Historical Lessons Learned:
What Might PFAS Site Closure Look Like?

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We Have Been Through This Before

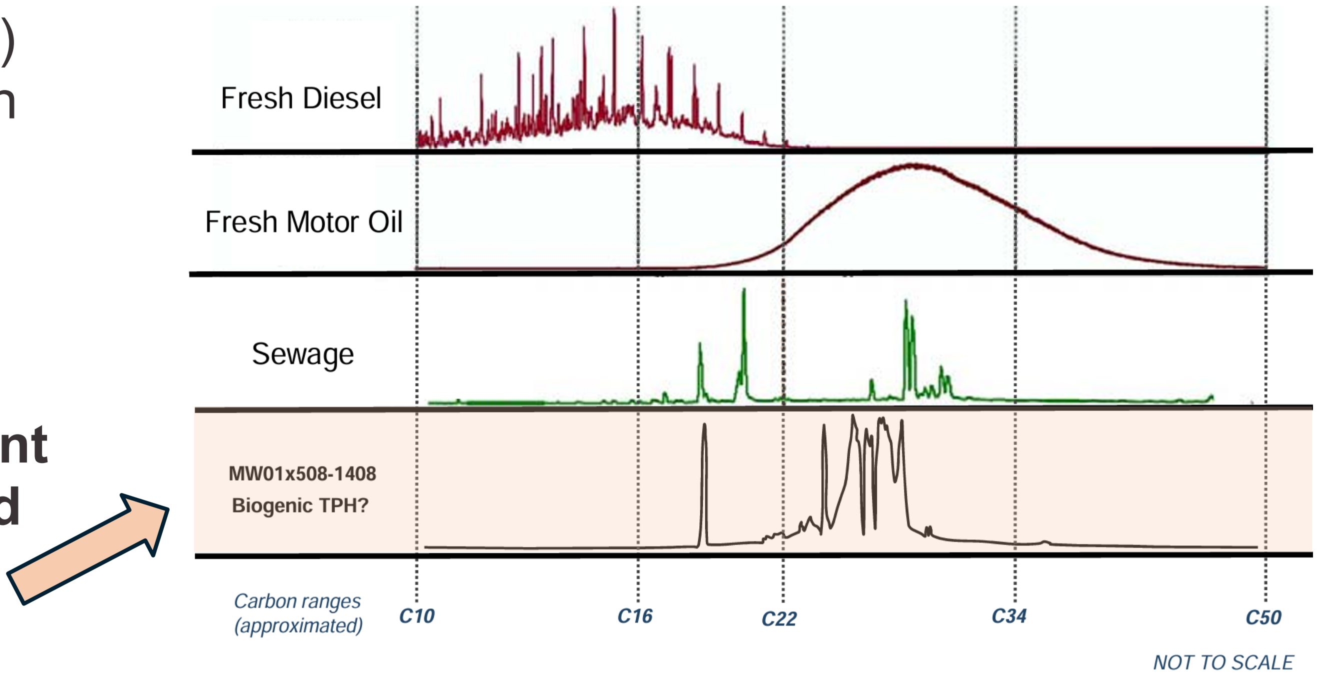
- **What are the key lessons learned from site closure of other contaminants?**
- I'll share my experiences based on:
  - 3 tiers of site closure complexity
  - Key considerations during PFAS investigation and remediation to support decision making

General Types of Site Closure

Closure Type		Description
1	**“No Risk”**	No unacceptable risk identified during the investigation phase
2	**“Simple” Remediation**	“Low” complexity remediation (e.g., tank removal, soil excavation, etc.)
3	**“Complex” Remediation**	Potentially decades of remediation activities required to achieve closure

"No Risk" Site Closure Example

- **Former Site CG508 at Travis AFB, CA**
  - Petroleum-only Contamination (POCO) site based on detection of TPH-MRO in groundwater
  - No soil source could be identified and no BTEX was detected
  - **Chromatogram pattern not consistent with motor oil but instead resembled sewage or manure (referencing Dr. Francine Kelly-Hooper's work)**



Chromatogram examples from:
Francine Kelly-Hooper, PhD

Restoration Program Manager's Meeting Minutes 21 January 2015

Blaming the Wrong "Source"?

- **TPH was not the result of an "oil spill", but instead multiple lines of evidence demonstrated this was a "non-site" and the site was closed**
  - A sewer line leak had occurred near the TPH-MRO detections
  - Decreased alkalinity and disinfection by-products observed in GW

- **Might we find similar scenarios at some PFAS sites where we initially blame the wrong "source"?**

Applying These Lessons Learned to PFAS

- How do we assess “background” PFAS?
- How can we be confident in determining when one source ends and another begins?

What Constitutes "Background"

- **First, we need to define "background" versus low-level point-source(s) of PFAS contamination**
- **Background PFAS** cannot be tied to any specific source, and is representative of "regional" PFAS releases
- **Low-level point source(s)** include many potential land uses tied to a specific use/release of PFAS

"Soup" of Potentially Similar PFAS Patterns at Low PPT Concentrations

Literature Review of Potential PFAS "Sources"

