NAVFAC
Naval Facilities Engineering Systems Command
EXWC Engineering and Expeditionary Warfare Center

Contextualizing PFAS Detections: Background and Forensics

Jeff Gamlin, PG, CHG, GSI Environmental Inc.

RITS 2025

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Information in this presentation is current as of 28 March 2025.

EXWC: Engineering and Expeditionary Warfare Center
NAVFAC: Naval Facilities Engineering Systems Command

Speaker Introduction

Jeff Gamlin, PG, CHG
Principal Hydrogeologist
GSI Environmental Inc.

CHG: Certified Hydrogeologist
PG: Professional Geologist
PFAS: per- and polyfluoroalkyl substances

EDUCATION

- Master of Science, Hydrogeology, 2002, *University of Nevada, Reno*
- Bachelor of Science, Geology, 1999, *University of California, Santa Barbara*

PROFESSIONAL EXPERIENCE

- ~25 years in the environmental remediation industry
- Has evaluated 70+ PFAS sites around the world
- Organizing Committee Member: PFAS Environmental Professionals Working Group

RECENT PUBLICATIONS

- Gamlin, J., Newell, C., Holton, C., Kulkarni, P., Skaggs, J., Adamson, D., Blotevogel, J., Higgins, C. 2024. “Data Evaluation Framework for Refining PFAS Conceptual Site Models.” *Groundwater Monitoring & Remediation.*
- Gamlin, J., Caird, R., Sachdeva, N., Miao, Y., Hutchison, C., Mahendra, S., De Long, S. 2024. “Developing a microbial community structure index (MCSI) as an approach to evaluate and optimize bioremediation performance.” *Biodegradation.*
- Gamlin, J., Javed, H., Newell, C., Stockwell, E., Caird, R., Scalia, J., Navarro, D., Awad, J. 2024. “Bridging the Technology Gap for Cost-Effective and Sustainable Treatment of Per- and Polyfluoroalkyl Substances in Surface Water and Stormwater.” *Remediation Journal.*

Presentation Overview

- Part 1: Introduction to the PFAS Analyte List
- Part 2: PFAS Forensics: Fate and Transport Considerations
- Part 3: PFAS Background Definitions
- Part 4: Key Considerations for Assessing Background PFAS
  - Lunch Break
- Part 5: Putting it All Together: Source Areas vs. Background
- Part 6: PFAS Background at Navy Installations
- Wrap-Up

PFAS Have a Lot of Acronyms…

- The next few slides will present a lot of acronyms…
- Don’t worry, this is just for reference, and you do not need to memorize
- We will break the PFAS acronyms into smaller “buckets” to make this easier to understand

(Image from Microsoft Office)

Introduction to the PFAS Analyte List

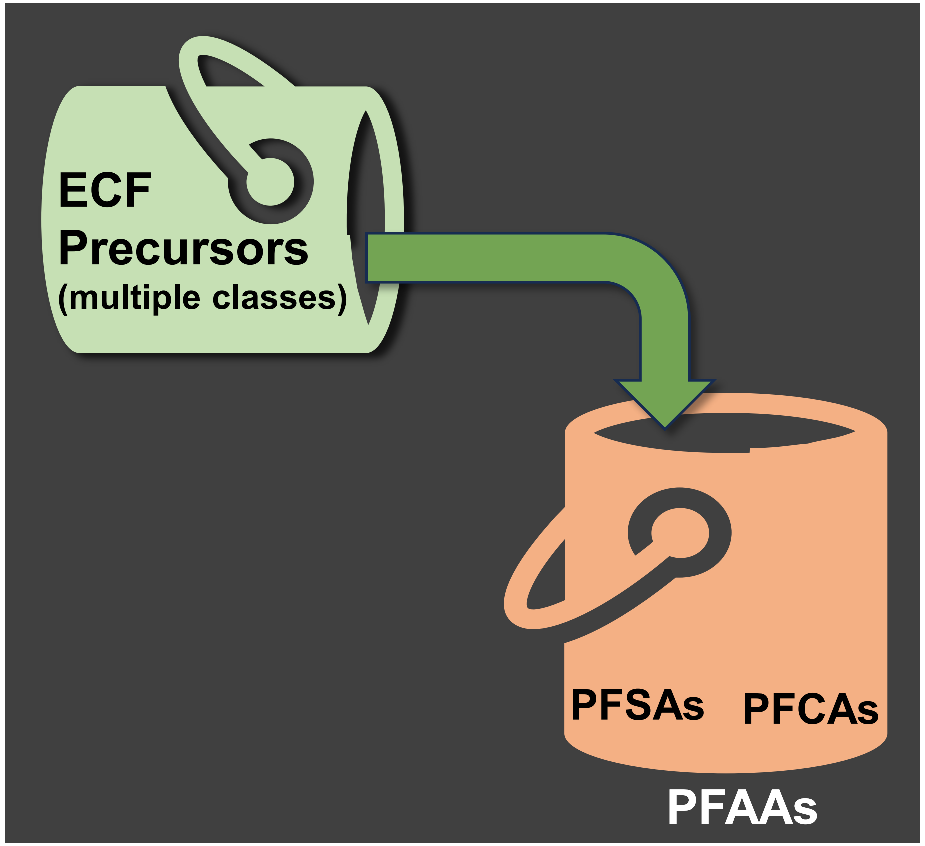
- General Acronym Definitions
  - We will focus on the EPA Method 1633 analyte list, since it is inclusive of PFAS in other DoD analyte lists
  - PFAAs: Perfluoroalkyl acids (perfluorinated)
    - PFSAs: Perfluoroalkyl sulfonic acids (e.g., perfluorooctane sulfonic acid - PFOS)
    - PFCAs: Perfluoroalkyl carboxylic acids (e.g., perfluorooctanoic acid - PFOA)
  - Precursors: PFAS that turn into other PFAS (polyfluorinated)
    - ECF: Electrochemical fluorination-based precursors
    - FT: Fluorotelomerization-based precursors
  - PFEAs: Per- and polyfluoroalkyl ether acids (“replacements”)

DoD: Department of Defense
EPA: United States Environmental Protection Agency

EPA Method 1633 Analyte List

ECF Precursors	PFSAs	PFCAs	FT Precursors	PFEAs
N-EtFOSE	PFDoDS	PFTeDA	8:2 FTS	11Cl-PF3OUdS
N-MeFOSE	PFDS	PFTrDA	6:2 FTS	9Cl-PF3ONS
N-EtFOSAA	PFNS	PFDoA	4:2 FTS	HFPO-DA
N-MeFOSAA	PFOS	PFUnA	7:3 FTCA	PFMBA
N-EtFOSA	PFHpS	PFDA	5:3 FTCA	PFMPA
N-MeFOSA	PFHxS	PFNA	3:3 FTCA	ADONA
FOSA	PFPeS	PFOA		NFDHA
	PFBS	PFHpA		PFEESA
		PFHxA		
		PFPeA		
		PFBA		

Generalized PFAS "Buckets" Part 1



ECF Precursors

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

PFSAs

- PFDoDS
- PFDS
- PFNS
- PFOS
- PFHpS
- PFHxS
- PFPeS
- PFBS

PFCAs

- PFTeDA
- PFTrDA
- PFDoA
- PFUnA
- PFDA
- PFNA
- PFOA
- PFHpA
- PFHxA
- PFPeA
- PFBA

Generalized PFAS "Buckets" Part 2

PFCAs

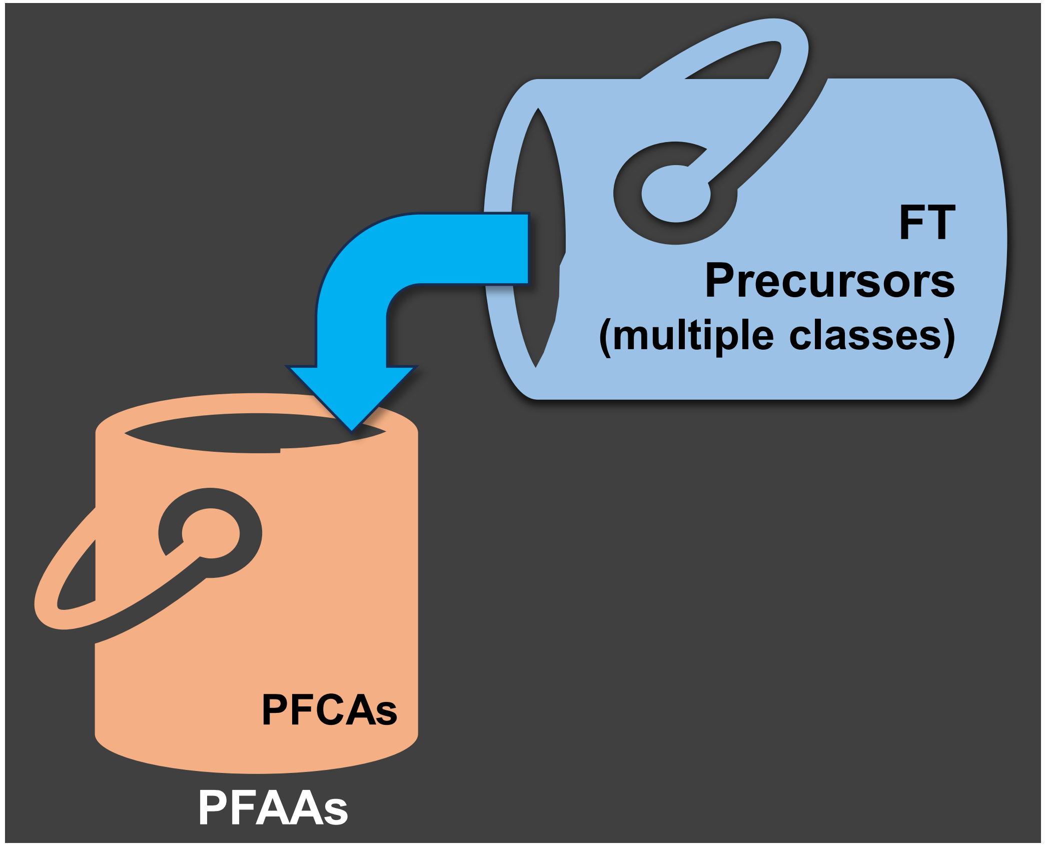
- PFTeDA
- PFTrDA
- PFDoA
- PFUnA
- PFDA
- PFNA
- PFOA
- PFHpA
- PFHxA
- PFPeA
- PFBA

