Geosyntec consultants

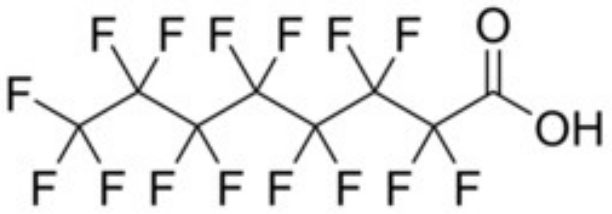
Navigating PFAS Site Characterization Complexities

Incorporating Anthropogenic Background, PFAS Analytical Methods, and Site History Forensics Into PFAS Delineation and Response

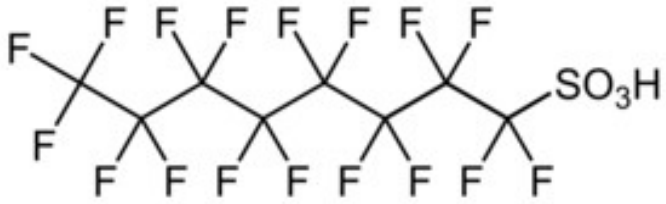
Thomas Wanzek, PhD | Scientist

Navigating PFAS Complexities: Multiple Lines of Evidence

- How do you delineate a ubiquitous contaminant?
- How do you determine what analytical tools are best suited to address your specific objectives?
- How do you develop defensible and compelling conclusions?



PFOA

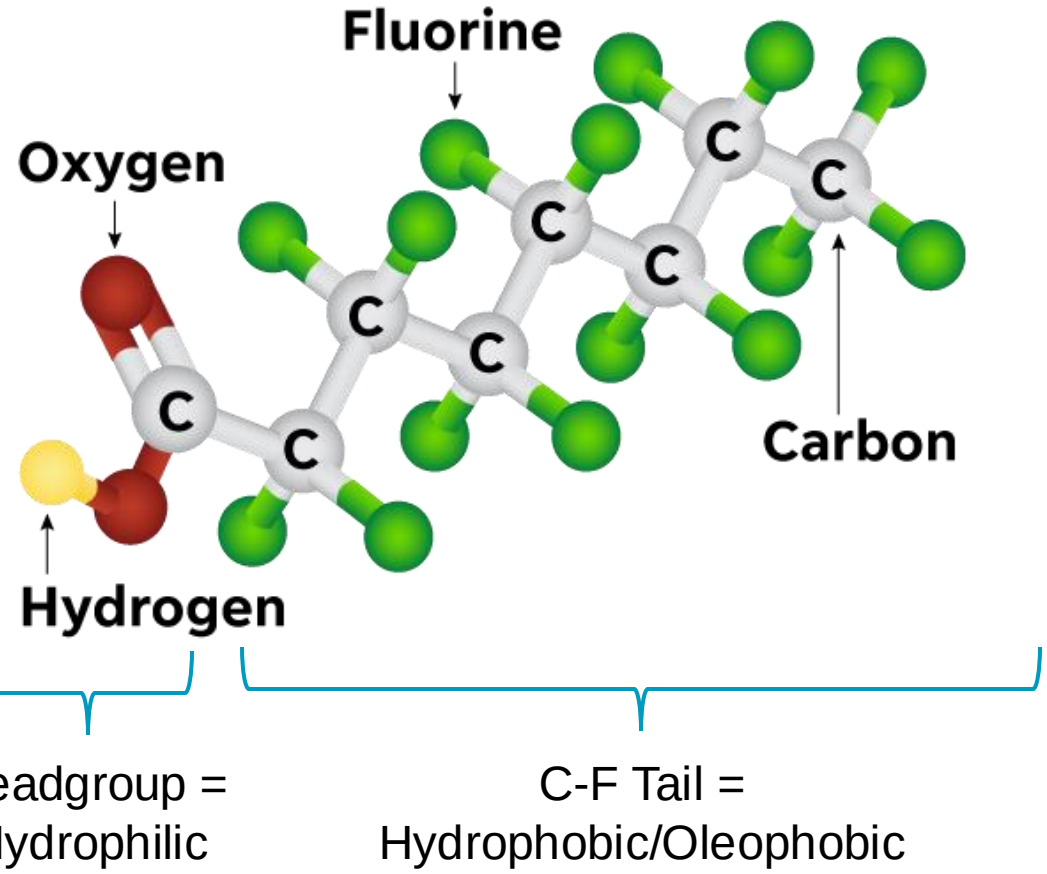


PFOS

Look for “Ask me about…”

What is a PFAS?

- PFAS are (mainly) composed of 7 elements
  - **C**arbon,
  - **F**luorine → highly electronegative (é withdrawing)
  - **O**xygen
  - **S**ulfur
  - **N**itrogen
  - **H**ydrogen
  - **Cl**orine
- Capable of
  - electrostatic
  - weak vdW (hydrophobic)
- C-F tail (and head group) *can* make them behave differently than other CoCs



Ask me about what makes PFAS interesting CoCs

Defining a PFAS…?

CF_3 and C_nF_{2n+1}
~200 PFAS

Buck 2011

C_nF_{2n} (n ≥ 3)
$C_nF_{2n}OC_mF_{2m}$ (m ≥ 1)
~4,700 PFAS

OECD 2018

$R\text{-}(CF_2)\text{-}CF(R')R''$
$R\text{-}CF_2OCF_2\text{-}R'$
$CF_3C(CF_3)R'R''$
~1,500 PFAS

EPA TSCA 2024

Based on % fluorination
~16,600 PFAS

EPA CompTox 2022 – 2024

CF_3 and CF_2
CF_2 w/o H/Cl/Br/I
~6 million PFAS

OECD 2021

Best Practices for Evaluating PFAS Complexities: Multiple Lines of Evidence

Employ a multiple lines of evidence approach to tell a single cohesive, defensible, and compelling story about the source(s) of a contaminant

Site History

- Operations (e.g., inputs, sales)
- Events (e.g., fires, floods)
- Ownership and corporate succession

Alternative Source(s) Investigation

- Local source(s)
- Downgradient status
- Background

Chemical Analyses

- Analytical method capabilities
- Contaminants of concern
- Marker compounds
- Source differentiation

Conceptual Site Model

- Magnitude and spatial distribution
- Transport pathways
- Compound transformation
- Contaminant fingerprinting
- Multivariate statistics