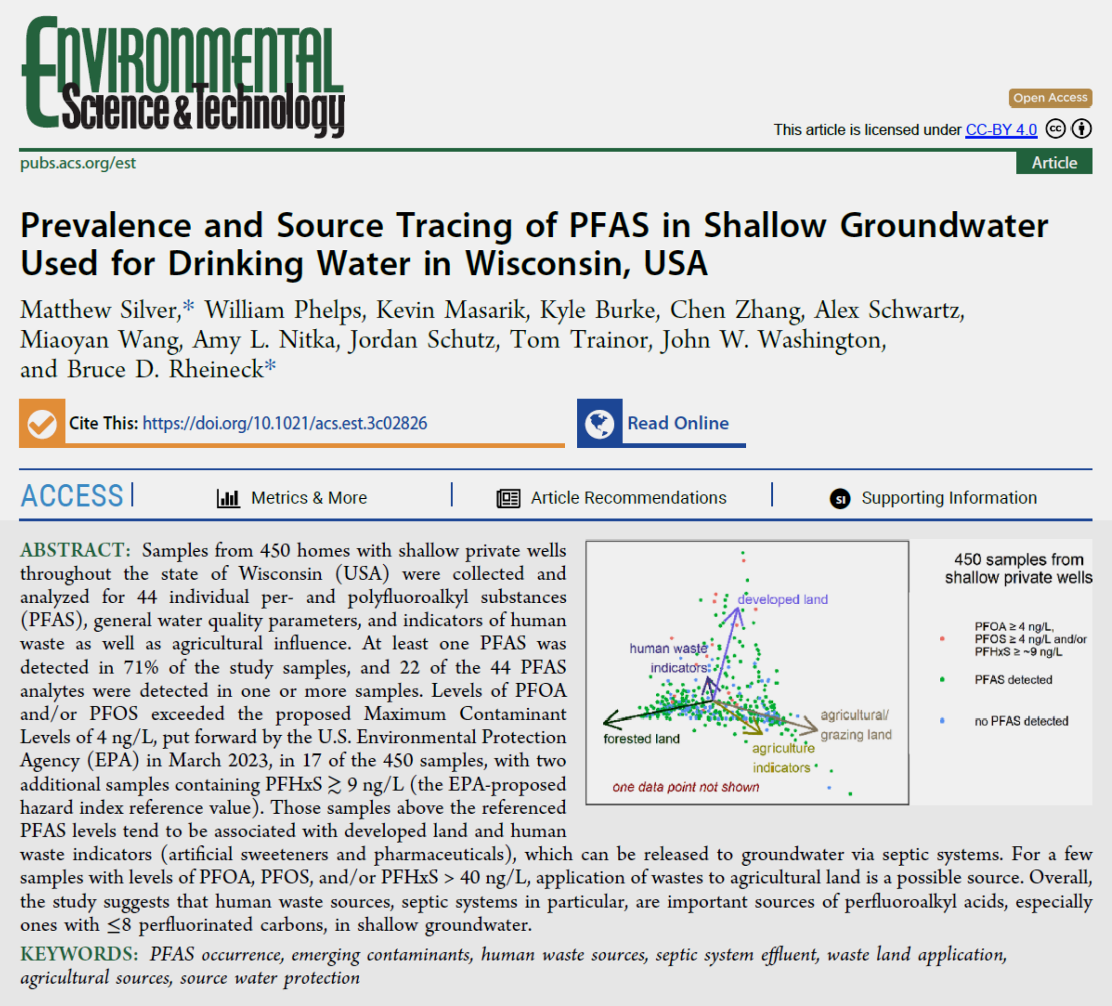
Potential Household Use / Background

- Precipitation
- Coatings and Adhesives
- Paper and Packaging Products
- Textiles and Carpets
- Cleaning Agents and Waxes
- Personal Care Products & Cosmetics
- Septage and Wastewater
- Pesticides and Herbicides
- Dry Cleaning
- Transportation Industry
- Metal Plating and Machining
- Plastics and Rubbers
- Printing, Etching, and Photography
- Concrete Manufacturing
- Energy Sector
- Medical Sector
- Electronics
- Building and Construction Industry
- Explosives, Propellants, and Ammunition
- Mining, Oil & Gas
- Landfills
- AFFF

Modified from Glüge et al. 2020 and Gaines 2023 – this list is not intended to be all-inclusive or applicable in some cases

What Might PFAS Background Look Like?

- Samples from 450 private wells **>3 miles** from Wisconsin DNR sites with actionable PFAS concentrations
- **“Those samples above the referenced PFAS levels tend to be associated with developed land and human waste indicators** (artificial sweeteners and pharmaceuticals), which can be released to groundwater via septic tanks.”



Environmental Science & Technology

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Prevalence and Source Tracing of PFAS in Shallow Groundwater Used for Drinking Water in Wisconsin, USA

Matthew Silver,* William Phelps, Kevin Masarik, Kyle Burke, Chen Zhang, Alex Schwartz, Miaoyan Wang, Amy L. Nitka, Jordan Schutz, Tom Trainor, John W. Washington, and Bruce D. Rheineck*

Cite This: https://doi.org/10.1021/acs.est.3c02826

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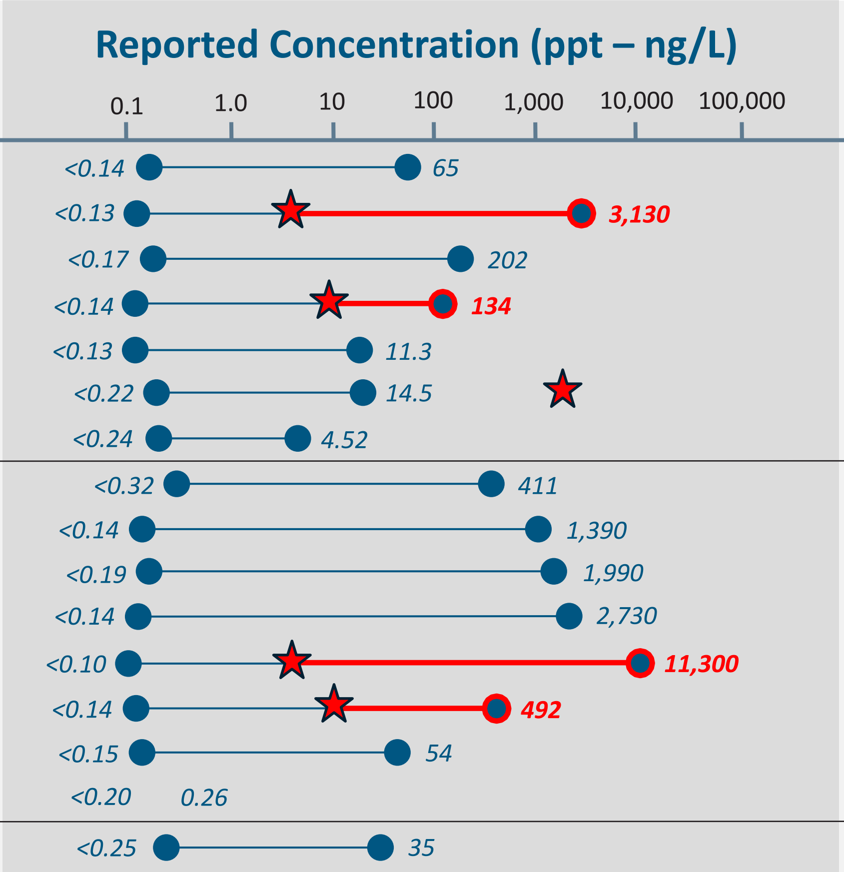
ABSTRACT: Samples from 450 homes with shallow private wells throughout the state of Wisconsin (USA) were collected and analyzed for 44 individual per- and polyfluoroalkyl substances (PFAS), general water quality parameters, and indicators of human waste as well as agricultural influence. At least one PFAS was detected in 71% of the study samples, and 22 of the 44 PFAS analytes were detected in one or more samples. Levels of PFOA and/or PFOS exceeded the proposed Maximum Contaminant Levels of 4 ng/L, put forward by the U.S. Environmental Protection Agency (EPA) in March 2023, in 17 of the 450 samples, with two additional samples containing PFHxS ≳ 9 ng/L (the EPA-proposed hazard index reference value). Those samples above the referenced PFAS levels tend to be associated with developed land and human waste indicators (artificial sweeteners and pharmaceuticals), which can be released to groundwater via septic systems. For a few samples with levels of PFOA, PFOS, and/or PFHxS > 40 ng/L, application of wastes to agricultural land is a possible source. Overall, the study suggests that human waste sources, septic systems in particular, are important sources of perfluoroalkyl acids, especially ones with ≤8 perfluorinated carbons, in shallow groundwater.

