS database from various discrete sources, transformation pathways, and use of multivariate analysis of high-resolution mass spectrometry data (ESTCP ER20-1375; Higgins et al.)
- Use of Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)(ESTCP ER20-1265; Blotevogel et al.)

Limitations of academic tools in applied settings

TOP Assay

- Reproducibility concerns
- Lack of site data

Source Library

- Incomplete library (Unknown number of possible source products)
- Unknown extent and nature of environmental transformation, fate and transport

HRMS Database

- Analytical method not widely available
- Temporal changes to source signatures

FT-ICR MS

- Analytical method not widely available
- Elevated detection limits

General trends in PFAS datasets

General observations

- Historical PFAS datasets contain limited number of analytes
- Temporal changes to source signatures cannot be captured
- May be unable to obtain additional samples
- Lack of complete geochemical characterization
- Lack of access to or logistical inability to perform specialized analytical methods
- Limited time to perform forensic analysis
- *Must maximize utility of available data to differentiate potential sources*

Historical data and lines of evidence

Importance of multiple lines of evidence

- Conceptual site models (CSM) – establish physical connectivity, definition of study area
- Historical records review (regional assessment) – identification of possible contributing source(s)
- Forensic chemistry of PFAS – chemical data to create a 4D understanding of physical fate and transport of PFAS
  - Chemical “marker” compounds – indication of comingled releases, industrial fingerprints
  - Isomeric analyses
  - PFAS signatures

Conceptual Site Models

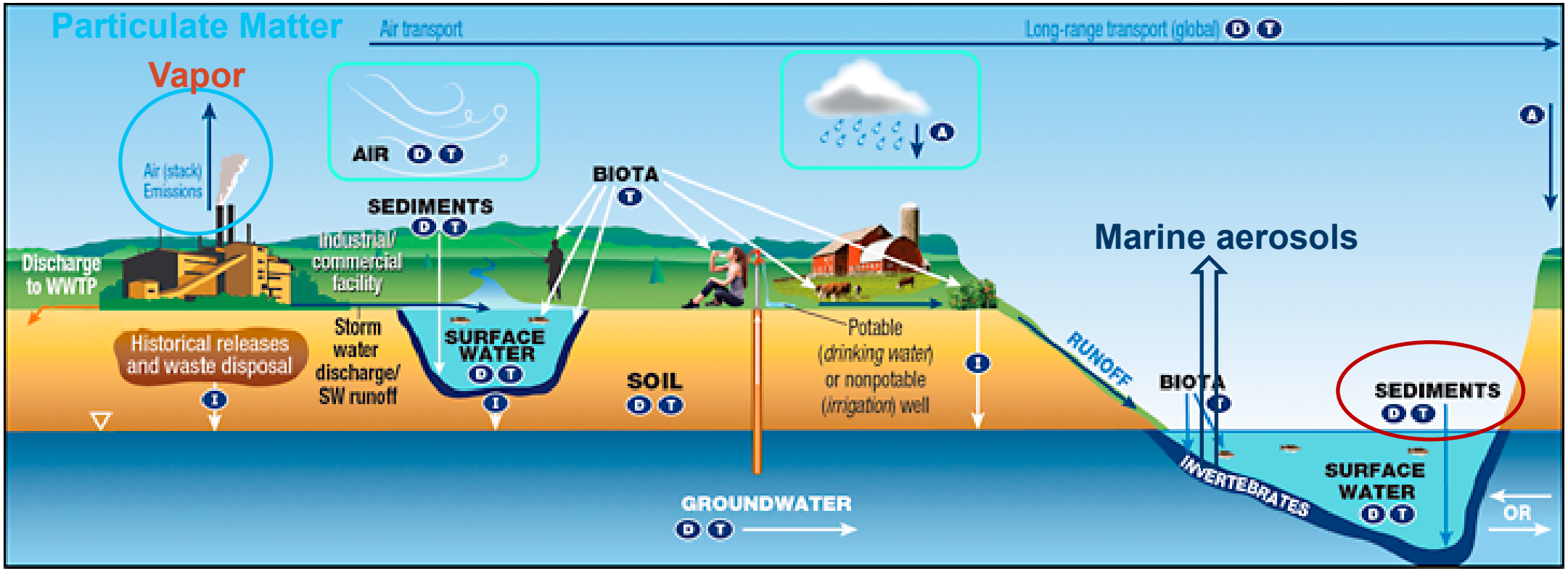
Based on historical site characterizations
Expanded to consider fate and transport properties of PFAS

"Can PFAS physically migrate from Point A to Point B?"
"What media are relevant?"
"What is or are the critical exposure or migration pathways?"

"What source(s) may be contributing to the detection of PFAS at this location?"