FT Precursors

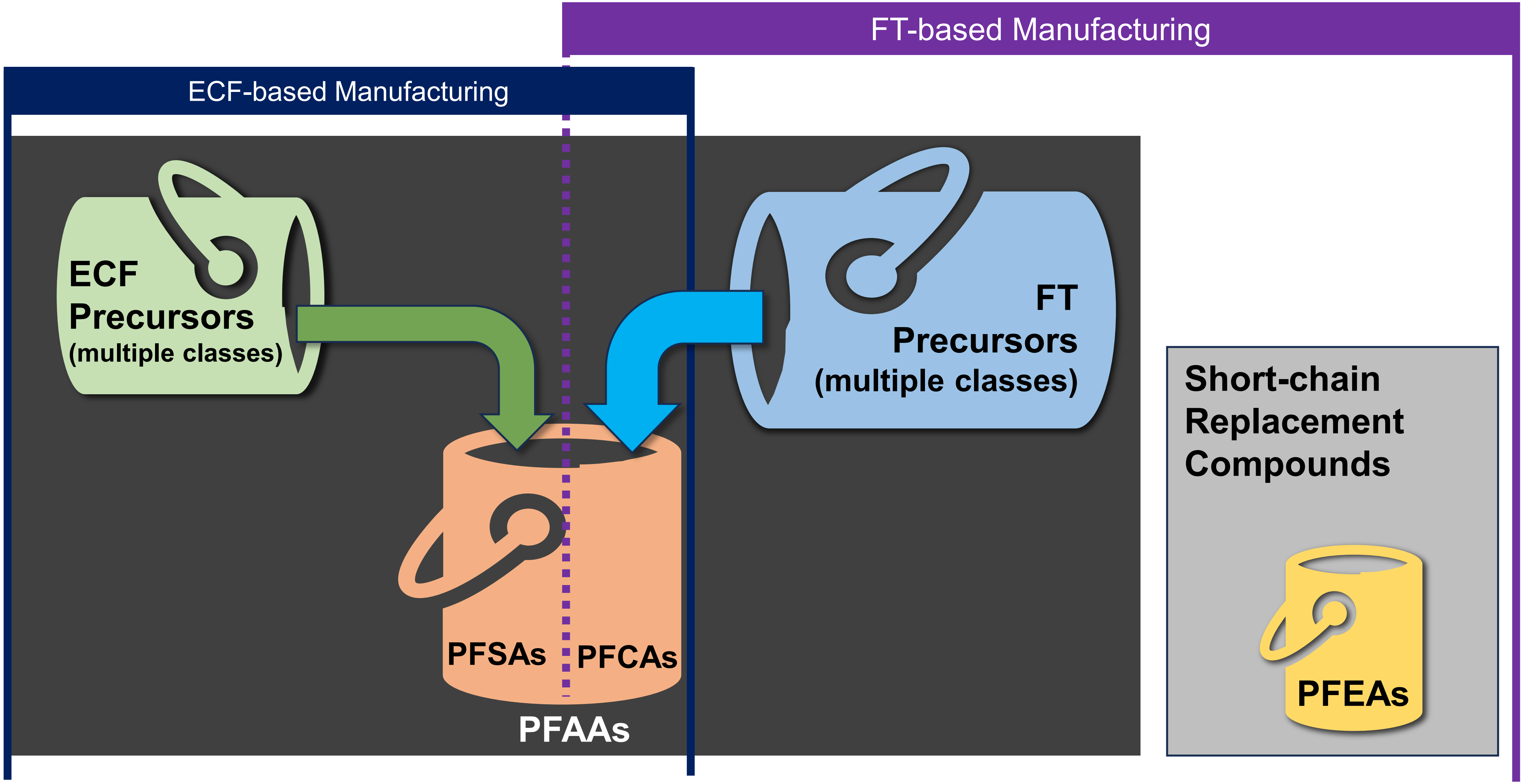
- 8:2 FTS
- 6:2 FTS
- 4:2 FTS
- 7:3 FTCA
- 5:3 FTCA
- 3:3 FTCA

PFEAs

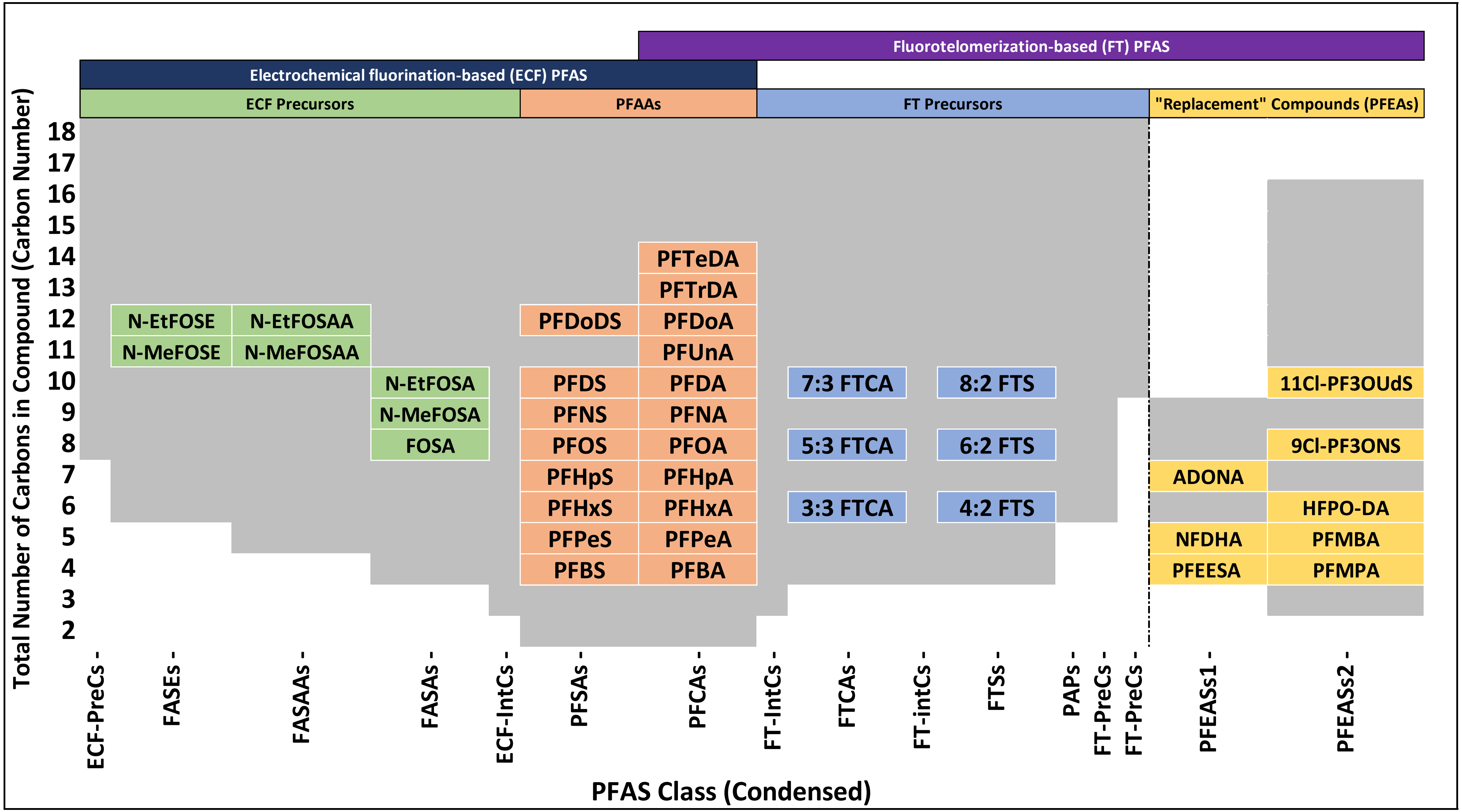
- 11Cl-PF3OUdS
- 9Cl-PF3ONS
- HFPO-DA
- PFMBA
- PFMPA
- ADONA
- NFDHA
- PFEESA



Generalized PFAS “Buckets” Combined



PFAS Family Tree (EPA Method 1633)



	ECF-PreCs	FASEs	FASAAs	FASAs	ECF-IntCs	PFSAs	PFCAs	FT-IntCs	FTCAs	FT-intCs	FTSs	PAPs	FT-PreCs	FT-PreCs	PFEASs1	PFEASs2
18																
17																
16																
15																
14							PFTeDA									
13							PFTrDA									
12		N-EtFOSE	N-EtFOSAA			PFDoDS	PFDoA									
11		N-MeFOSE	N-MeFOSAA				PFUnA									
10				N-EtFOSA		PFDS	PFDA		7:3 FTCA		8:2 FTS					11Cl-PF3OUdS
9				N-MeFOSA		PFNS	PFNA									
8				FOSA		PFOS	PFOA		5:3 FTCA		6:2 FTS					9Cl-PF3ONS
7						PFHpS	PFHpA								ADONA	
6						PFHxS	PFHxA		3:3 FTCA		4:2 FTS					HFPO-DA
5						PFPeS	PFPeA								NFDHA	PFMBA
4						PFBS	PFBA								PFEESA	PFMPA
3																
2																

Note: Dark grey cells are approximate representations of other PFAS not analyzed by EPA Method 1633