KEYWORDS: *PFAS occurrence, emerging contaminants, human waste sources, septic system effluent, waste land application, agricultural sources, source water protection*

Groundwater Background near Septic Sources



Matrix	Reference	Detected Compound	Reported Concentration (ppt – ng/L)	Detection Frequency	Geometric Mean (ppt)
Groundwater	Silver et al. (2023) (Wisconsin Septic Sites) n = 40 locations	**FOSA**	*<0.14* *65*	15%	0.20
		PFOS	*<0.13* ***3,130***	20%	0.26
		PFHpS	*<0.17* *202*	5%	0.21
		PFHxS	*<0.14* ***134***	35%	0.31
		PFPeS	*<0.13* *11.3*	8%	0.16
		PFBS	*<0.22* *14.5*	35%	0.39
		PFPrS	*<0.24* *4.52*	5%	0.28
		PFBA	*<0.32* *411*	53%	0.90
		PFPeA	*<0.14* *1,390*	28%	0.30
		PFHxA	*<0.19* *1,990*	23%	0.32
		PFHpA	*<0.14* *2,730*	23%	0.26
		PFOA	*<0.10* ***11,300***	53%	0.75
		PFNA	*<0.14* ***492***	13%	0.24
		PFDA	*<0.15* *54*	8%	0.19
		PFUnA	*<0.20* *0.26*	3%	0.20
		6:2 FTS	*<0.25* *35*	3%	0.28
		Sum of PFAS	*<0.10* *21,839*	75%	4.1

★ = *USEPA MCL*

Exceedances in Red Font

Geomean calculated using MDL value for non-detects

Global Groundwater Background Study

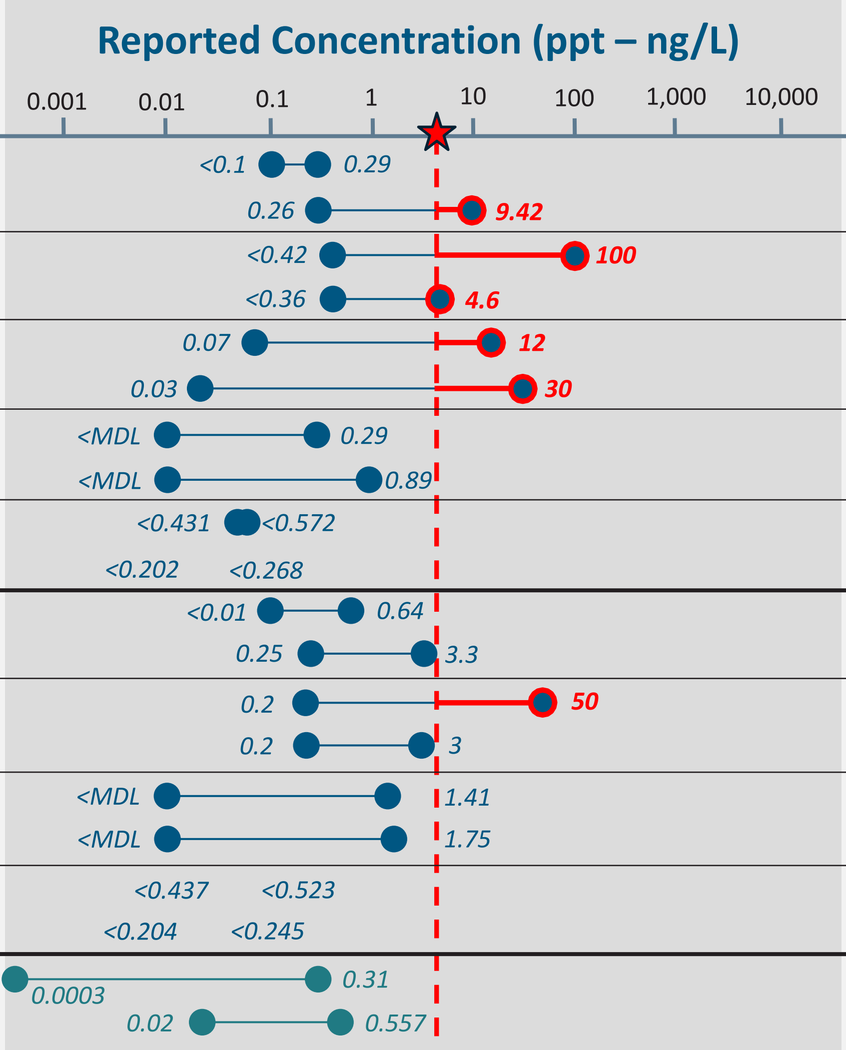
Matrix	Reference	Detected Compound	Reported Concentration (ppt – ng/L)		Detection # and Frequency	Mean (ppt)
Groundwater	Johnson et al. (2022) (Global Study) Range = 95% CI (min) to Max n = 5,990 locations* **No known PFAS sources*	**FOSA**	*1.0*	*95*	154 (2%)	1.0
		PFDS	*0.36*	*6.9*	71 (1%)	0.66
		PFNS	*NR*		0 (0%)	NR
		PFOS	***48***	***20,000***	1,043 (17%)	**46**
		PFHpS	*0.36*	*10*	67 (1%)	0.70
		PFHxS	*1.0*	***56***	732 (12%)	6.0
		PFPeS	*NR*		0 (0%)	NR
		PFBS	*1.9*	*143*	668 (11%)	8.9
		PFBA	*1.2*	*90.3*	478 (8%)	5.7
		PFPeA	*1.0*	*290*	720 (12%)	5.0
		PFHxA	*1.1*	*299*	755 (13%)	4.1
		PFHpA	*1.0*	*61*	774 (13%)	6.3
		PFOA	***5***	***1,800***	1,051 (18%)	**13**
		PFNA	*1.6*	***620***	677 (11%)	3.4
		PFDA	*0.09*	*34*	670 (11%)	0.42
		PFUnA	*0.21*	*28*	304 (5%)	0.53
		PFDoA	*0.12*	*13.7*	308 (5%)	0.32
		PFTrDA	*0.14*	*5.9*	115 (2%)	0.27
		PFTeDA	*0.07*	*9.2*	291 (5%)	0.19
		4:2 FTS	*0.38*		30 (1%)	0.38
		6:2 FTS	*1.2*	*118*	223 (4%)	1.8
		8:2 FTS	*1.1*		30 (1%)	1.1
		Gen X	*0.06*		30 (1%)	0.06