PFAS exposure routes

Ref: L. Trozzolo 2021



Sediments - considered final repository of PFAS

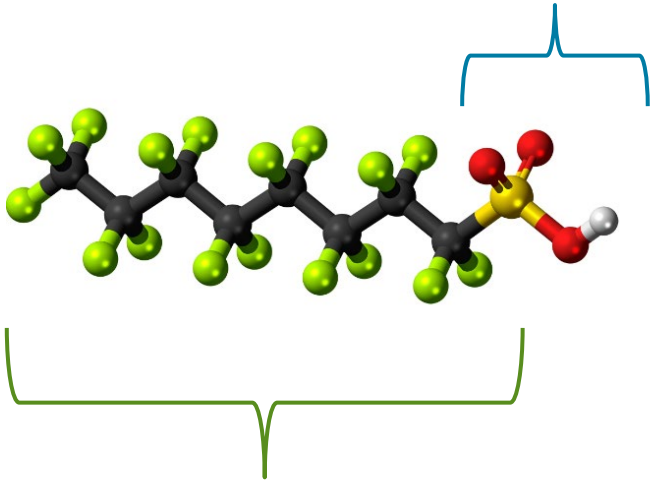
General chemistry

- **PFAS**
  - **Nonpolymers**
    - **Perfluoroalkyl substances**
      - Perfluoroalkyl acids (PFAAs)
      - Perfluoroalkyl carboxylic acids/ Perfluoroalkyl carboxylates (PFCAs)
      - Perfluoroalkane sulfonic acids/ Perfluoroalkane sulfonates (PFSAs)
      - Perfluoroalkyl ether acids
      - Perfluoroalkane sulfonyl fluorides (PASFs)
      - Perfluoroalkane sulfonamides (FASAs)
      - Perfluoroalkanoyl fluorides (PFAs)
      - Perfluoroalkyl iodides (PFAIs)
      - Perfluoroalkyl aldehydes (PFALs)
    - **Polyfluoroalkyl substances**
      - Fluorotelomer substances
      - Perfluoroalkane sulfonamido substances
      - Polyfluoroalkyl ether acids
      - Chloropolyfluoroalkyl ether acids
      - Chloropolyfluoroalkyl acids
  - **Polymers**
    - Fluoropolymers
    - Polymeric Perfluoropolyethers (PFPE)
    - Side-chain fluorinated polymers