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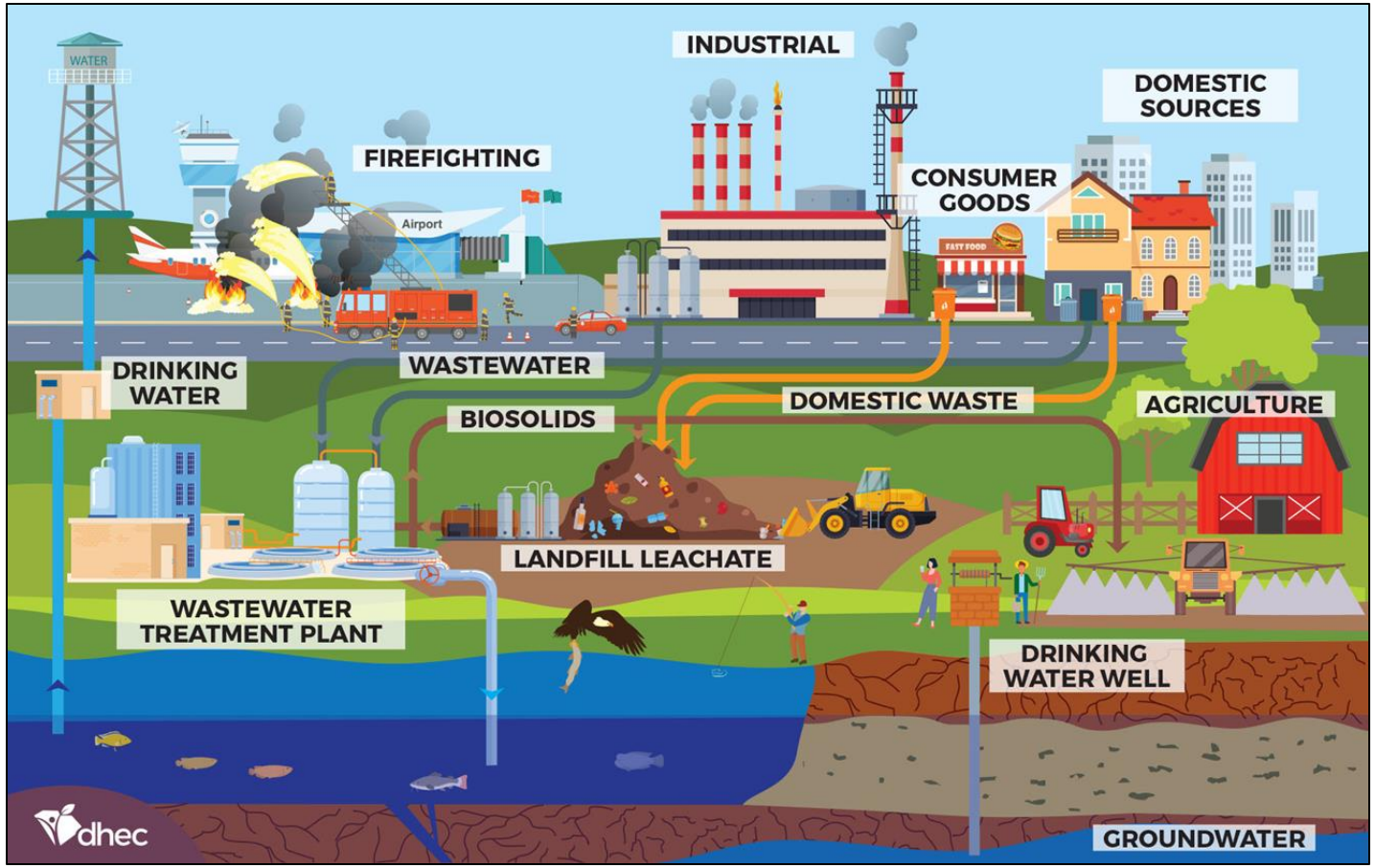
Why Should We Consider PFAS Background/Site History?

- Timeframe and ubiquity
  - More than 70-year history of production and uses across innumerable industries, products, and materials
- Magnitude
  - Historical emissions of PFCA and PFSAs estimated at 1,000s to 10,000s of metric tons
- Mobility and recalcitrance
  - Long range transport from sources and cycling in the environment



Source: *https://scdhec.gov/environment/polyfluoroalkyl-substances-pfas*

Potential PFAS Sources

Products

- Aqueous film forming foams (AFFF)
- Stain repellants
- Textiles, including water resistant apparel/equipment
- Carpets
- Personal care products
- Pesticides
- Cleaning products
- Pigments, dyes, and inks
- Packaging, paper, and cardboard
- Adhesives
- Explosives and ammunition
- Floor waxes and sealants
- Glass etching
- Industrial surfactants
- Leather
- Medical devices
- Plastics & Polymer manufacturing
- Rubber
- Semiconductors
- Performance chemicals (e.g., hydraulic fluids, jet fuels)

Industries

- Transportation (e.g., automobiles, aircraft, aerospace)
- Metal plating and finishing
- Automotive (e.g., anti-fogging agents)
- Building and construction – weather resistant coatings
- Electronics manufacturing
- Fire fighting/training facilities
- Oil and gas recovery
- Wire manufacturing and coating
- Mining (e.g., odor and dust suppression, surfactants)
- Photography (e.g., film, paper, plates)

Disposal Practices

- Wastewater treatment plants
- Biosolids
- Septic systems
- Landfills (e.g., leachate, odor and dust suppression)

Source: Gaines, L.G. 2023. Historical and current usage of per-and polyfluoroalkyl substances (PFAS): A literature review. *American Journal of Industrial Medicine*, *66*(5), pp.353-378.
Kotthoff M, Muller J, Jurling H, Schlummer M, Fiedler D. Perfluoroalkyl and polyfluoroalkyl substances in consumer products. Environ Sci Pollut Res Int. 2015;22(19):14546-14559.

What is Anthropogenic Background?

- Natural background
  - Geologic forces deposit a naturally occurring substance at a location
- Anthropogenic background
  - Non-specific human activities deposit a natural or synthetic substance at a location
- Regulatory exemptions
  - For impacts linked to urban fill, biosolids, pesticides, higher standards in industrialized areas

Anthropogenic Background means those levels of oil and hazardous material that would exist in the absence of the disposal site of concern and which are:

(a) attributable to atmospheric deposition of industrial process or engine emissions and are ubiquitous and consistently present in the environment at and in the vicinity of the disposal site of concern;

(b) attributable to Historic Fill;

(c) associated with sources specifically exempt from the definitions of disposal site or release as those terms are defined in MGL c. 21E and 310 CMR 40.0006;

(d) releases to groundwater from a public water supply system; or

(e) petroleum residues that are incidental to the normal operation of motor vehicles.

***Source**: Massachusetts Department of Environmental Project (MassDEP)*

The Department defines DAP as follows:

"Diffuse anthropogenic pollution" or "DAP" means contamination from broadly distributed contaminants, often arising from multiple sources. DAP generally arises from atmospheric deposition, but may also contain contributions from random, non-attributable, non-point sources.

***Source**: New Jersey Department of Environmental Protection (NJDEP)*

Guidance on Quantifying Site-Specific Background

2002 USEPA Office of Solid Waste and Emergency Response (OSWER 9285.6-07P)

The primary goal of the CERCLA program is to protect human health and the environment from current and potential threats posed by uncontrolled releases of hazardous substances, pollutants, and contaminants. Contamination at a CERCLA site may originate from releases attributable to the CERCLA site in question, as well as contamination that originated from other sources, including natural and/or anthropogenic sources not attributable to the specific site releases under investigation (EPA, 1995a). In some cases, the same hazardous substance, pollutant, and contaminant associated with a release is also a background constituent. These constituents should be included in the risk assessment, particularly when their concentrations exceed risk-based concentrations. In cases where background levels are high or present health risks, this information may be important to the public. Background information is important to risk managers because the CERCLA program, generally, does not clean up to concentrations below natural or anthropogenic background levels.