★ *= USEPA MCL*

Exceedances in Red Font

Summary of Select Precipitation Studies

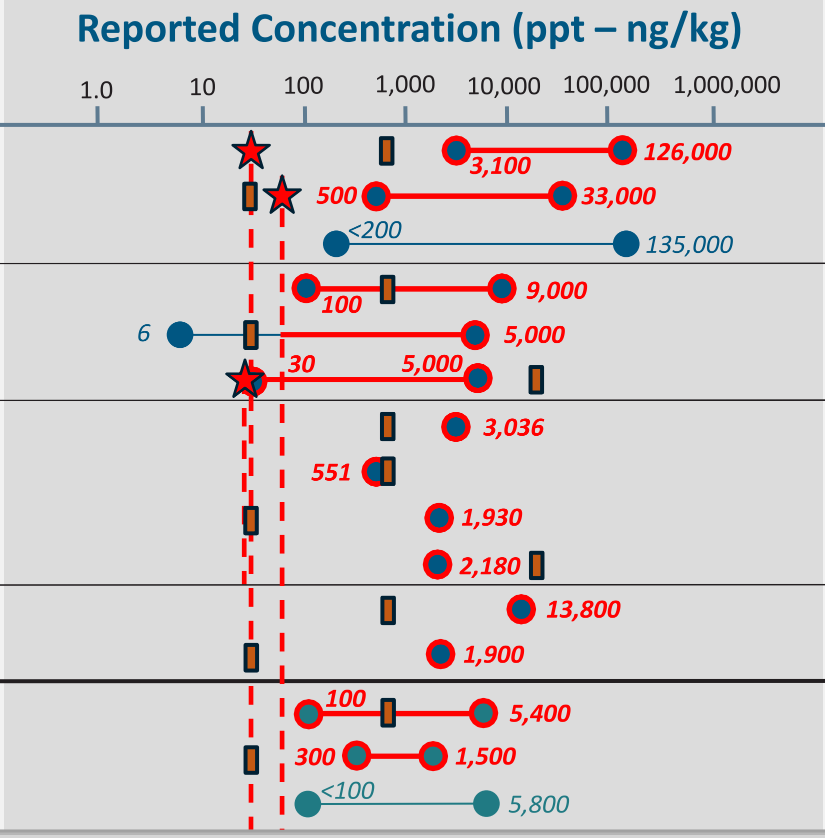
Focused on U.S. Studies (Antarctica provided for reference)



Matrix & Reference	Reference and Sample Dates	Detected Compound	Reported Concentration (ppt – ng/L)	Locations (# of Samples)	Median (ppt)	
Precipitation	Kwok et al. (2010) 2006-2008	**PFOS**	<0.1 – 0.29	Albany, NY (6)	0.18	**Urban**
★ = *USEPA MCL*		**PFOA**	0.26 – 9.42		3.4	
Exceedances in Red Font	Shimizu et al (2021) 2018-2019	**PFOS**	<0.42 – 100	Wilmington, NC (24)	N/A	
		PFOA	<0.36 – 4.6		N/A	
	Pike et al. (2021) 2019	**PFOS**	0.07 – 12	Willoughby, OH (11)	8	
		PFOA	0.03 – 30		1	
	Pfotenhauer et al. (2022) 2020	**PFOS**	<MDL – 0.29	Wisconsin (3 sites) (25)	0.06-0.12	
		PFOA	<MDL – 0.89		0.13-0.22	
	Olney et al. (2023) 2021	**PFOS**	<0.431 <0.572	MA (17 sites) (32)	N/A	
		PFOA	<0.202 <0.268		N/A	
	Kwok et al. (2010) 2006-2008	**PFOS**	<0.01 – 0.64	Slingerlands, NY (6)	0.27	**Rural**
		PFOA	0.25 – 3.3		1.79	
	Pike et al. (2021) 2019	**PFOS**	0.2 – 50	OH (2 sites), WY (1 site) (18)	2-20	
		PFOA	0.2 – 3		0.6-2	
	Pfotenhauer et al. (2022) 2020	**PFOS**	<MDL – 1.41	Wisconsin (5 sites) (63)	0.04-0.26	
		PFOA	<MDL – 1.75		0.13-0.33	
	Olney et al. (2023) 2021	**PFOS**	<0.437 <0.523	MA (8 sites) (17)	N/A	
		PFOA	<0.204 <0.245		N/A	
	Casas et al. (2021) 2017-2018	**PFOS**	0.0003 – 0.31	Antarctica (20)	0.0055	
		PFOA	0.02 – 0.557		0.2195	

Summary of Select Soil Background Studies

Focused on U.S. Studies (remote locations provided for reference)