Family hierarchy legend

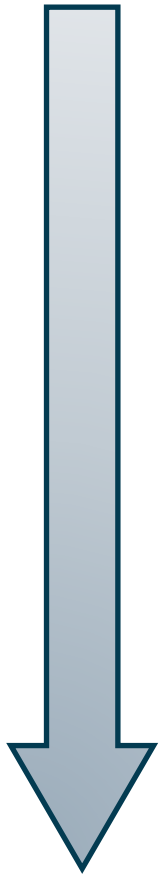
- Family
- Class
- Group
- Subgroup

"Head" is soluble in water



"Tail" is insoluble in both water and liquid

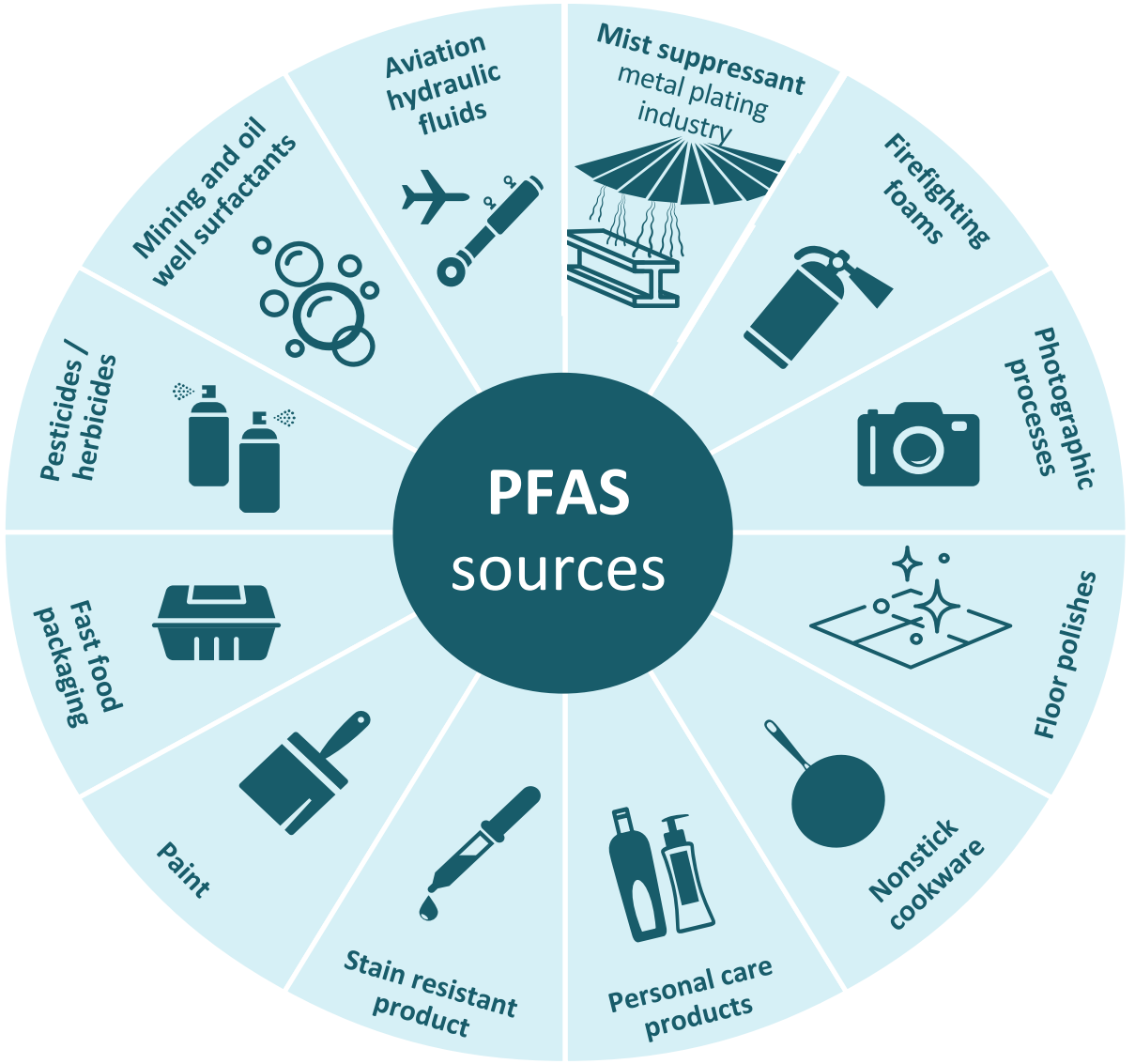
Brief production history



- 1940s – non-stick coatings (primarily polytetrafluoroethylene a.k.a. Teflon)
- 1950s – PFOS-based stain and water-resistant products
- 1950s-1960s – PFOA-based protective coatings
- 1960s – PFOS-based firefighting foams
- 1970s – waterproof fabrics (primarily PFTE)
- 1980s – production of architectural resins containing other PFAS
- 1990s – production of firefighting foams with fluorotelomers
- 2000s – U.S. reduction of PFOS, PFOA, and select other PFAS

Widely used in consumer and industrial products

- PFAS are not naturally occurring
- PFAS used in wide range of consumer and industrial products
- Exact number and types of products containing PFAS is unknown
- Not classified as hazardous = not listed on Safety Data Sheets or ingredient lists
- Most studied PFAS are PFOA and PFOS, then PFHxS, and PFNA.
- **PFOA and PFOS now phased out of production in U.S., but still found in products and waste streams.**



Municipal/Department of Defense sources – AFFF related

- Fire stations and firefighting training areas