Quantifying Background

PFOS and PFOA Concentrations Detected in Locations with No Known PFAS Source in Various Media

		PFOS			PFOA		
		Median	Min	Max	**Median**	Min	Max
Surface water	ng/L	**10**	0.3	348	**18**	0.4	1,030
Groundwater	ng/L	**30**	0.2	140	**15**	0.8	450
Rainwater*	ng/L	**3.2**	0.1	50	**18**	0.07	121
Marine water	ng/L	**0.2**	0.001	756	**0.3**	0.001	1,629
Soil	ng/kg	**2,700**	3	162,000	**3,100**	10	189,000

Table 1 is adapted from data in Johnson et al. (2022).
*Most samples included in the meta-analysis by Johnson et al. (2022) were collected from within metropolitan areas.
ng/L – nanograms per liter
ng/kg – nanograms per kilogram

USEPA RSLs for PFOS and PFOA in Various Media (THQ = 1.0)

		PFOS	PFOA
Residential Tapwater	ng/L	4	4
Residential Soil*	ng/kg	6,300	1,900
Soil to GW*	ng/kg	30.5	60.8

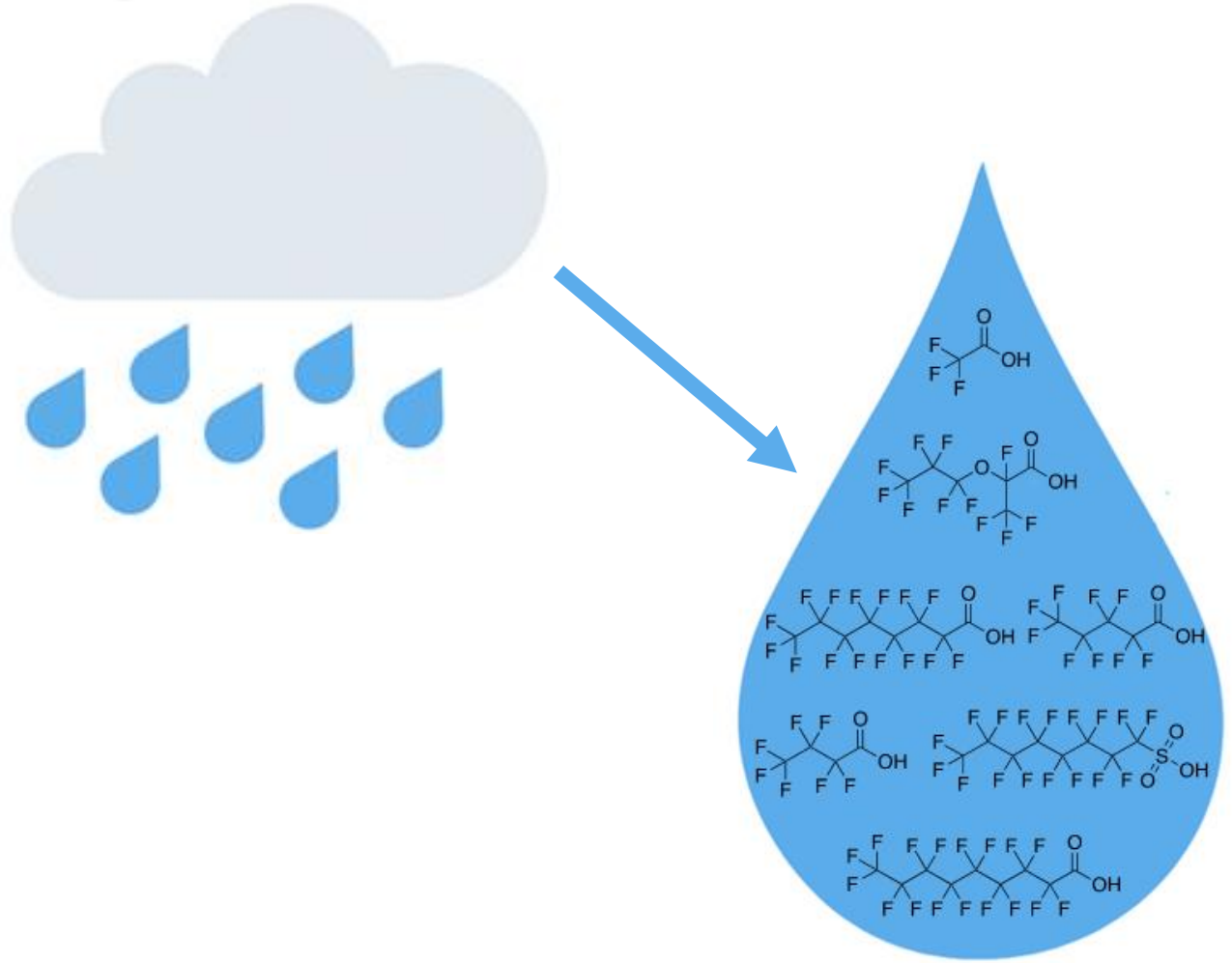
*MCL-based SSL

***Source**:* Johnson et al., (2022). Global distributions, source-type dependencies, and concentration ranges of per- and polyfluoroalkyl substances in groundwater. *Science of the Total Environment*, *841*.

How Do We Consider Anthropogenic Background?

- Source attribution of PFAS concentrations within the range of non-point source background **may not be possible**

- Need to account for background in the how we approach plume delineation ***and*** the conceptual site model