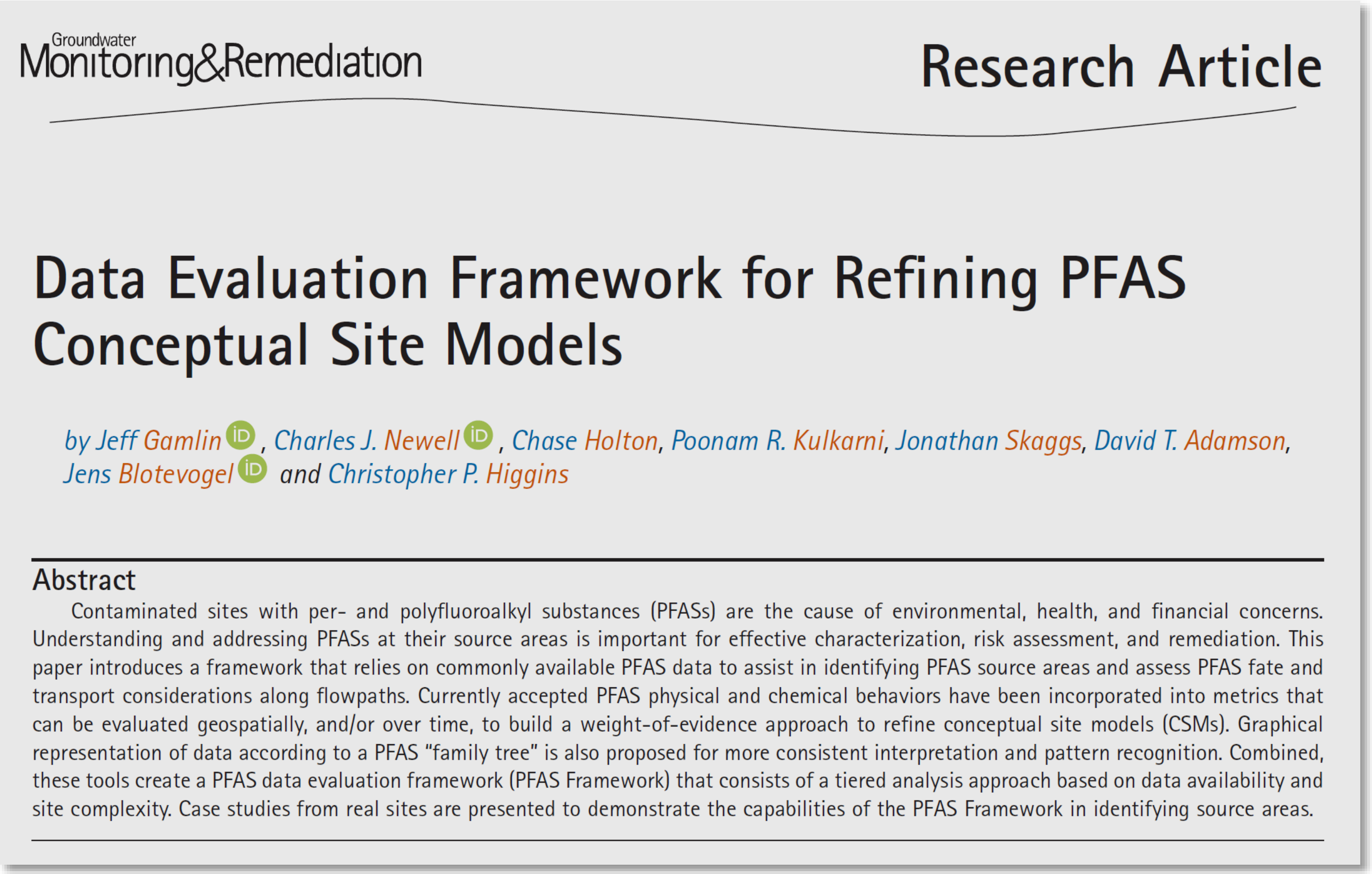
Matrix	Reference	Detected Compound	Reported Concentration (ppt – ng/kg)	Location	Range or Threshold Value?
Soil	Brousseau et al. (2020)	**PFOS**	3,100 126,000	United States (5 locations)	Range of Max C's for PFOS & PFOA; Detection Range for Sum
		PFOA	500 33,000		
		Sum of PFAS	<200 135,000		
	Zhu et al. (2022)	**PFOS**	100 9,000	Vermont	Range
		PFOA	6 5,000		
		PFNA	30 5,000		
	Sanborn, Head & Assoc. (2022)	**PFOS** (urban)	3,036	Maine	Threshold
		PFOS (non-urban)	551		
		PFOA	1,930		
		PFNA	2,180		
	Anderson and Modiri (2024)	**PFOS**	13,800	U.S. DoD Study	Threshold (Max)
		PFOS	1,900		Threshold (Min)
	Brousseau et al. (2020)	**PFOS**	100 5,400	Tierra Del Fuego, & Antarctica (1), Nepal (1)	Range of Max C's for PFOS & PFOA; Detection Range for Sum
		PFOA	300 1,500		
		Sum of PFAS	<100 5,800		

USEPA SSLs (May 2024)	*PFOS*	*PFOA*	*PFNA*
– –★ *Protection of MCLs*	*30.5*	*60.8*	*25*
▮ *Residential Soil*	*630*	*19*	*19,000*

Cancer or HQ = 0.1 (ppt – ng/kg)

Exceedances in Red Font

PFAS Data Evaluation Framework



Groundwater Monitoring&Remediation

Research Article

Data Evaluation Framework for Refining PFAS Conceptual Site Models

by Jeff Gamlin, Charles J. Newell, Chase Holton, Poonam R. Kulkarni, Jonathan Skaggs, David T. Adamson, Jens Blotevogel and Christopher P. Higgins