- Airports and marine ports
  - Runways, taxiways, maintenance ramps, and aprons (and associated drainage features)
  - Plane or drone crash sites
  - Crash debris storage areas
  - Aircraft fuel purge stations
  - Refueler truck ramp and parking areas
  - Bulk fuel storage areas with “foam lines”
  - Hangar fire-suppression systems
- Engine testing/ manufacturing
- Tank farms and oil refineries

High concentration, short duration releases (acute)

More about AFFF

- AFFF
  - Fire crew use and foam deluge systems
  - More recent formulations (since 2006) contain shorter-chain PFAS compounds
- PFAS present at grams/liter concentrations in AFFF –
  - It takes 37 MILLION gallons of water to dilute the PFOS content in 1 liter of AFFF to 70 ng/L (the EPA Health Advisory Level).

Secondary sources – non-AFFF related

- Private industrial sites – examples: West Virginia, Ohio
- Industrial waste landfills – industrial wastes from PFAS producers
- Municipal landfills
- Wastewater treatment plants and associated infrastructure
- Agricultural application of biosolids
- Industrial and consumer use of PFAS-containing products

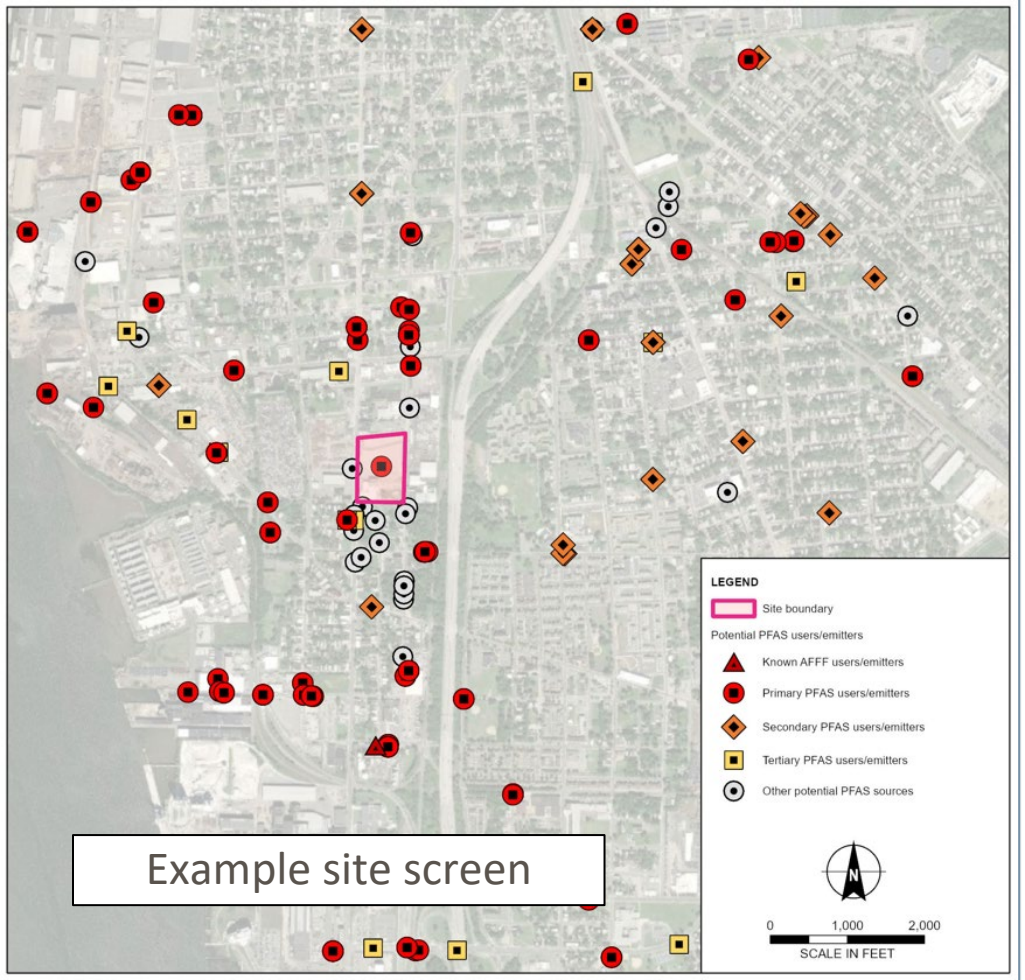
Could be low or high concentration, but are long-duration releases (chronic)