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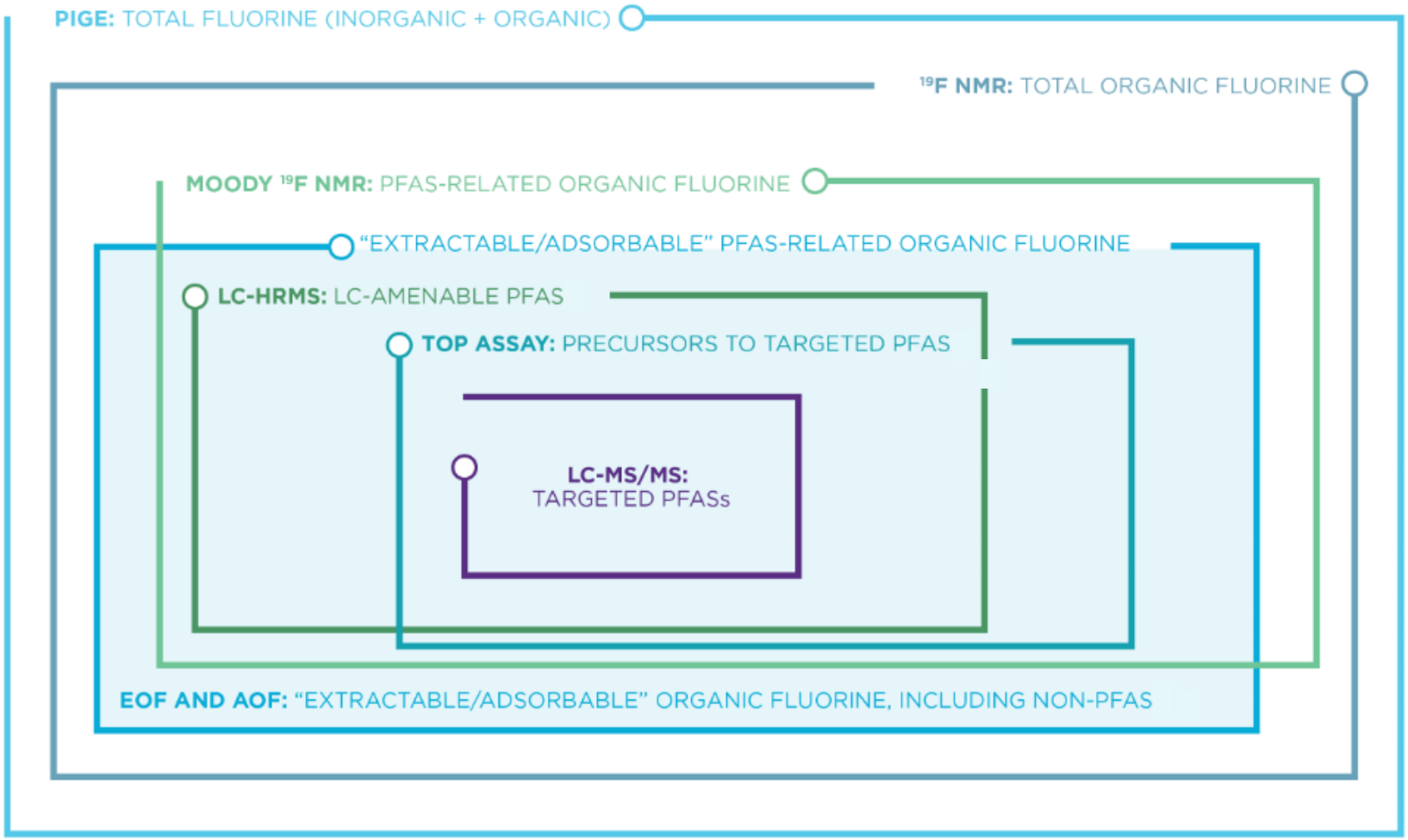
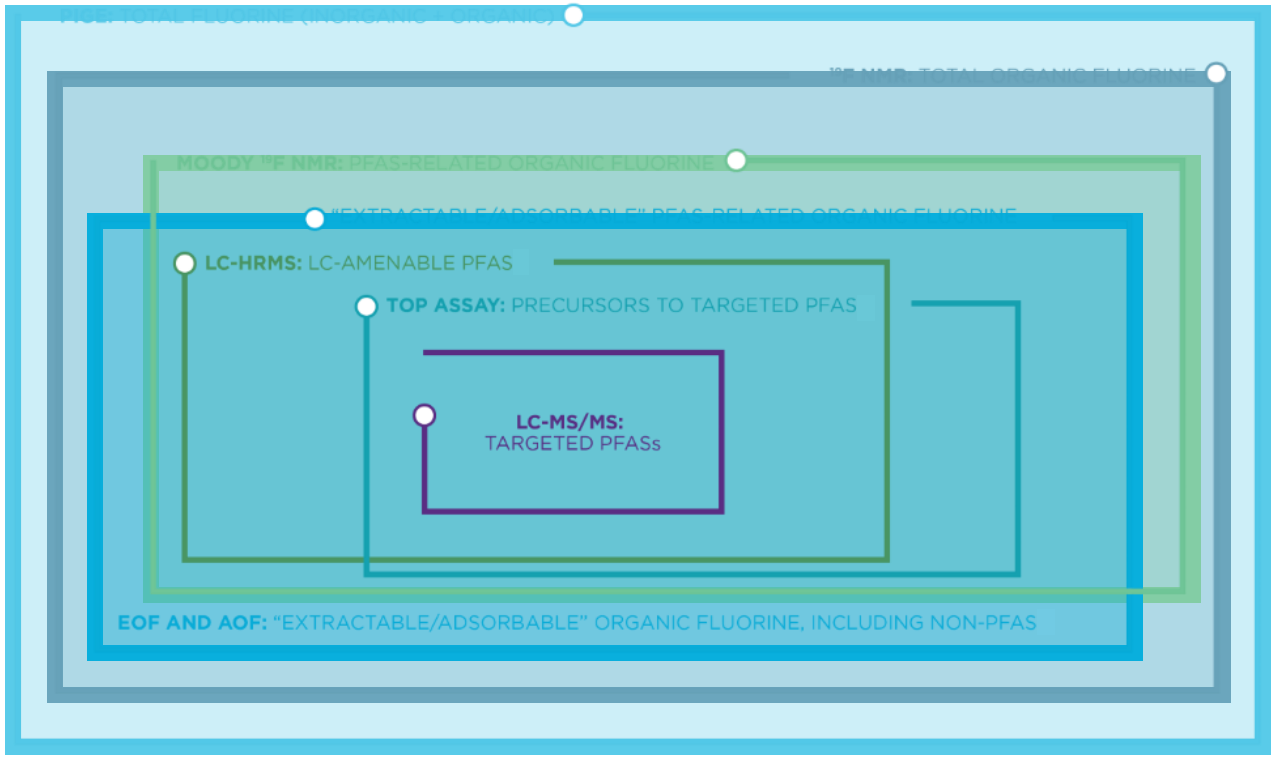
Selecting the Right Tool for the Job