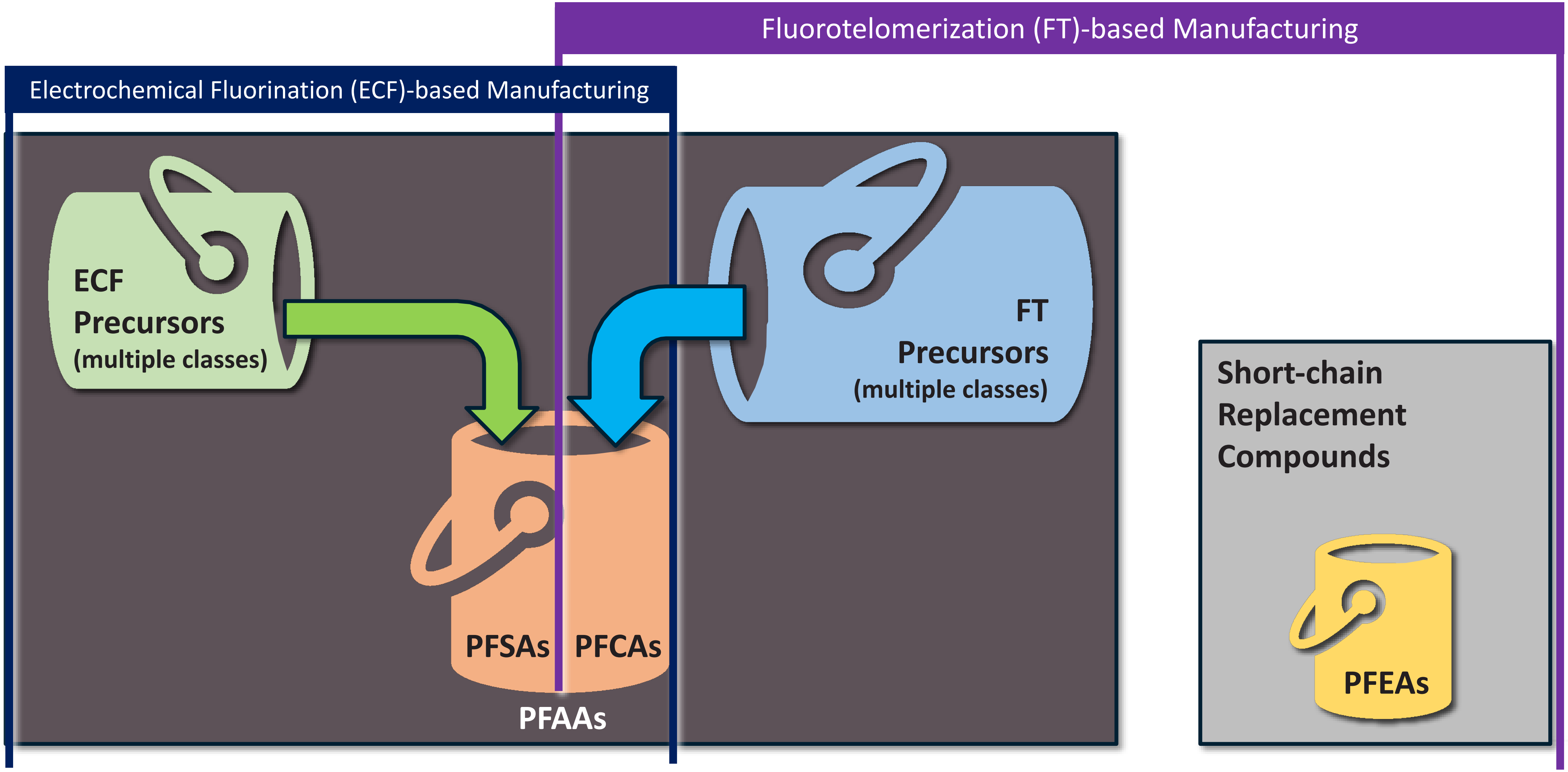
Abstract

Contaminated sites with per- and polyfluoroalkyl substances (PFASs) are the cause of environmental, health, and financial concerns. Understanding and addressing PFASs at their source areas is important for effective characterization, risk assessment, and remediation. This paper introduces a framework that relies on commonly available PFAS data to assist in identifying PFAS source areas and assess PFAS fate and transport considerations along flowpaths. Currently accepted PFAS physical and chemical behaviors have been incorporated into metrics that can be evaluated geospatially, and/or over time, to build a weight-of-evidence approach to refine conceptual site models (CSMs). Graphical representation of data according to a PFAS "family tree" is also proposed for more consistent interpretation and pattern recognition. Combined, these tools create a PFAS data evaluation framework (PFAS Framework) that consists of a tiered analysis approach based on data availability and site complexity. Case studies from real sites are presented to demonstrate the capabilities of the PFAS Framework in identifying source areas.

- **PFAS Framework based on multiple lines of evidence**
  - Look for Gamlin et al. (2024) **DOI:10.1111/gwmr.12666**

Environmental PFAS "Buckets"

by Manufacturing Process and Chemical Class



Fluorotelomerization (FT)-based Manufacturing

Electrochemical Fluorination (ECF)-based Manufacturing

Short-chain Replacement Compounds

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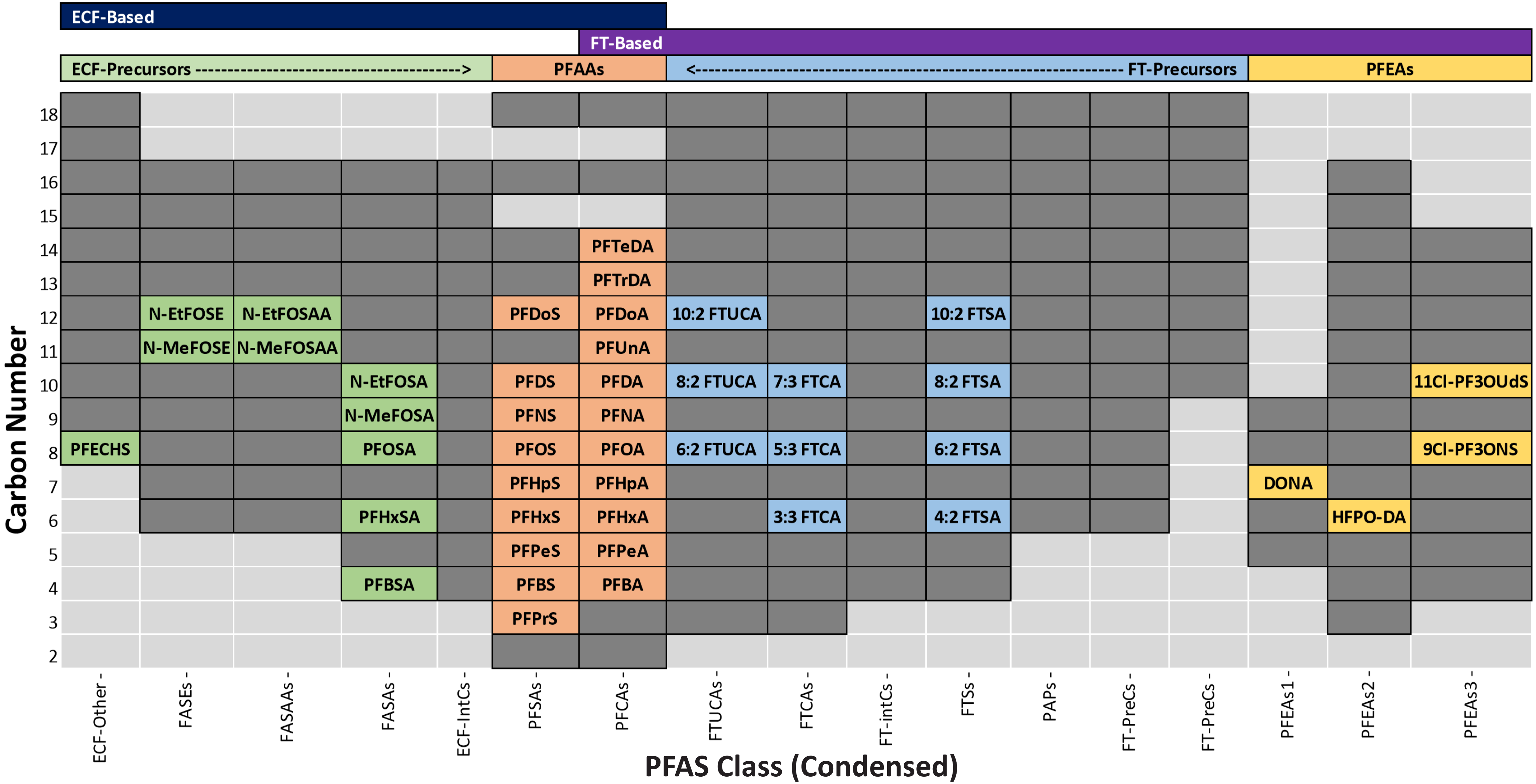
PFAS Family Tree – Based on Silver et al. (2023) Analyte List