Partial PFAS user/emitter screening list

Known AFFF users (3%)	**Known or suspected PFAS users/emitters (97%)**		
Fire training facilities	Landfills	Carpet treatment	Flexible circuit board manufacturers
Airports	Wastewater Treatment Plants	Molded plastics	Paints
Military installations	Chrome platers	Dry cleaners	Lithography
Tank farms	Incineration facilities	Car washes	Biosolids (farms)
	Semiconductors	Pesticides/herbicides usage	Auto parts manufacturing
	Paper facilities (recycling & manufacturing)	Electronics manufacturing	Battery manufacturing/recycling

Screening for potential sources

- Multiple potential sources may be present
- Consider CSM
  - Groundwater gradient
  - Site history
  - Other remedial activities
- Consideration of regional background



Example site screen

Forensic chemistry of PFAS

Chemical marker compounds

- Comingled contaminants indicative of specific processes
  - Fuel-related (tank farms, refineries, etc.) – volatile organics, petroleum hydrocarbons
  - Chrome platers – chromium, solvents
  - Historic contaminated sites – contaminants of concern (COCs) indicative of particular site plume
- PFAS-specific analytes
  - Landfills (generally) – 5:3 fluorotelomer carboxylic acid (FTCA)
  - Chrome platers – PFOS and/or 6:2 fluorotelomer sulfonate (FTS)
  - Process-specific – indication of precursors and daughter products

Precursor transformation

- Many PFAS can transform into other PFAS

  Precursors → Terminal products

- Precursor may not be directly detectable, historically reported, or persistent
- Terminal products are NOT unique to a single precursor
- Understanding of relationship to terminal products is key!

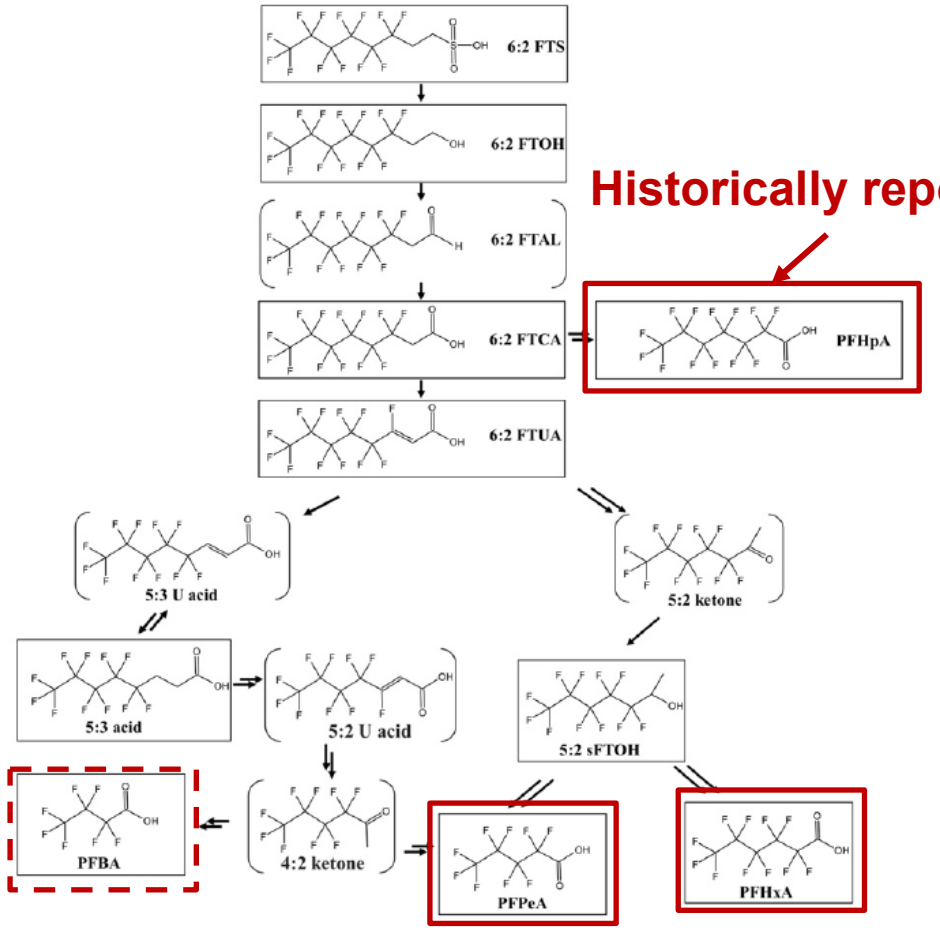
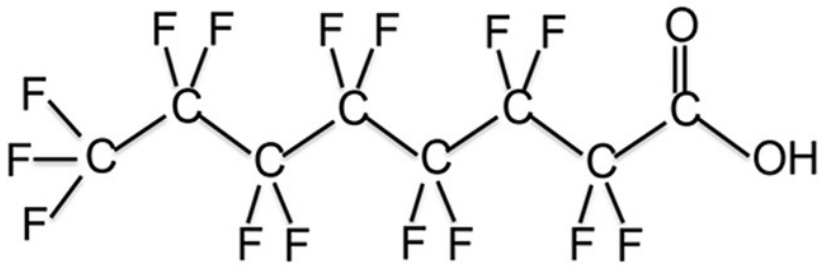