Selecting the Right Tool for the Job

Analytical Method Category 1: Bulk Fluorine

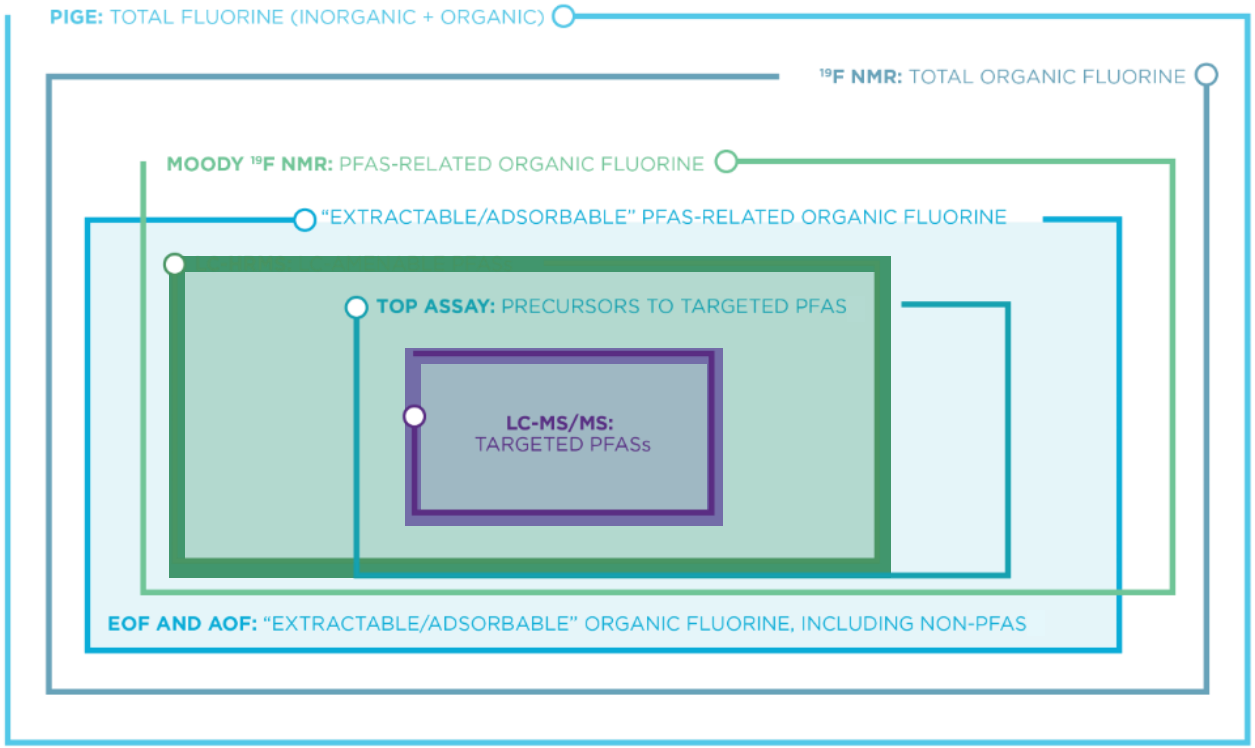
- Does not quantify/identify individual fluorinated (i.e., PFAS) compounds
  - Combustion ion chromatography (CIC) (organic and inorganic F)
  - Particle induced gamma ray emission (PIGE)
  - 19F Nuclear Magnetic Resonance
  - Adsorbable organic fluorine (AOF) + CIC (**USEPA Method 1621**)
  - Extractable organic fluorine (EOF) + CIC



Selecting the Right Tool for the Job

Analytical Method Category 2: Compound-Specific or Targeted Analyses

- Quantifies/identifies individual PFAS
  - Liquid chromatography + mass spectrometry (LC-MS)
    - **USEPA Method 1633**
  - Gas chromatography + mass spectrometry (GC-MS)



Ask me about the TOP Assay

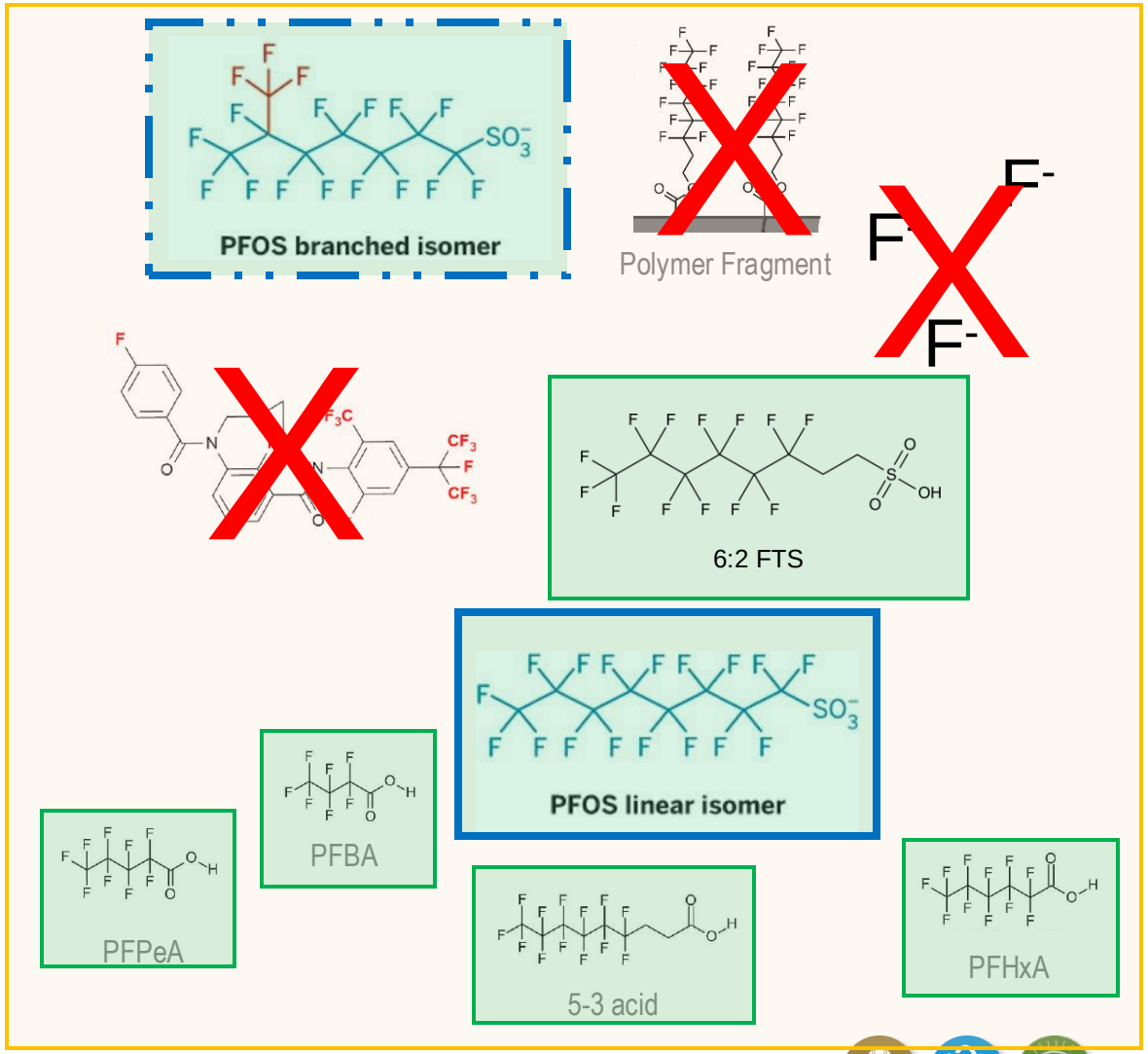
What TF/TOF Can (and Can't) Tell You

Total Fluorine/Total Organic Fluorine (orange)			
C-F bond Fluoride	Thumbs up/down	Units: nmol F/area or nmol F/volume	Higher MDL (~300 – 1,500 ppt)