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Objective

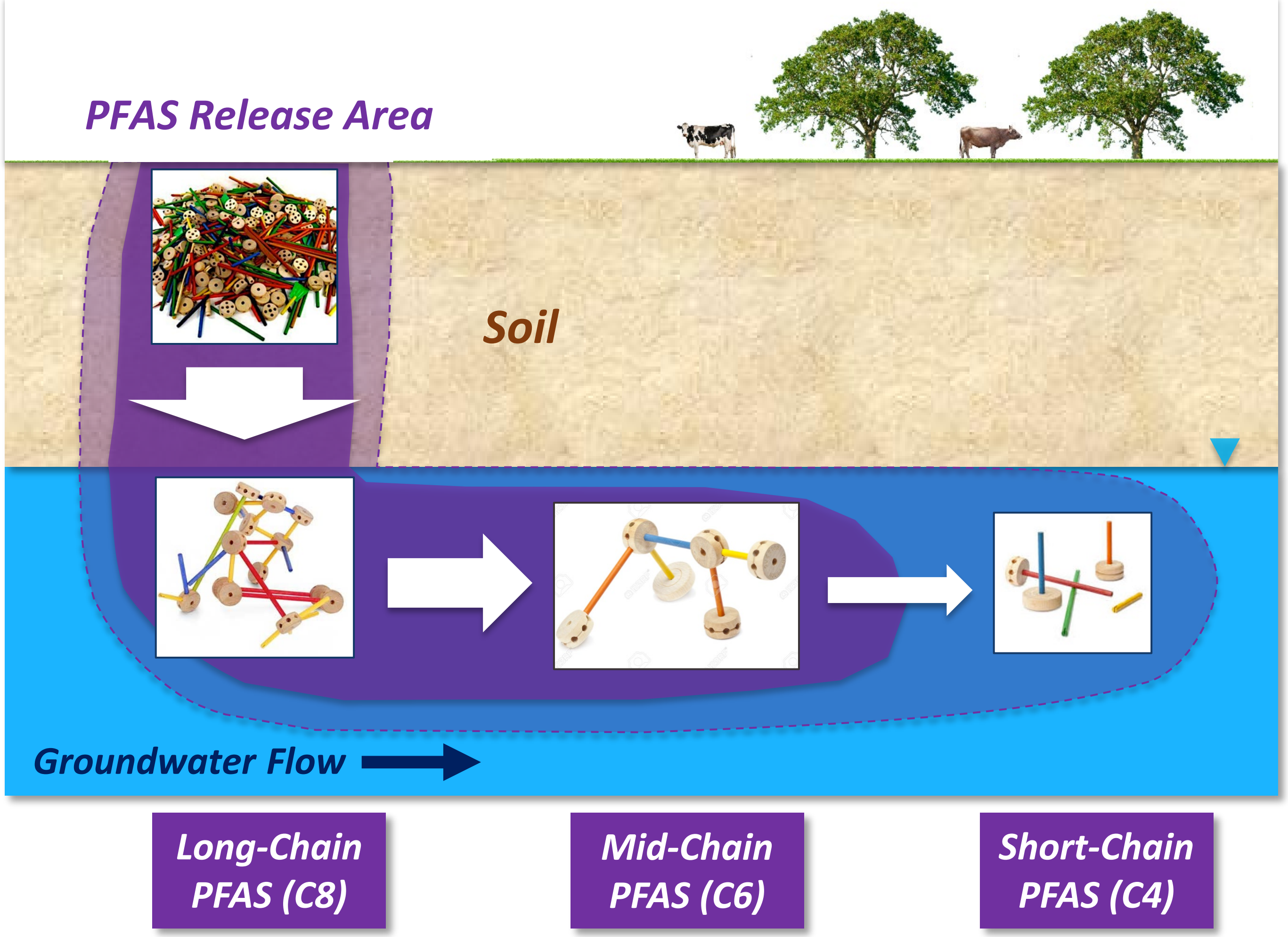
- Explain how PFAS fate and transport mechanisms can affect PFAS patterns over time/distance

(Image from Microsoft Office)

Basics of PFAS Environmental Behavior

Tinker toys represent complexity of PFAS along route of migration

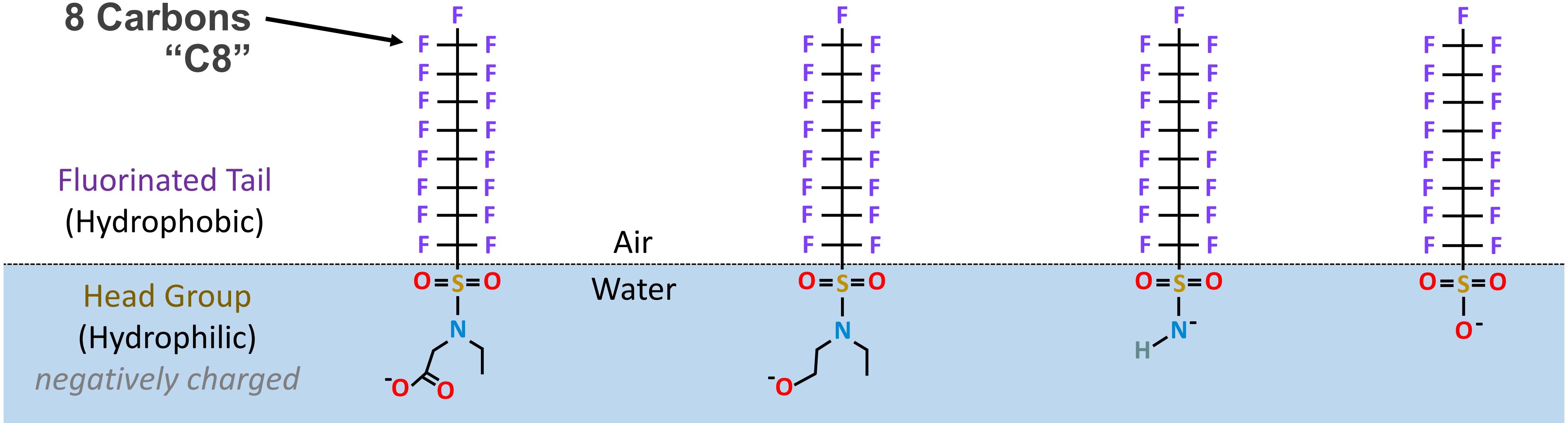
- Environmental factors cause long-chain PFAS to “stick” closer to source areas
- This causes PFAS patterns to change along routes of migration



Precursor Transformation to PFOS

Transformation Pathway (Rhodes et al. 2008) →

N-EtFOSE → N-EtFOSAA → FOSA → PFOS



Tail with 8 Carbons "C8"

Fluorinated Tail
(Hydrophobic)

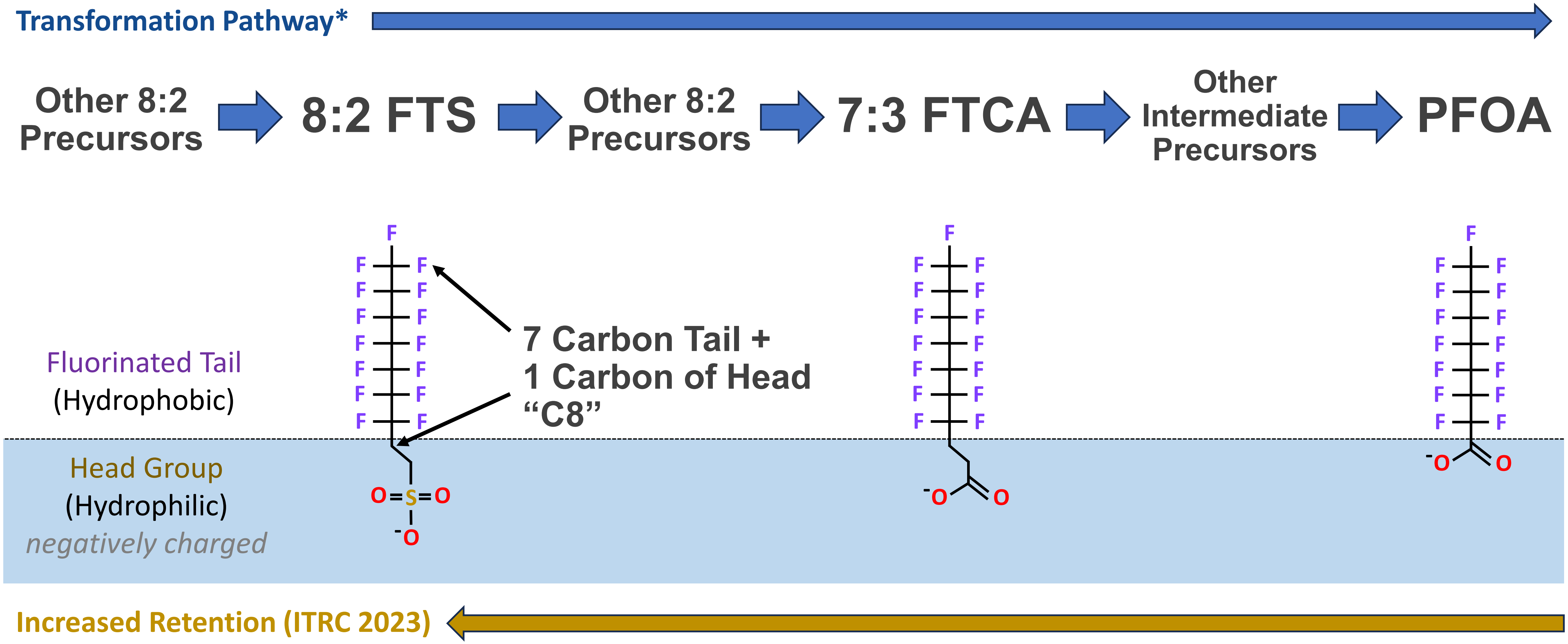
Air

Water

Head Group
(Hydrophilic)
negatively charged

Increased Retention (ITRC 2023) ←

Precursor Transformation to PFOA



Transformation Pathway*

Other 8:2 Precursors → **8:2 FTS** → **Other 8:2 Precursors** → **7:3 FTCA** → **Other Intermediate Precursors** → **PFOA**

Fluorinated Tail
(Hydrophobic)

Head Group
(Hydrophilic)
negatively charged

**7 Carbon Tail +
1 Carbon of Head
"C8"**

Increased Retention (ITRC 2023)

*(Harding-Marjanovic et al. 2015), (Dasu et al. 2012, 2013), (Li et al. 2018)