Fig. S1. Aerobic biotransformation pathways of 6:2 FTS in AFFF-impacted soils proposed in the previous study (Yan et al., 2024). The compounds in the rectangular boxes were detected by LC-MS/MS analysis, and the compounds in the brackets are proposed transformation products. The solid arrows represent the biotransformation steps expected to occur based on the present and previous studies. The double arrows represent multiple enzymatic steps involved.

Isomeric analyses – linear and branched

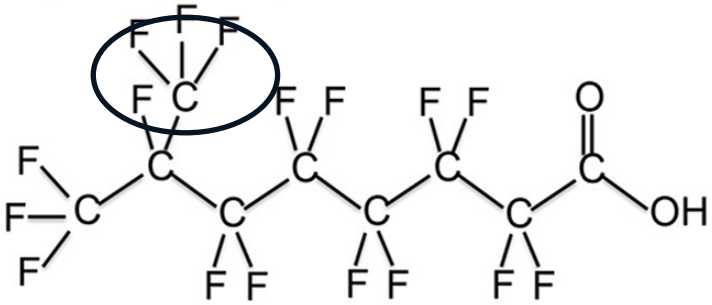
Product of both electrochemical fluorination (ECF) and fluorotelomerization (FT) synthesis

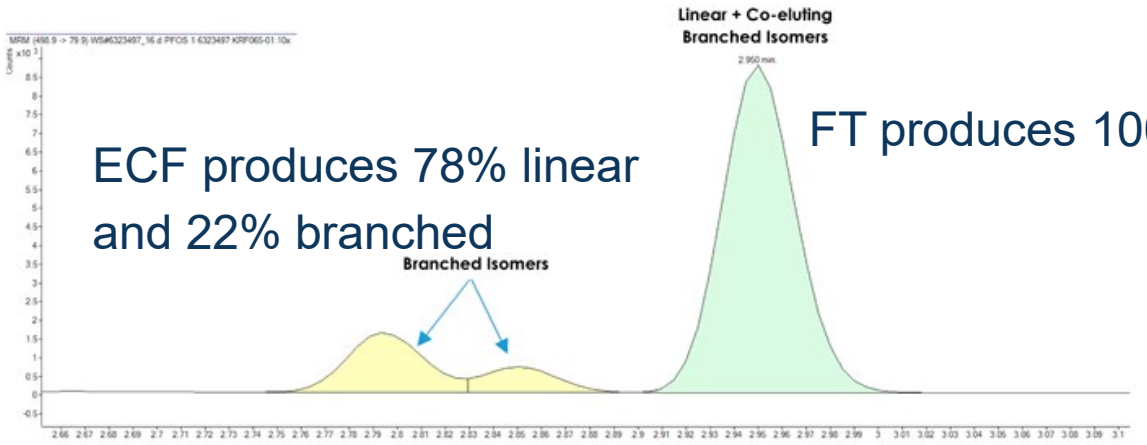
Linear PFOA



Product of ECF only

Branched PFOA





ECF produces 78% linear and 22% branched

FT produces 100% linear

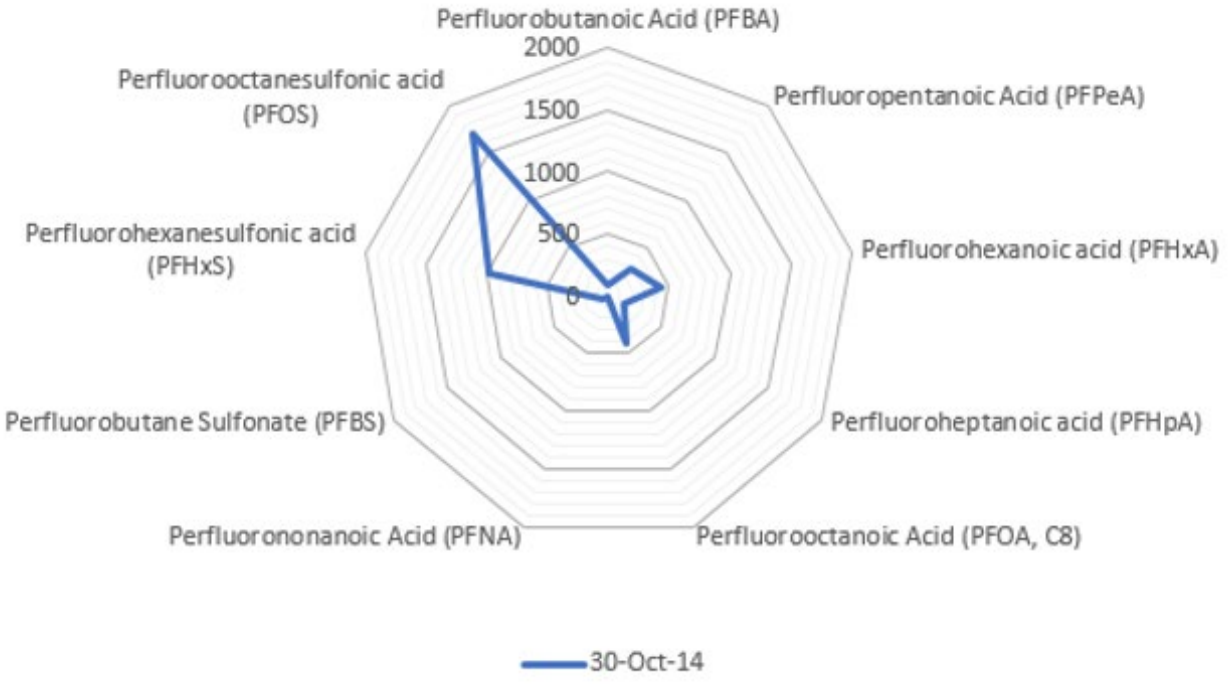
Identifies manufacturing process – NOT specific products

Does not account for environmental fractionation

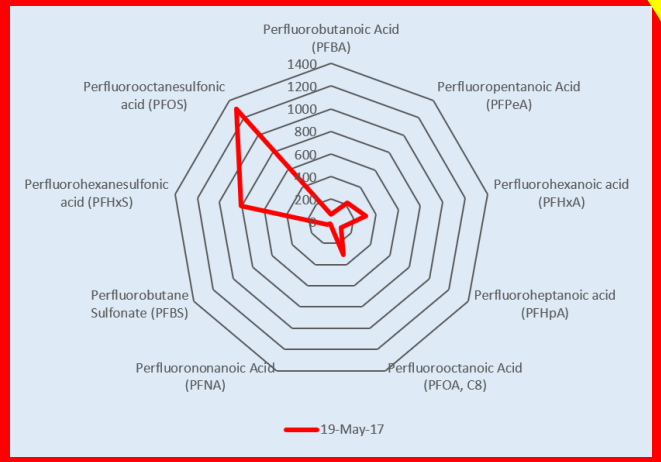
Construction of PFAS signatures

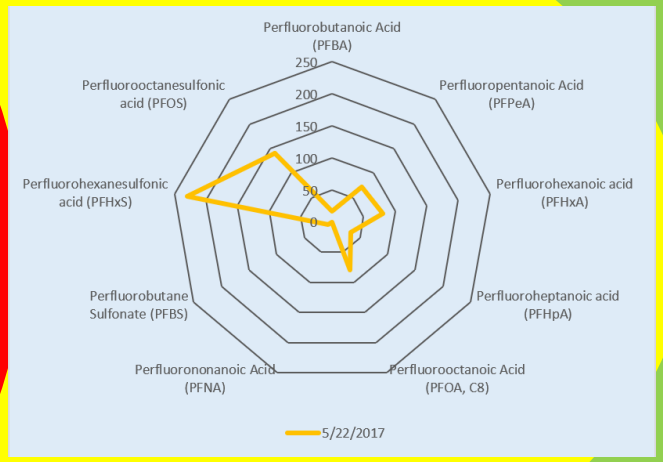
- Variety of graphical presentations of PFAS data
- Key functions:
  - Generate obvious visual comparisons
  - Examine changes *over time* for individual monitoring locations
  - Examine changes *over distance* to assess whether the distribution and ratios of PFAS compounds change

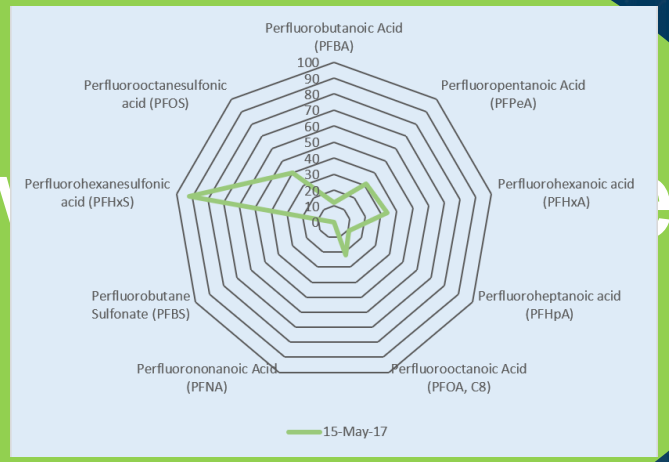
Radar plot fingerprints



- Radar plots
  - 9 PFAS – historically reported
  - Separated carboxylates and sulfonates
  - Plotted concentrations for each compound
- Assess concentrations and fingerprints over time and/or distance
- Can be modified to represent other sets of PFAS compounds







DOWNGRADIENT

Use of PFAS fingerprints

- PFAS fingerprints are a strong line of evidence:
  - Identify and distinguish multiple sources
  - Support allocation of response costs and liabilities
- Because PFAS fingerprints are:
  - Consistent and reproducible over time
  - Insensitive to decreasing concentrations over distance from source area