Compound Specific (green)			
Individual molecule information	PFBA PFPeA PFHxA 5:3 FTCA 6:2 FTS PFOS (Br *and* L)	Units: mass/volume or mass/mass	Lower MDL (~0.3-10 ppt)*

*For aqueous matrices using USEPA Method 1633

Ask me about short/ultra short PFAS



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Site History Forensics

Site History Data

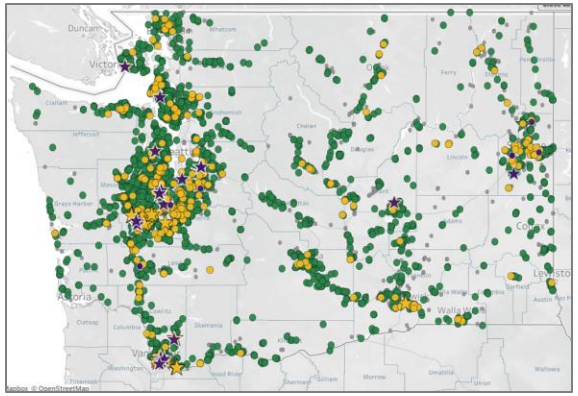
- Records of spills or major events such as fires
- Facility plans/process drawings
- Historical operations noted in Sanborn maps, newspapers, company publications, etc.

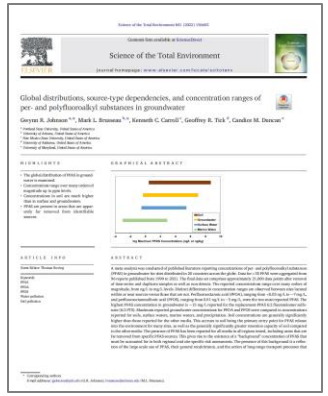
Document Retrieval

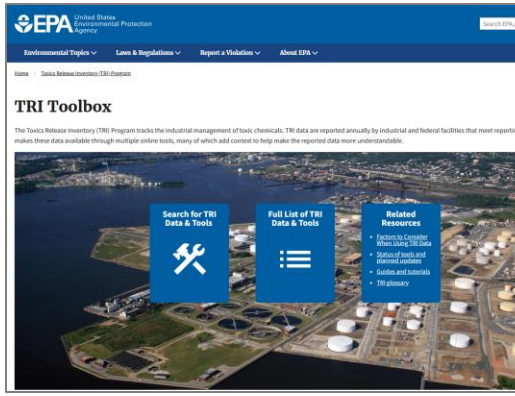
- Historical archives
- Local and university libraries
- Federal government repositories
- Freedom of Information Act (FOIA or state-equivalent) requests
- Public websites and data repositories

Literature and Report Review

- Associate PFAS with industrial processes or products
- Basis for a PFAS fingerprint library





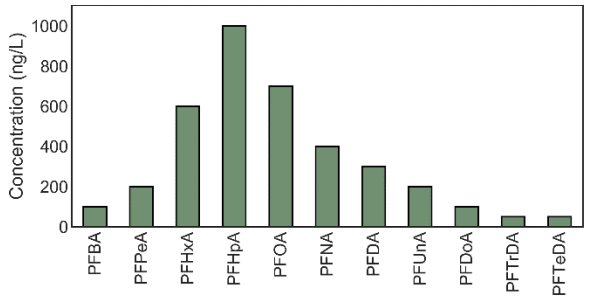


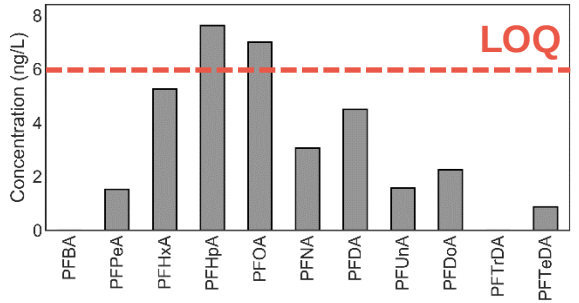
Sources:
USEPA. PFAS Analytic Tools. Available at https://awsedap.epa.gov/public/extensions/PFAS_Tools/PFAS_Tools.html.
Washington DOH. 2025. PFAS Testing Results Dashboard. https://doh.wa.gov/data-and-statistical-reports/washington-tracking-network-wtn/pfas/dashboard
USEPA. Toxics Release Inventory (TRI) Toolbox. Available at https://www.epa.gov/toxics-release-inventory-tri-program/tri-toolbox.
Johnson, G.R., Brusseau, M.L., Carroll, K.C., Tick, G.R. and Duncan, C.M., 2022. Global distributions, source-type dependencies, and concentration ranges of per-and polyfluoroalkyl substances in groundwater. Science of the Total Environment, 841, p.156602.

Complicating Factors: Detection Limits and Relative Low Concentration Ranges of Background