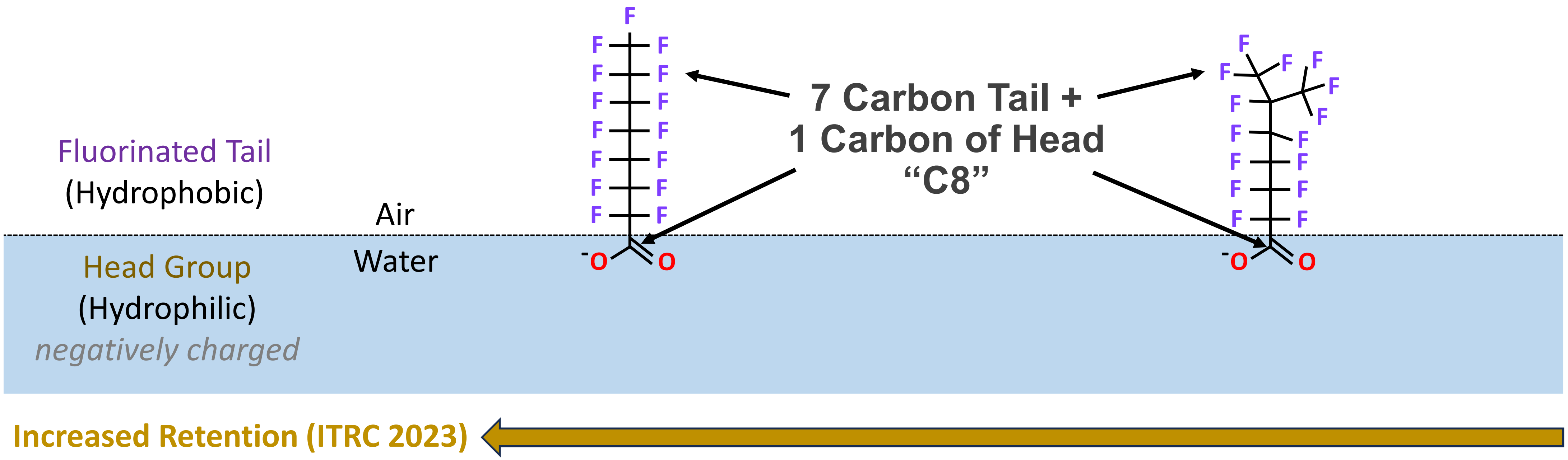
Branched and Linear Isomers

Linear PFOA

(ECF or FT-based)

Branched PFOA

(ECF-based)



7 Carbon Tail +
1 Carbon of Head
“C8”

Fluorinated Tail
(Hydrophobic)

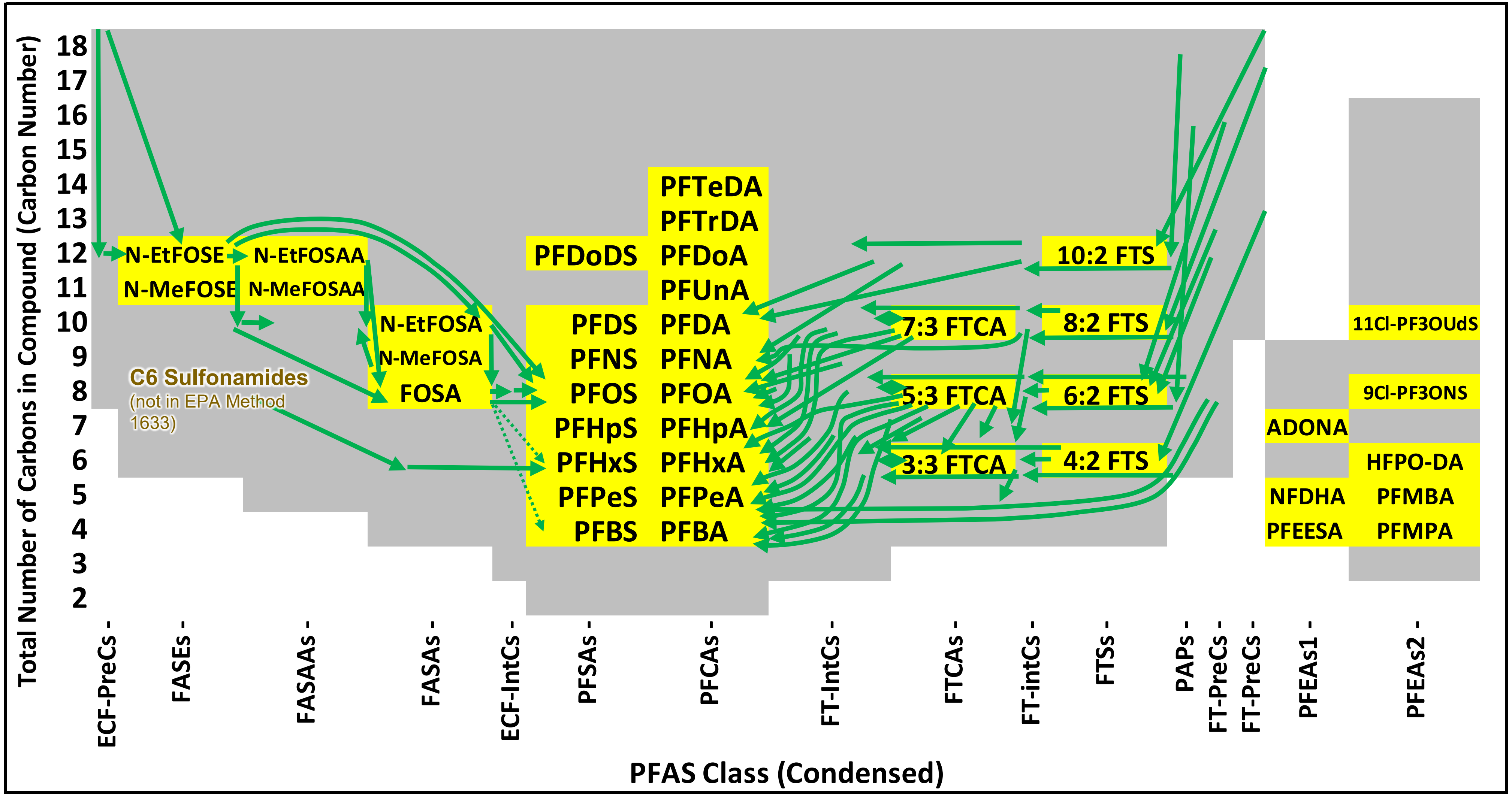
Air

Water

Head Group
(Hydrophilic)
negatively charged

Increased Retention (ITRC 2023)