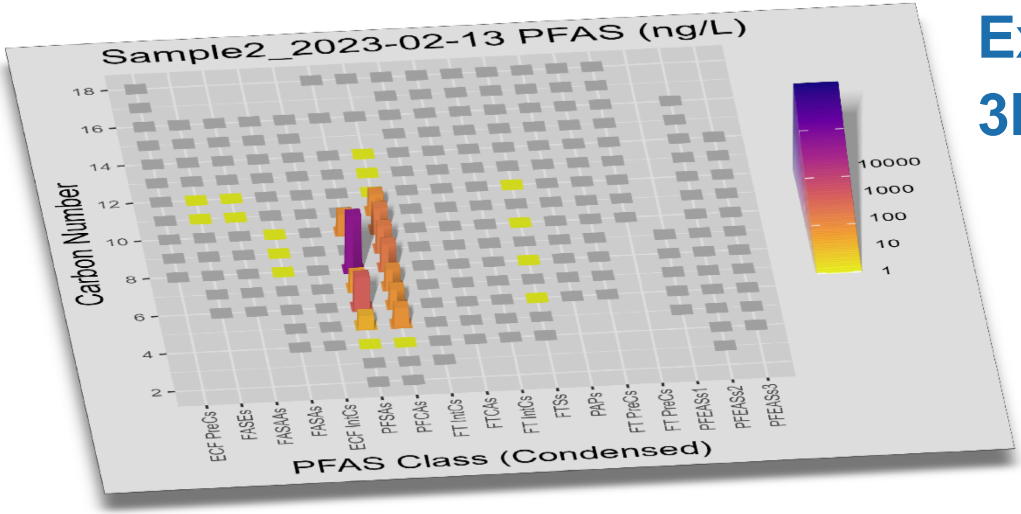


	ECF-Other	FASEs	FASAAs	FASAs	ECF-IntCs	PFSAs	PFCAs	FTUCAs	FTCAs	FT-intCs	FTSs	PAPs	FT-PreCs	FT-PreCs	PFEAs1	PFEAs2	PFEAs3
18	■					■	■	■	■	■	■	■	■	■			
17	■							■	■	■	■	■	■	■			
16	■	■	■	■	■	■	■	■	■	■	■	■	■	■		■	
15	■	■	■	■	■			■	■	■	■	■	■	■		■	
14	■	■	■	■	■	■	PFTeDA	■	■	■	■	■	■	■		■	■
13	■	■	■	■	■	■	PFTrDA	■	■	■	■	■	■	■		■	■
12	■	N-EtFOSE	N-EtFOSAA	■	■	PFDoS	PFDoA	10:2 FTUCA	■	■	10:2 FTSA	■	■	■		■	■
11	■	N-MeFOSE	N-MeFOSAA	■	■	■	PFUnA	■	■	■	■	■	■	■		■	■
10	■	■	■	N-EtFOSA	■	PFDS	PFDA	8:2 FTUCA	7:3 FTCA	■	8:2 FTSA	■	■	■		■	11Cl-PF3OUdS
9	■	■	■	N-MeFOSA	■	PFNS	PFNA	■	■	■	■	■	■		■	■	■
8	PFECHS	■	■	PFOSA	■	PFOS	PFOA	6:2 FTUCA	5:3 FTCA	■	6:2 FTSA	■	■		■	■	9Cl-PF3ONS
7		■	■	■	■	PFHpS	PFHpA	■	■	■	■	■	■		DONA	■	■
6		■	■	PFHxSA	■	PFHxS	PFHxA	■	3:3 FTCA	■	4:2 FTSA	■	■		■	HFPO-DA	■
5				■	■	PFPeS	PFPeA	■	■	■	■				■	■	■
4				PFBSA	■	PFBS	PFBA	■	■	■	■					■	■
3						PFPrS	■	■	■							■	
2						■	■										

Note: Dark grey cells are approximate representations of other PFAS compounds not analyzed.