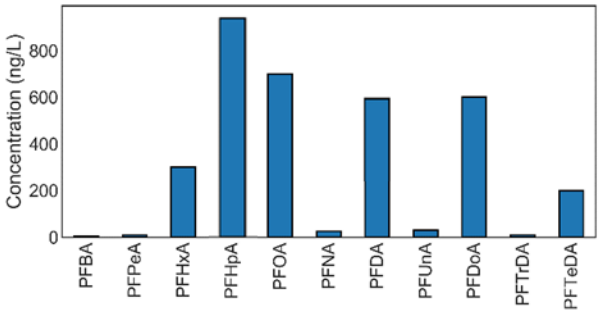
Fate and Transport

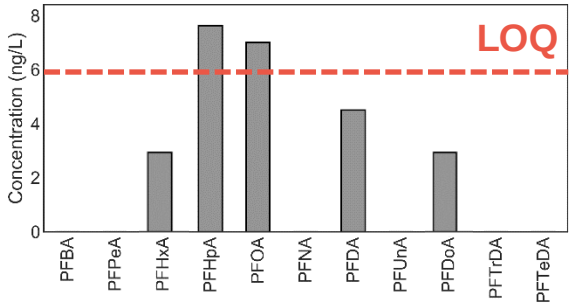
Point Source 1



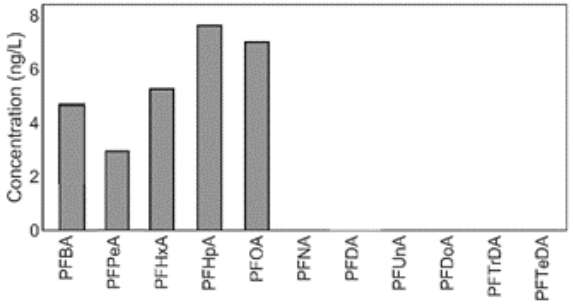


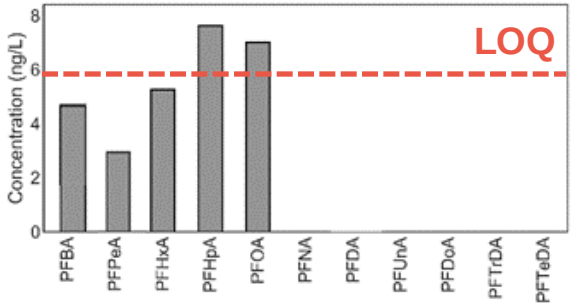
Point Source 2



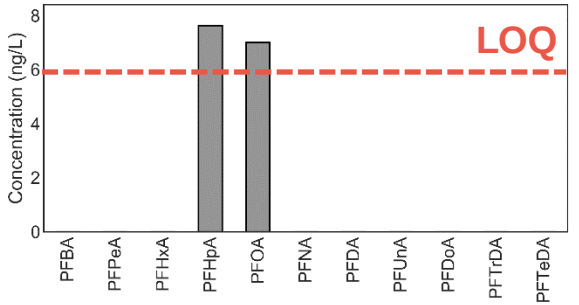


Regional Background





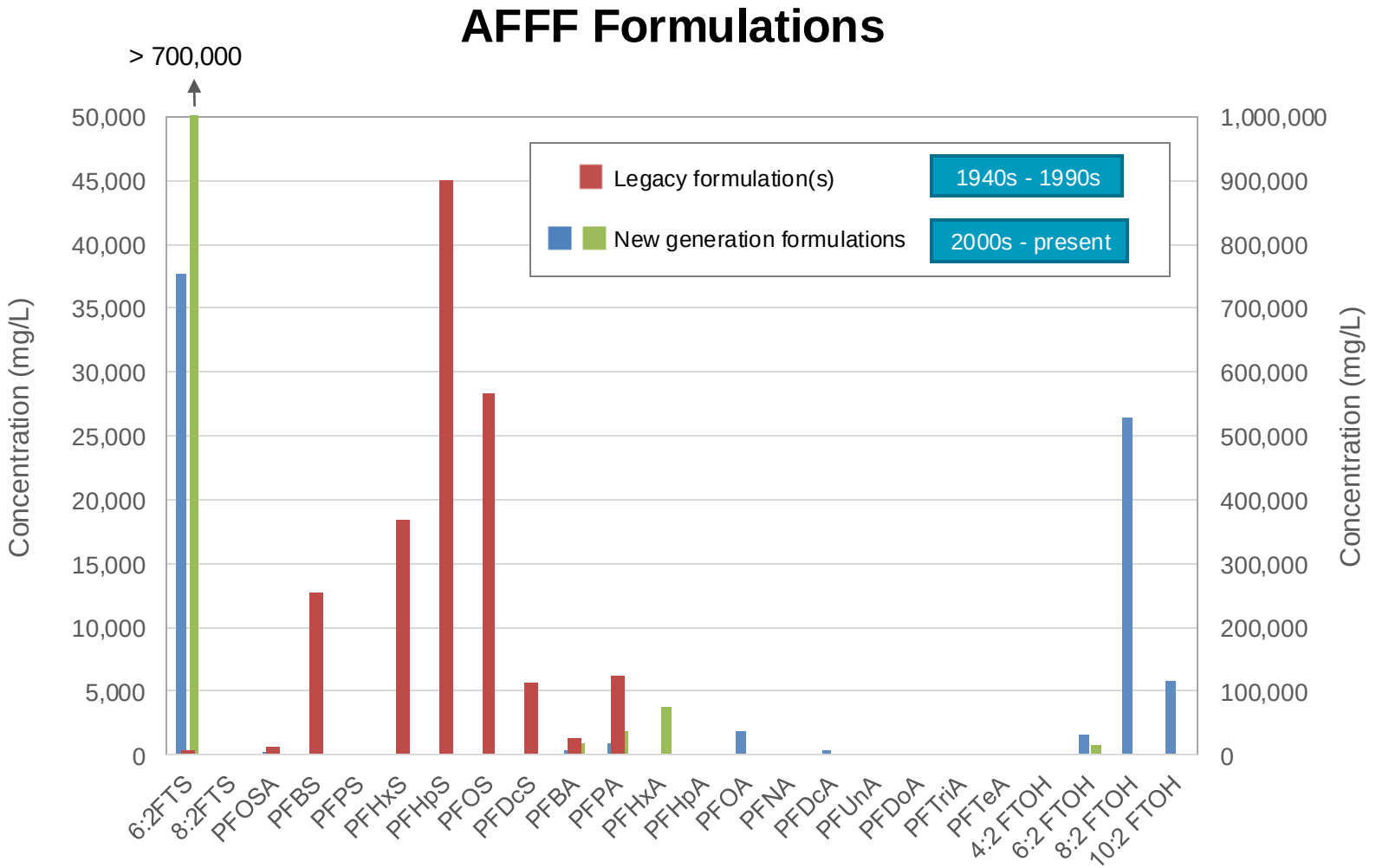
The apparent fingerprint for each source is the same



Complicating Factors: PFAS Formulations Have Changed Over Time

- Fingerprints for a single source type can change over time
- Fingerprints for a given product can differ among manufacturers
- Number of PFAS that can be evaluated has changed over time

Ask me about PFAS transformation



Source: Herzke et al. (2012). Perfluoroalkyl and Polyfluoroalkyl substances (PFASs) in consumer products in Norway–A pilot study. *Chemosphere*, *88*(8), 980-987.