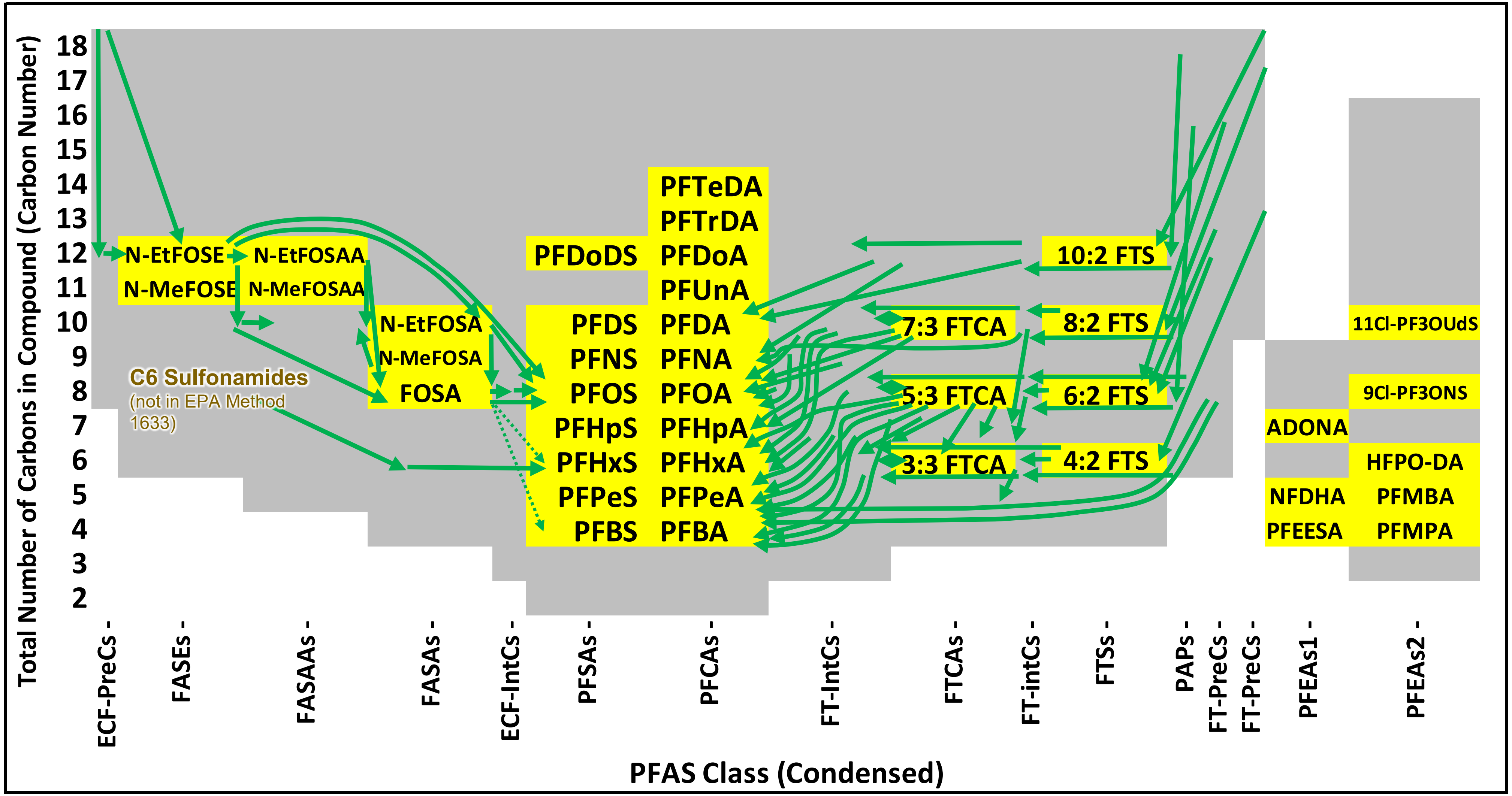
Precursor Transformation Overview



Arrows represent precursor transformation step, based on literature

Arrows the start in the gray space represent precursors not in EPA Method 1633

Retention and Precursor Transformation



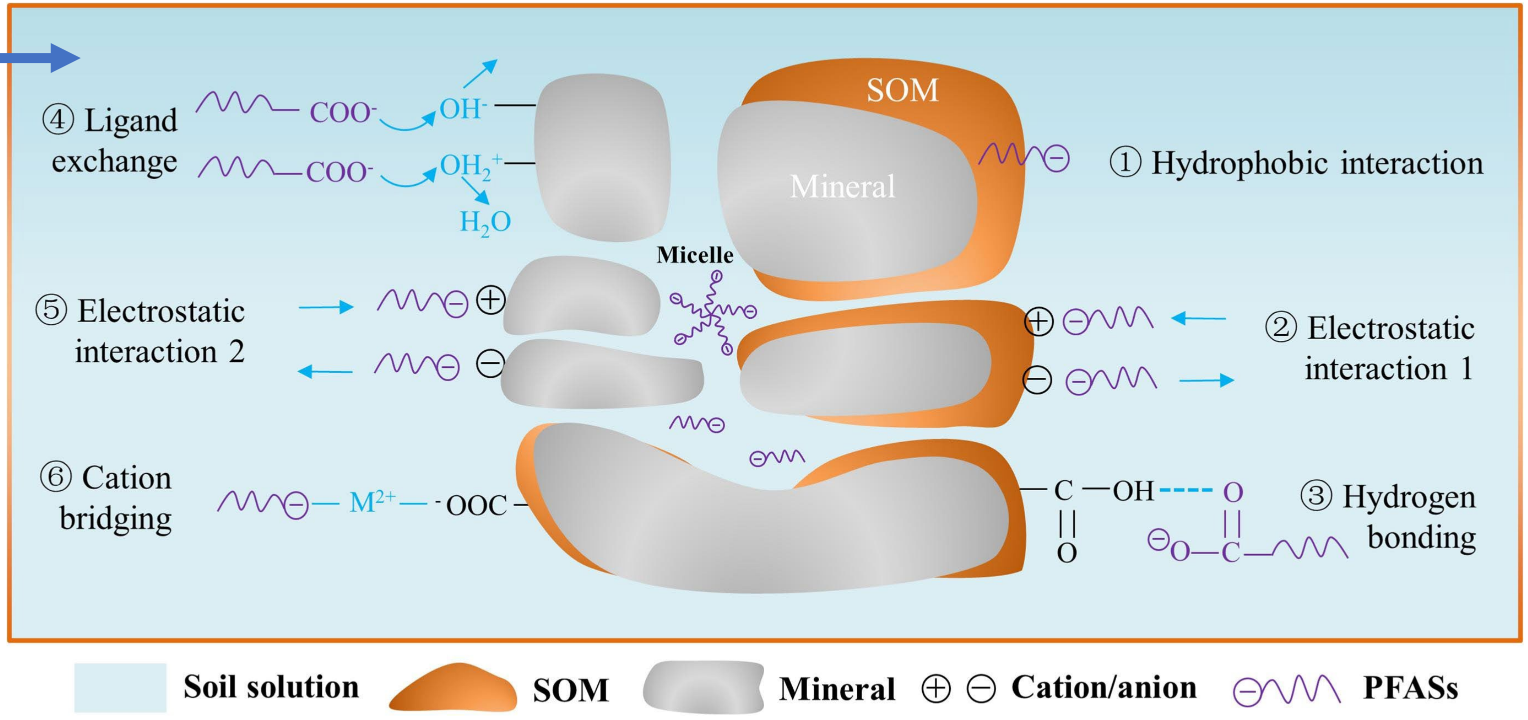
Greater Retention

Less Retention

Retention Considerations

- Retention can be caused by sorption, air/water partitioning, or other factors

- Example of sorption →
  - PFAS sorb to organic carbon on soils (more carbons = generally more sorption)



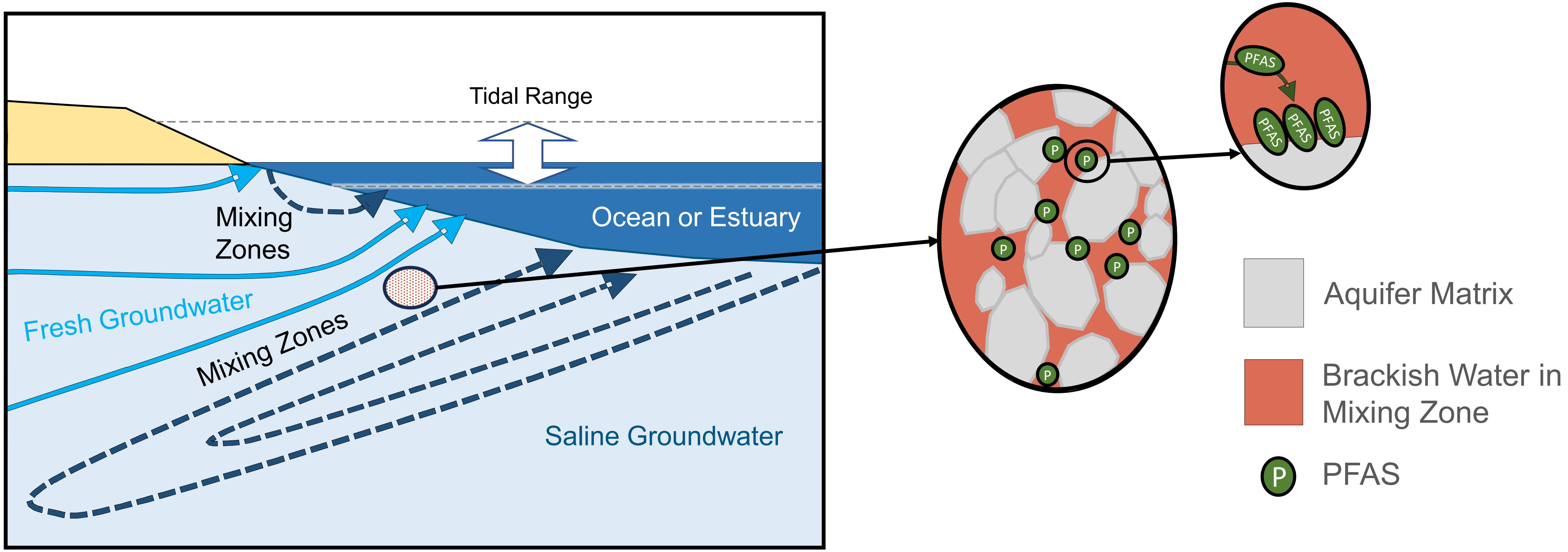
(Mei et al. 2021)

SOM: soil organic material

Other Retention Considerations

PFAS “Salting Out”

If a freshwater PFAS plume enters a mixing zone, it can trigger the salting out process that retains PFAS in aquifer matrix



For more information, see Final Report for SERDP Project ER22-3275 and Newell et al. 2022

PFAS Patterns

KEY POINT

Retention and precursor transformation affect PFAS patterns along routes of migration.

(Image from Microsoft Office)

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Knowledge Pre-Check: Questions 1–3

- Does the EPA definition of Background apply to PFAS?

  A) Yes B) No

- Does the 2004 Navy Policy on Background apply to PFAS?

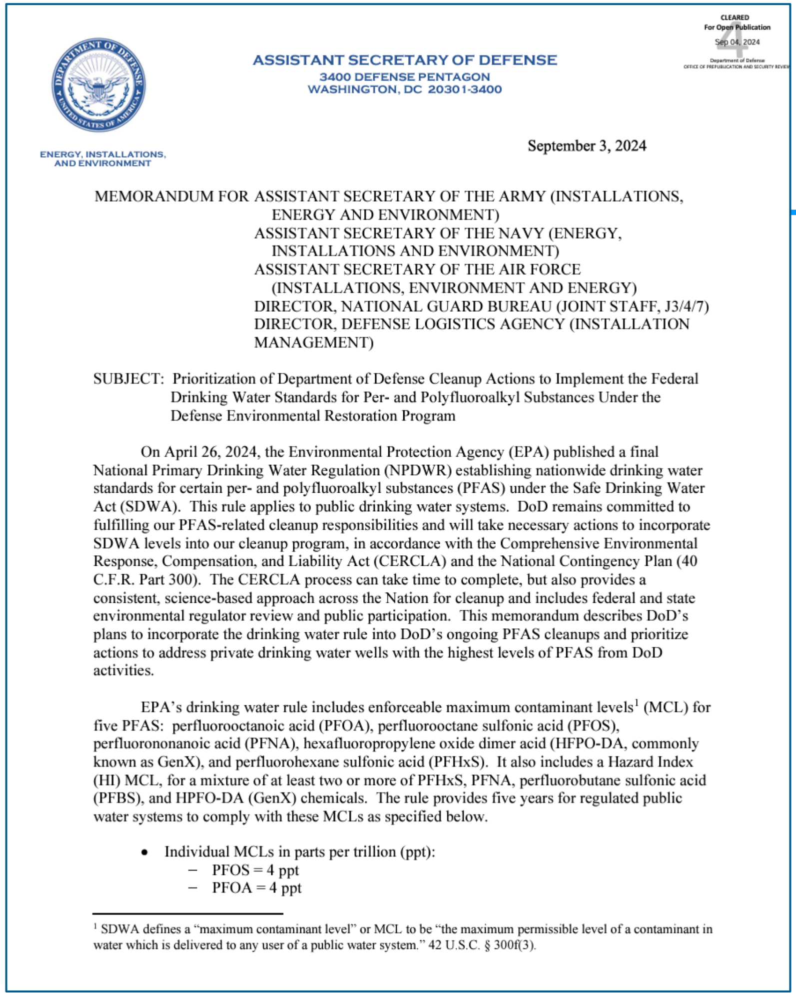
  A) Yes B) No

- Will Background PFAS be a component of remedial decision-making at DoD facilities?