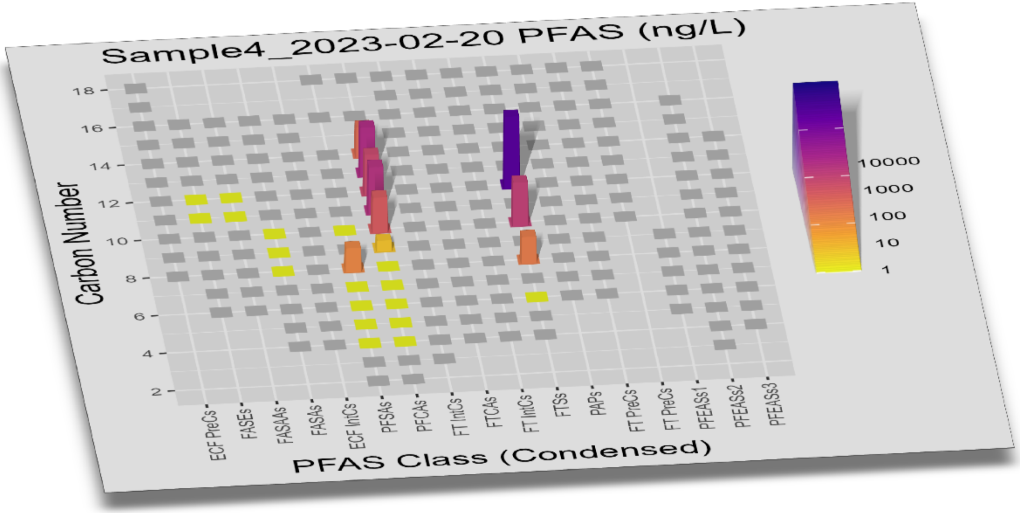
PFAS Family Tree Graphs

Examples of AFFF patterns within environmental water samples

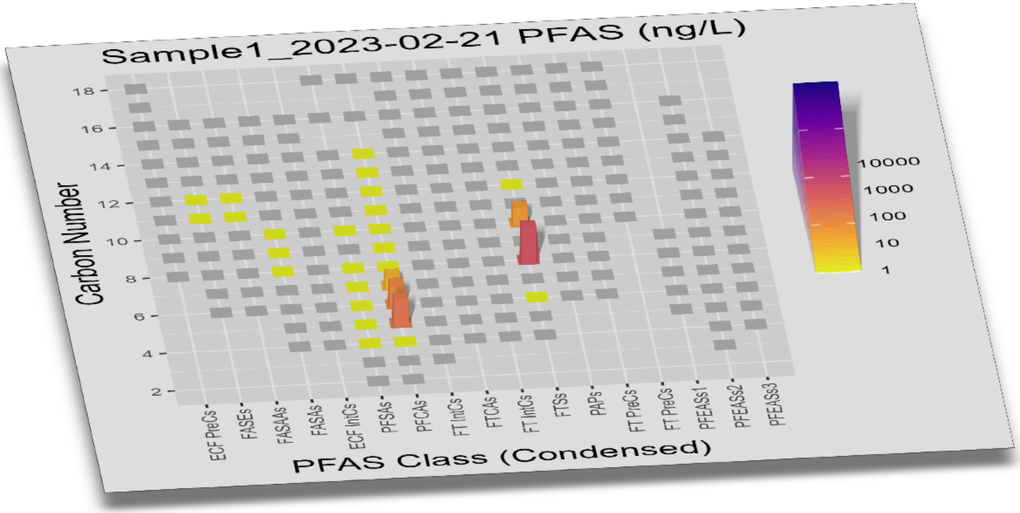


Example of 3M LightWater Pattern

"Heavy" FT-based AFFF Pattern

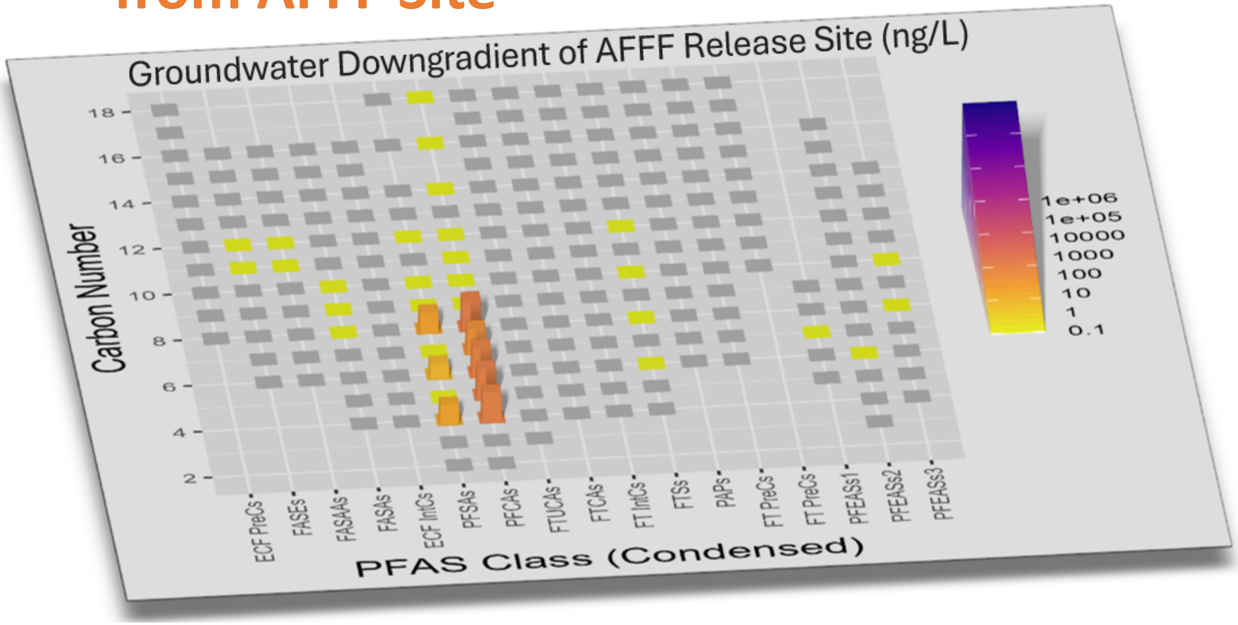


"C6" AFFF Pattern

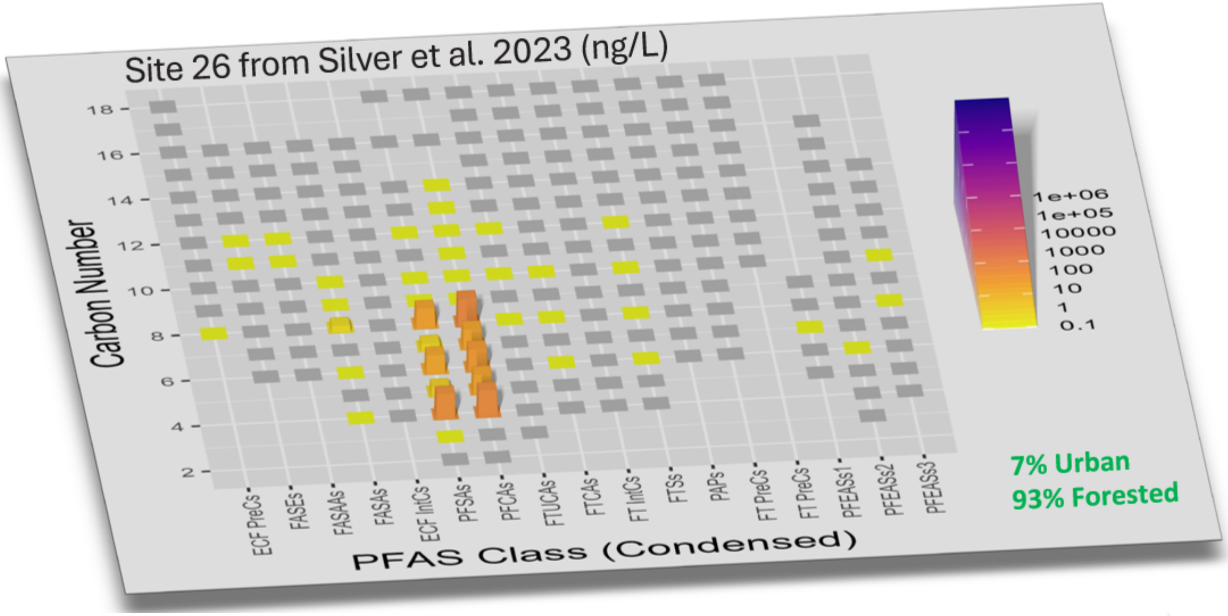


PFAS Background Patterns versus
PFAS Patterns Downgradient of AFFF Release Sites

PFAS Pattern from AFFF Site



Background PFAS Pattern from Silver et al. 2023



7% Urban
93% Forested

If PFAS background patterns can resemble downgradient AFFF plumes, PFAS patterns alone may not be sufficient to identify/separate differing sources.

Key Considerations for PFAS Sites

- **Understanding PFAS sources at low PPT levels requires <u>multiple lines of evidence</u>**
- **We need better tools to communicate complex topics with stakeholders**
  - PFAS Data Evaluation Framework paper

    DOI:10.1111/gwmr.12666

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