Example: Site History Forensics is an Important First Step

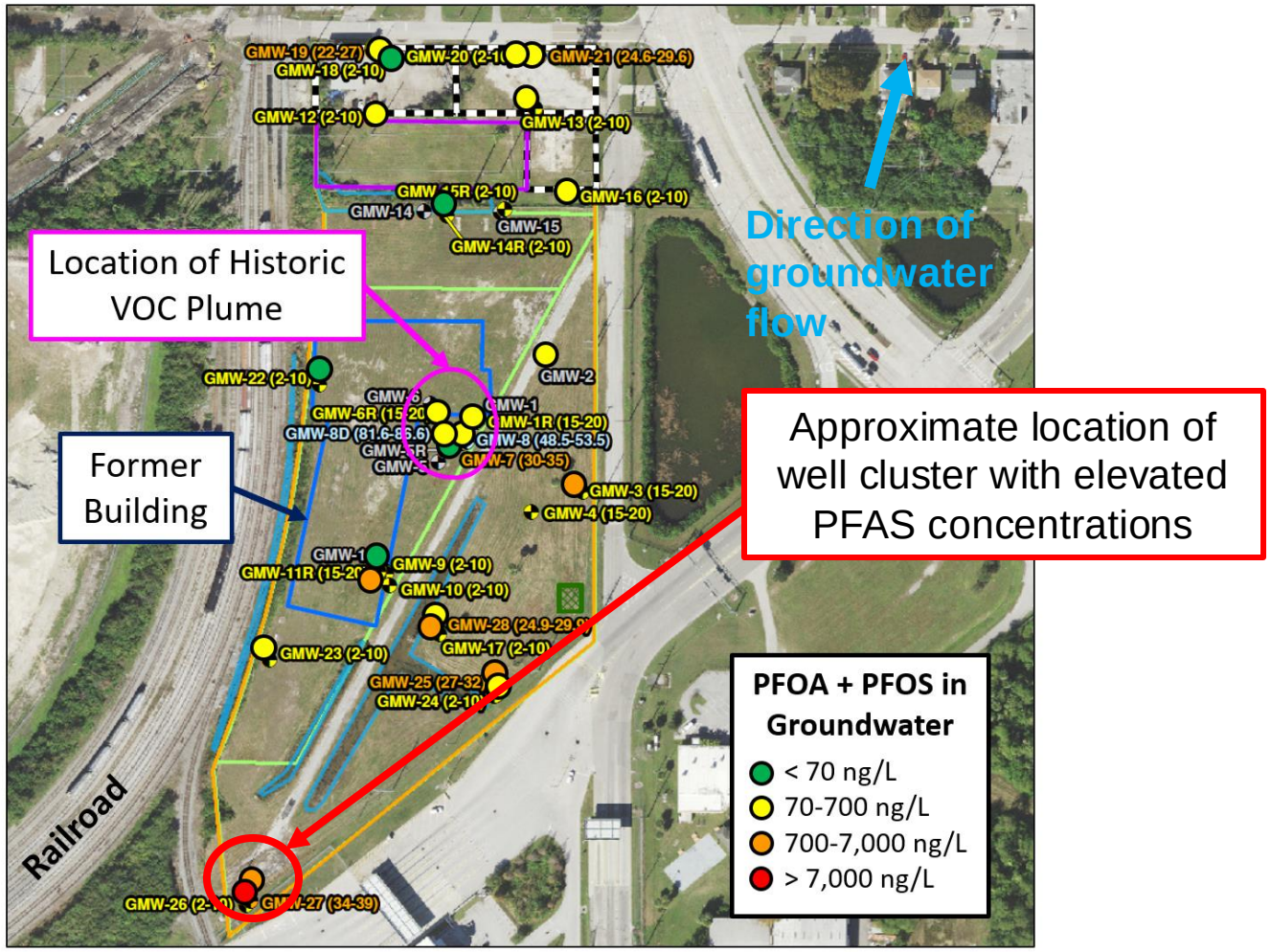
- Historic/mature site
- Client operations included
  - Hydraulic machine assembly
  - Parts cleaning
- TCE plume under client's property
- PFAS detections in wells:

  ~10 – 150 ng/L
- Request for PFAS sampling on site

Example: Site History Forensics is an Important First Step

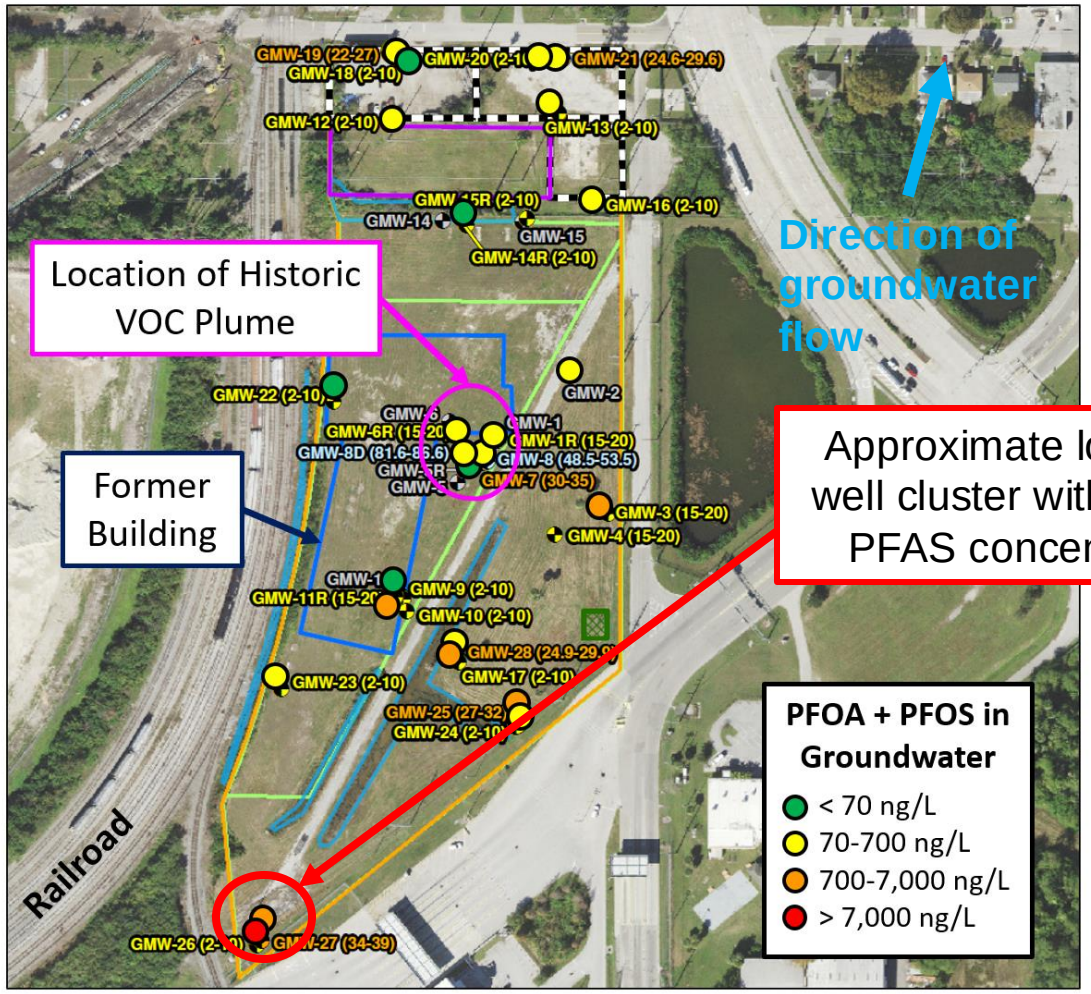
- Literature review:
  - No link between PFAS~TCE
- Second historical records review
  - No record of PFAS use
  - No record of PFAS containing materials
- Neighboring property:
  - Aircraft parts maintenance/assembly
- Future steps:
  - Collect samples (if necessary)
  - Fingerprinting analysis?

Example: Off-site PFAS Source?



- Historic/mature site
- VOC plume under client's property
- Request for PFAS sampling *prior* to site closure
- Highest PFAS concentrations were off-site
- Conducted second historical records review

Example: Off-site PFAS Source?



Best Practices for Evaluating PFAS Complexities: Key Takeaways

- Consideration of (regional) PFAS anthropogenic background is critical
  - A key component of CSM development and delineation of PFAS impacts
- Need to strategically select the appropriate PFAS analytical method(s)
  - Understanding the advantages or limitations of different analytical tools to answer specific questions
- A multiple lines of evidence approach is the best practice when evaluating PFAS complexities
  - Understanding site history; evaluation of potential PFAS sources; incorporating fate and transport of PFAS

A multiple lines of evidence approach is a best practice for addressing PFAS site characterization

Contact Information

Thank you!

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