  A) Yes B) No

DoD Memorandum on Background PFAS

- **PFAS background assessments will be a component of remedial decision-making at DoD facilities**
  - September 3, 2024, memo on prioritization of DoD Cleanup Actions to implement PFAS MCLs



CLEARED
For Open Publication
Sep 04, 2024
Department of Defense
OFFICE OF PREPUBLICATION AND SECURITY REVIEW

ASSISTANT SECRETARY OF DEFENSE
3400 DEFENSE PENTAGON
WASHINGTON, DC 20301-3400

ENERGY, INSTALLATIONS,
AND ENVIRONMENT

September 3, 2024

MEMORANDUM FOR ASSISTANT SECRETARY OF THE ARMY (INSTALLATIONS, ENERGY AND ENVIRONMENT)
ASSISTANT SECRETARY OF THE NAVY (ENERGY, INSTALLATIONS AND ENVIRONMENT)
ASSISTANT SECRETARY OF THE AIR FORCE (INSTALLATIONS, ENVIRONMENT AND ENERGY)
DIRECTOR, NATIONAL GUARD BUREAU (JOINT STAFF, J3/4/7)
DIRECTOR, DEFENSE LOGISTICS AGENCY (INSTALLATION MANAGEMENT)

SUBJECT: Prioritization of Department of Defense Cleanup Actions to Implement the Federal Drinking Water Standards for Per- and Polyfluoroalkyl Substances Under the Defense Environmental Restoration Program

On April 26, 2024, the Environmental Protection Agency (EPA) published a final National Primary Drinking Water Regulation (NPDWR) establishing nationwide drinking water standards for certain per- and polyfluoroalkyl substances (PFAS) under the Safe Drinking Water Act (SDWA). This rule applies to public drinking water systems. DoD remains committed to fulfilling our PFAS-related cleanup responsibilities and will take necessary actions to incorporate SDWA levels into our cleanup program, in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the National Contingency Plan (40 C.F.R. Part 300). The CERCLA process can take time to complete, but also provides a consistent, science-based approach across the Nation for cleanup and includes federal and state environmental regulator review and public participation. This memorandum describes DoD's plans to incorporate the drinking water rule into DoD's ongoing PFAS cleanups and prioritize actions to address private drinking water wells with the highest levels of PFAS from DoD activities.

EPA's drinking water rule includes enforceable maximum contaminant levels[1] (MCL) for five PFAS: perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), hexafluoropropylene oxide dimer acid (HFPO-DA, commonly known as GenX), and perfluorohexane sulfonic acid (PFHxS). It also includes a Hazard Index (HI) MCL, for a mixture of at least two or more of PFHxS, PFNA, perfluorobutane sulfonic acid (PFBS), and HPFO-DA (GenX) chemicals. The rule provides five years for regulated public water systems to comply with these MCLs as specified below.

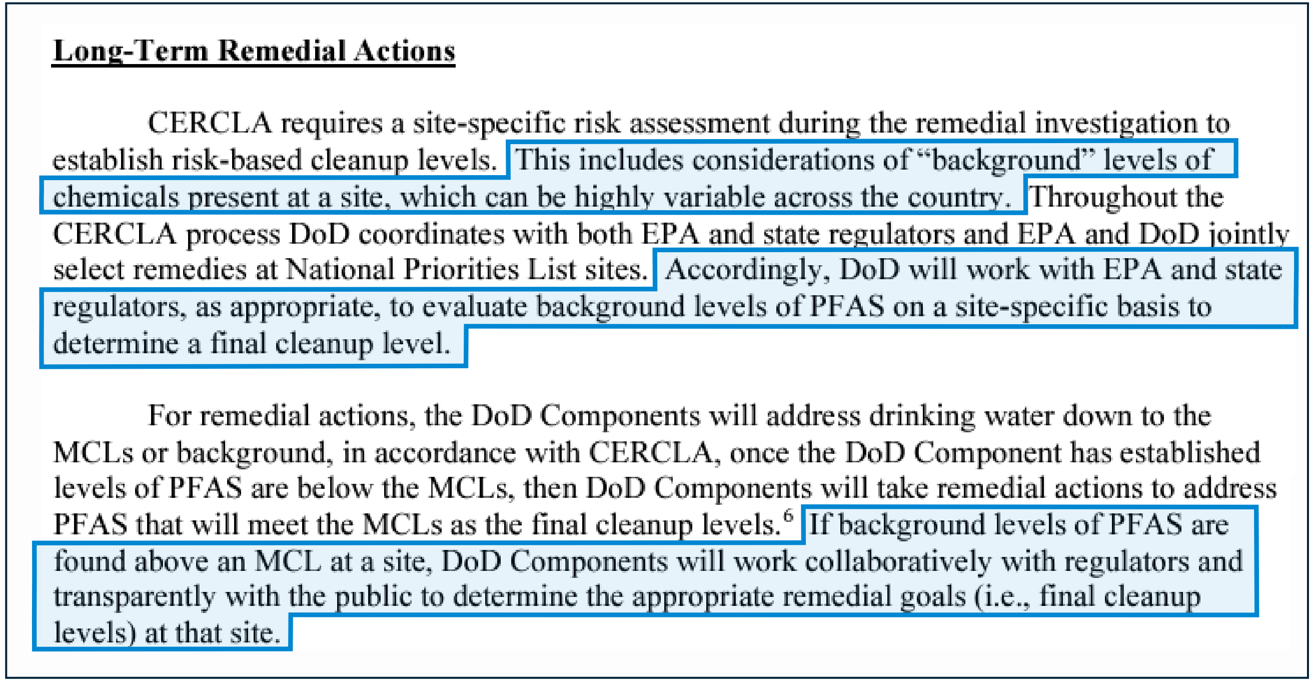
- Individual MCLs in parts per trillion (ppt):
  - PFOS = 4 ppt
  - PFOA = 4 ppt

---

[1] SDWA defines a "maximum contaminant level" or MCL to be "the maximum permissible level of a contaminant in water which is delivered to any user of a public water system." 42 U.S.C. § 300f(3).

(DoD 2024)

MCL: maximum contaminant level



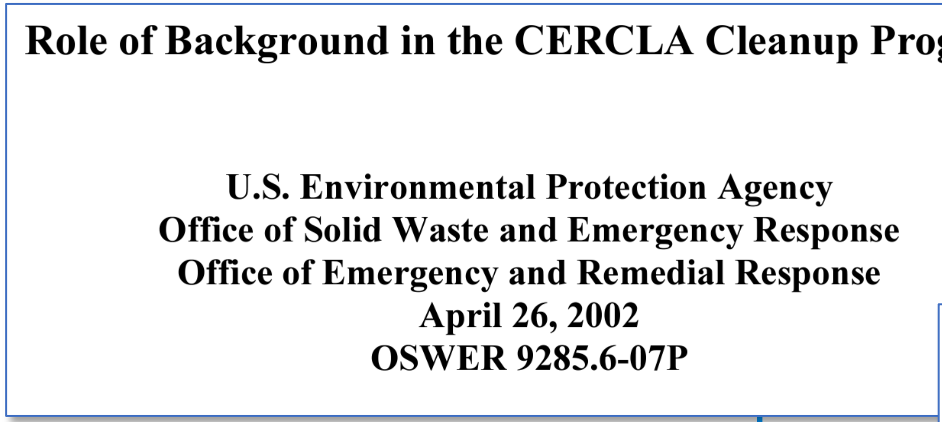
Long-Term Remedial Actions

CERCLA requires a site-specific risk assessment during the remedial investigation to establish risk-based cleanup levels. This includes considerations of "background" levels of chemicals present at a site, which can be highly variable across the country. Throughout the CERCLA process DoD coordinates with both EPA and state regulators and EPA and DoD jointly select remedies at National Priorities List sites. Accordingly, DoD will work with EPA and state regulators, as appropriate, to evaluate background levels of PFAS on a site-specific basis to determine a final cleanup level.

For remedial actions, the DoD Components will address drinking water down to the MCLs or background, in accordance with CERCLA, once the DoD Component has established levels of PFAS are below the MCLs, then DoD Components will take remedial actions to address PFAS that will meet the MCLs as the final cleanup levels.[6] If background levels of PFAS are found above an MCL at a site, DoD Components will work collaboratively with regulators and transparently with the public to determine the appropriate remedial goals (i.e., final cleanup levels) at that site.

(DoD 2024)

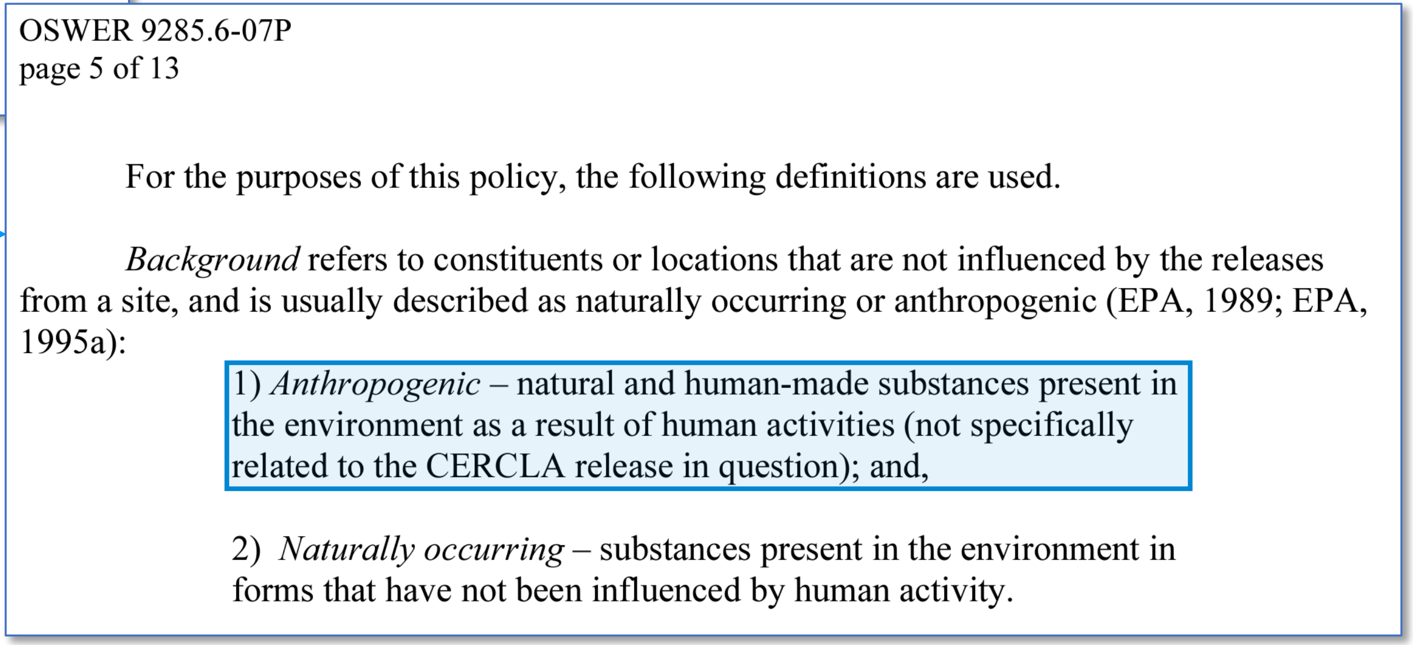
EPA Definition of Background



Role of Background in the CERCLA Cleanup Program

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Office of Emergency and Remedial Response
April 26, 2002
OSWER 9285.6-07P

(EPA 2002)



OSWER 9285.6-07P
page 5 of 13

For the purposes of this policy, the following definitions are used.