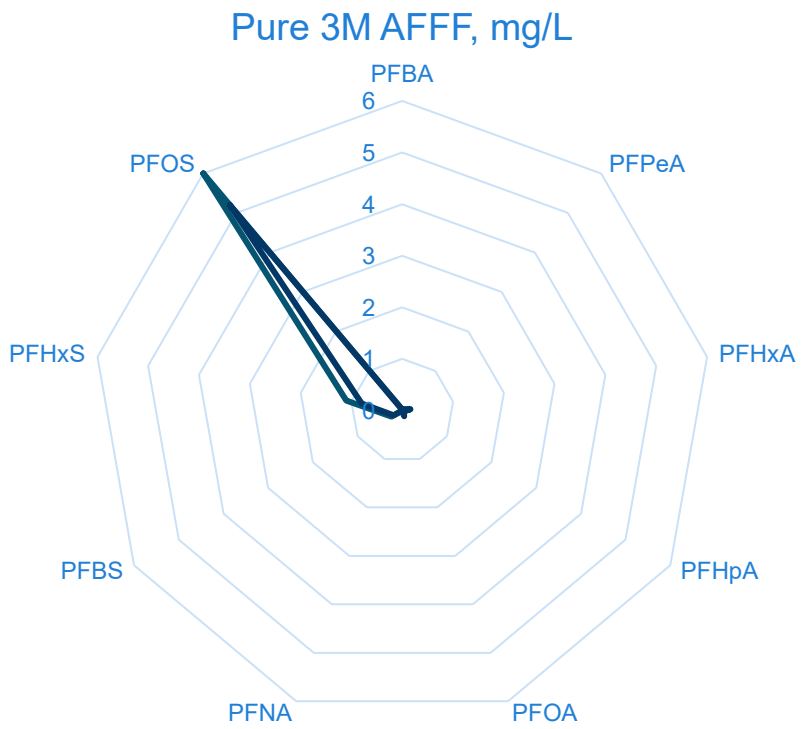
Example case study

What do we have?

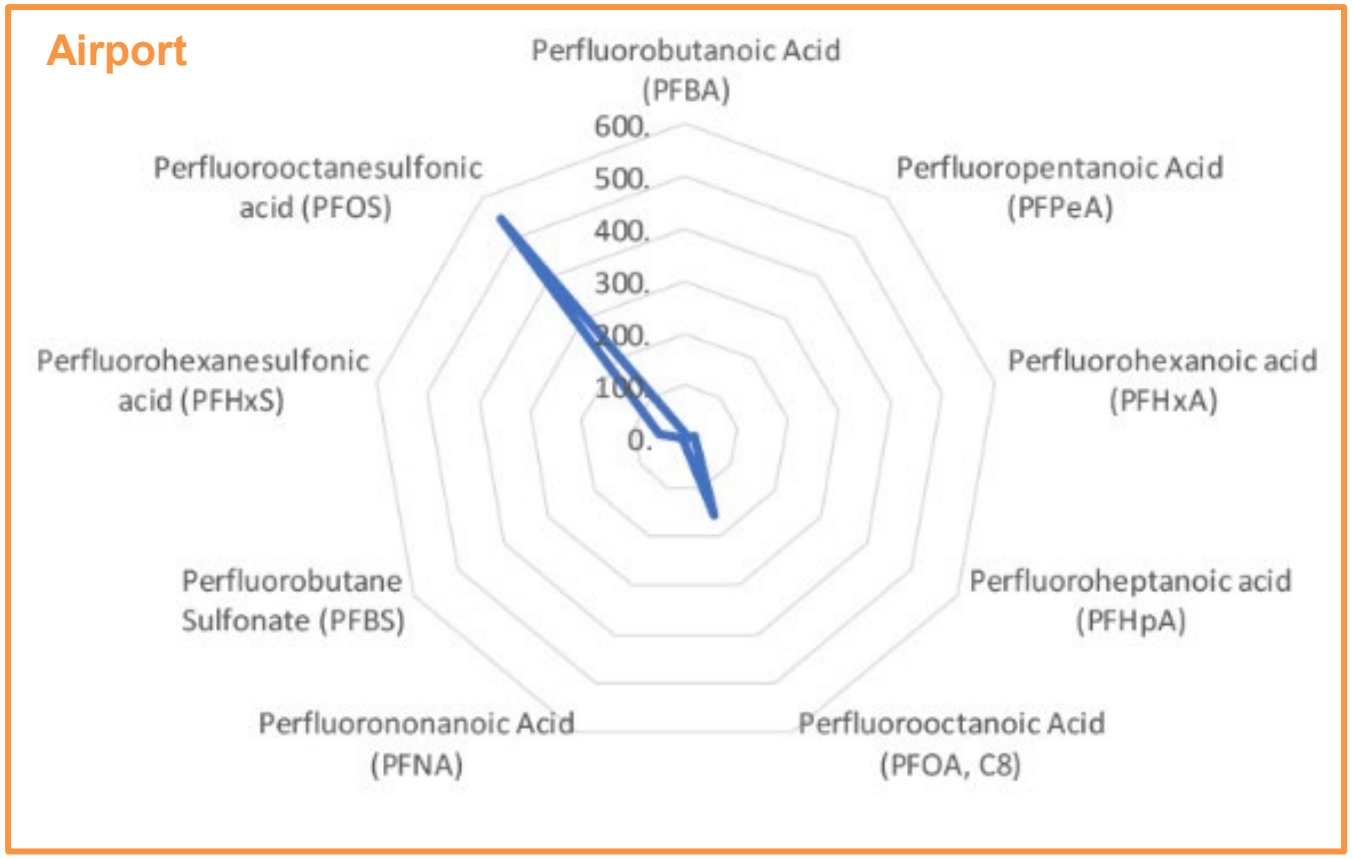
- General groundwater flow direction or historical CSM
- Known AFFF use at a facility/installation
- EPA Method 537.1 Analytical Data from multiple possible source areas
  - Airport
  - Former landfill
  - WWTP
  - Production well