Background refers to constituents or locations that are not influenced by the releases from a site, and is usually described as naturally occurring or anthropogenic (EPA, 1989; EPA, 1995a):

1) *Anthropogenic* – natural and human-made substances present in the environment as a result of human activities (not specifically related to the CERCLA release in question); and,

2) *Naturally occurring* – substances present in the environment in forms that have not been influenced by human activity.

(EPA 2002)

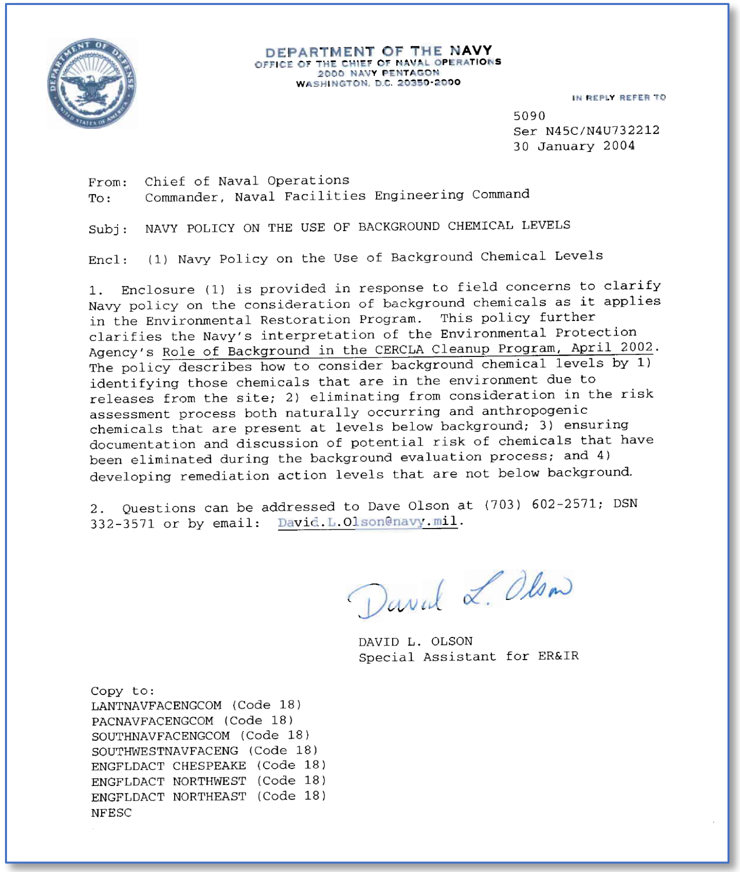
CERCLA: Comprehensive Environmental Response, Compensation, and Liability Act
OSWER: Office of Solid Waste and Emergency Response

Definitions of Background PFAS

- **Anthropogenic PFAS** not related to the CERCLA site in question are defined as ***Background*** under OSWER 9285.6-07P
    - The term “Background” does apply to PFAS
- Background PFAS can potentially be from **nonpoint source(s) and/or point source(s)**
    - Nonpoint sources may include precipitation, urban runoff, runoff from agricultural land with biosolids application, etc.
    - The greatest concentrations may or may not be closest to background PFAS sources; therefore**, site-specific conditions should always be considered**

2004 Navy Policy on Background

- Key Points
  - Site chemical levels should be compared to background levels (this applies to PFAS)
  - **Site-related** COPCs are carried through to the **baseline risk assessment**
  - **Non-site-related** COPCs should be compared to risk-based screening benchmarks and **discussed in the risk characterization section**
  - **Site cleanup remedial goals are not set below background levels**



DEPARTMENT OF THE NAVY
OFFICE OF THE CHIEF OF NAVAL OPERATIONS
2000 NAVY PENTAGON
WASHINGTON, D.C. 20350-2000

IN REPLY REFER TO
5090
Ser N45C/N4U732212
30 January 2004

From: Chief of Naval Operations
To: Commander, Naval Facilities Engineering Command

Subj: NAVY POLICY ON THE USE OF BACKGROUND CHEMICAL LEVELS

Encl: (1) Navy Policy on the Use of Background Chemical Levels

1. Enclosure (1) is provided in response to field concerns to clarify Navy policy on the consideration of background chemicals as it applies in the Environmental Restoration Program. This policy further clarifies the Navy's interpretation of the Environmental Protection Agency's Role of Background in the CERCLA Cleanup Program, April 2002. The policy describes how to consider background chemical levels by 1) identifying those chemicals that are in the environment due to releases from the site; 2) eliminating from consideration in the risk assessment process both naturally occurring and anthropogenic chemicals that are present at levels below background; 3) ensuring documentation and discussion of potential risk of chemicals that have been eliminated during the background evaluation process; and 4) developing remediation action levels that are not below background.

2. Questions can be addressed to Dave Olson at (703) 602-2571; DSN 332-3571 or by email: David.L.Olson@navy.mil.

David L. Olson

DAVID L. OLSON
Special Assistant for ER&IR

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ENGFLDACT NORTHWEST (Code 18)
ENGFLDACT NORTHEAST (Code 18)
NFESC

(Navy 2004)

COPC(s): chemical(s) of potential concern

NAVFAC Background Guidance Documents

Human Health Risk Assessment	NAVFAC Resources on Human Health Risk Assessment Navy human health risk assessment policies and guidance including background
Background Chemicals	Navy Policy on the Use of Background Chemical Levels (January 2004) Clarifies the Navy's position on consideration of background chemical levels
Soil Background	NAVFAC Guidance for Environmental Background Analysis Volume I: Soil (April 2002) Provides instructions for characterizing background conditions at sites where past uses of the property have resulted in actual or suspected chemical releases to soil
Sediment Background	NAVFAC Guidance for Environmental Background Analysis: Volume II Sediment (April 2003) Provides instructions for the characterization of background conditions at sediment sites where past uses of the property may have resulted in chemical releases
Groundwater Background	NAVFAC Guidance for Environmental Background Analysis Volume III: Groundwater (April 2004) Provides instructions for characterizing groundwater background conditions and comparing datasets for impacted groundwater based on statistical methods and geochemical relationships
Indoor Air Background	NAVFAC Guidance for Environmental Background Analysis Volume IV: Vapor Intrusion Pathway (April 2011) Reviews methodologies for assessing potential background sources to indoor air as a part of the assessment of the vapor intrusion pathway

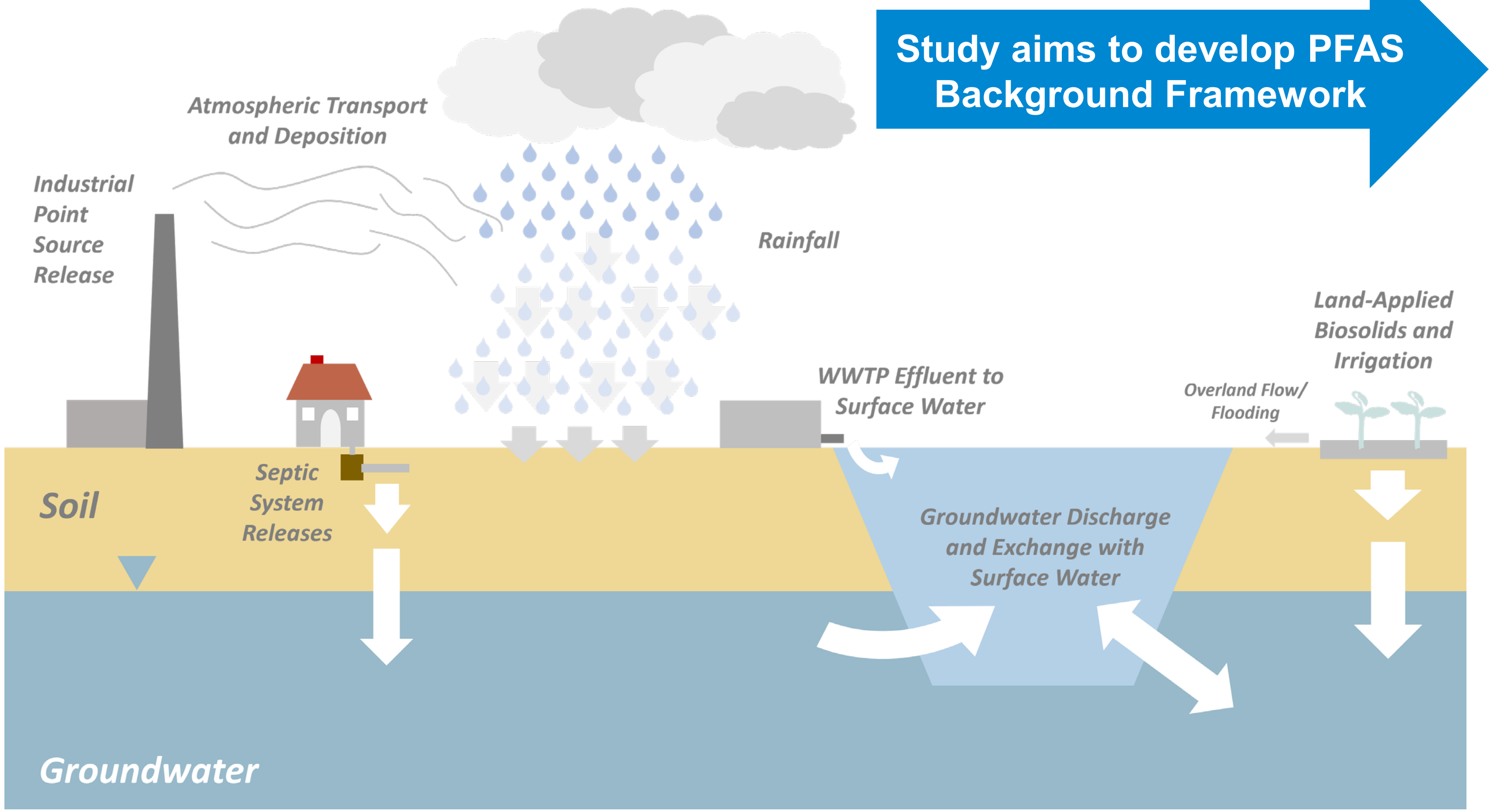
Background PFAS: Guidance and Research

- Guidance specific to conducting PFAS background studies has yet to be developed
- **ESTCP Project ER25-8813** aims to develop a framework for evaluating background PFAS
  - Joint effort by GSI, CDM Smith, and Colorado School of Mines (Dave Adamson is the Principal Investigator)
  - Project expected to begin soon

ESTCP: Environmental Security Technology Certification Program

ESTCP Project ER25-8813

Key Question *– How do we better identify the likely background sources of PFAS?*



Study aims to develop PFAS Background Framework

Key Elements *of Framework for Evaluating Background PFAS*

- How to develop PFAS-specific hypothesis testing and data quality objectives for the site
- Identifying potential regional and nonpoint source contributors to background PFAS
- Tiered approach for media-specific sampling and analysis plans, where higher tiers are associated with higher levels of effort
- Approaches for evaluating data to distinguish background sources and document contributions

Poll Questions 1–3 (Answers)

- Does the EPA definition of Background apply to PFAS?