Source identification (for illustration purposes only)

AFFF vs airport radar plots

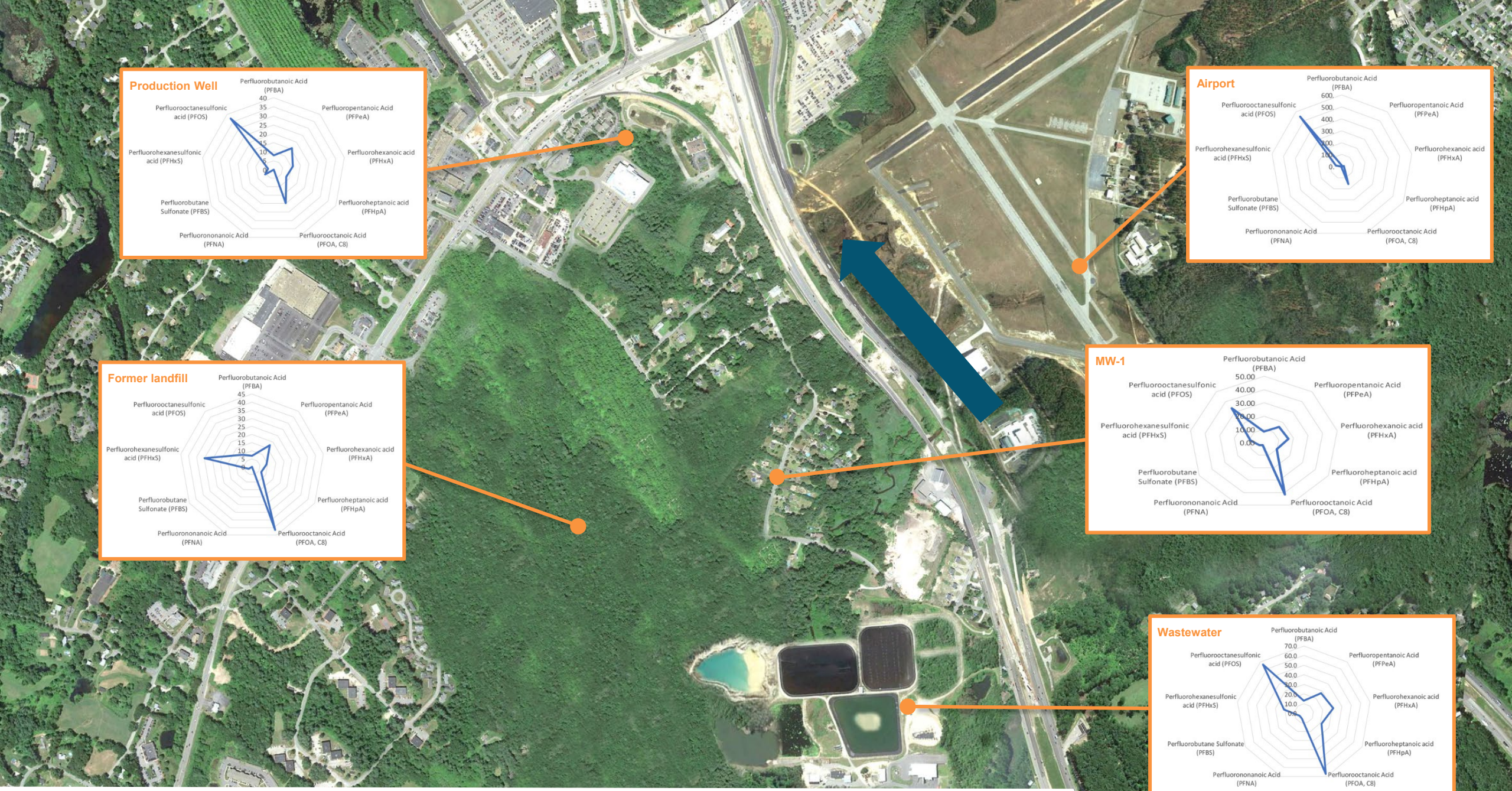


Pre-1976, 3M AFFF “contained high concentrations of [PFCAs] and their derivatives” (Houtz et al, 2013)



Generate CSM

- Identify and address data gaps
- Sample existing wells
- Advance new probes, wells, etc.
- Update CSM
- ***Prioritize use of empirical data (i.e., tracer contaminants) to verify fate and transport assumptions***



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Tiffany Thomas, Ph.D.

Principal Chemist
tnthomas@haleyaldrich.com

HALEY ALDRICH

Q&A