  A) Yes B) No

- Does the 2004 Navy Policy on Background apply to PFAS?

  A) Yes B) No

- Will Background PFAS be a component of remedial decision-making at DoD facilities?

  A) Yes B) No

Naval Facilities Engineering Systems Command
EXWC Engineering and Expeditionary Warfare Center

Break

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Objective

- We will review peer-reviewed research articles that provide insights regarding the potential presence/sources of background PFAS

(Image from Microsoft Office)

Knowledge Pre-Check: Questions 4–6

- Can PFAS in precipitation exceed EPA MCLs?

  A) Yes B) No

- What sources of PFAS may contribute to background?

  A) Septic Tanks B) Biosolids C) Precipitation D) All of the above

- Will every PFAS background assessment rely on the same approach?

  A) Yes B) No

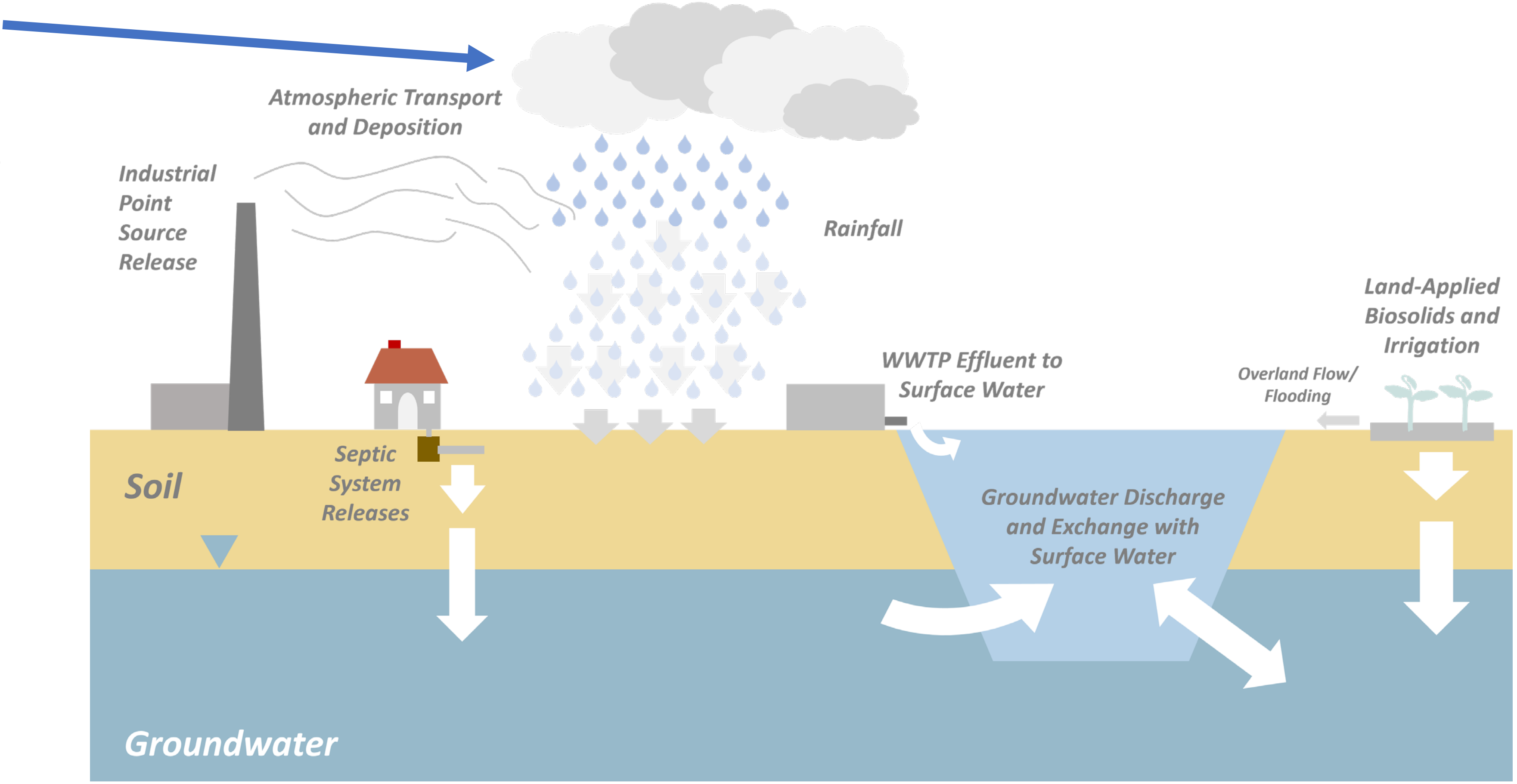
What Does the Scientific Literature Say?

- Can PFAS in precipitation exceed the EPA MCLs?
- What are some potential sources of background PFAS?
- What background concentration ranges might be observed?

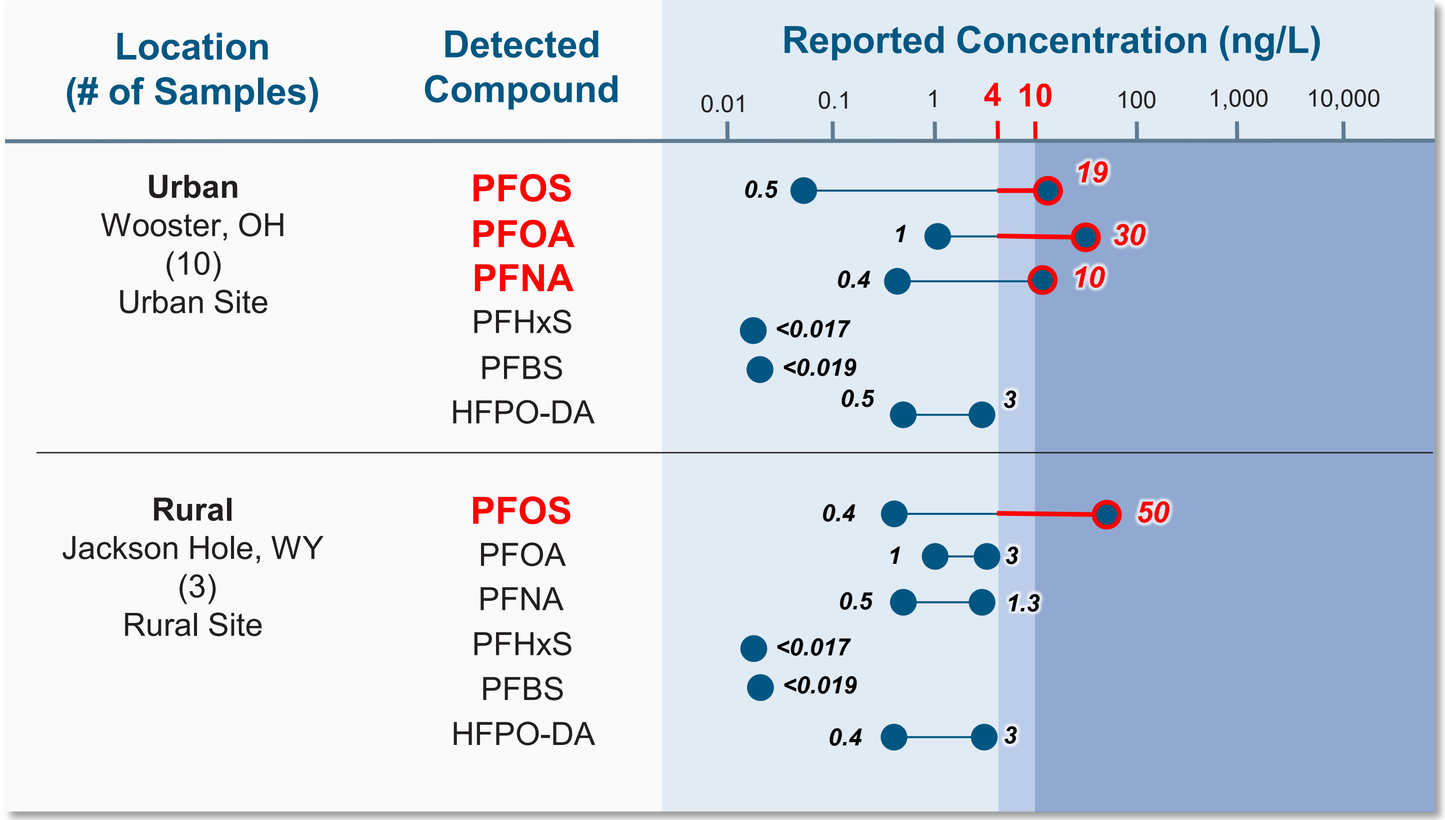
(Image from Microsoft Office)

PFAS in Precipitation

- Precipitation can be a source of background PFAS



Example Summary of PFAS in Precipitation



EPA MCL:
PFOS, PFOA = 4 ng/L
PFHxS, PFNA, HFPO-DA = 10 ng/L
Red Font = Precipitation Exceeds MCL

Data from:
Pike et al. (2021)

HFPO-DA: hexafluoropropylene oxide dimer acid
ND: nondetect

ng/L: nanograms per liter
PFOA: perfluorooctanoic acid
PFOS: perfluoroctanesulfonic acid

PFHxS: perfluorohexanesulfonic acid
PFNA: perfluorononanoic acid

PFAS in Precipitation

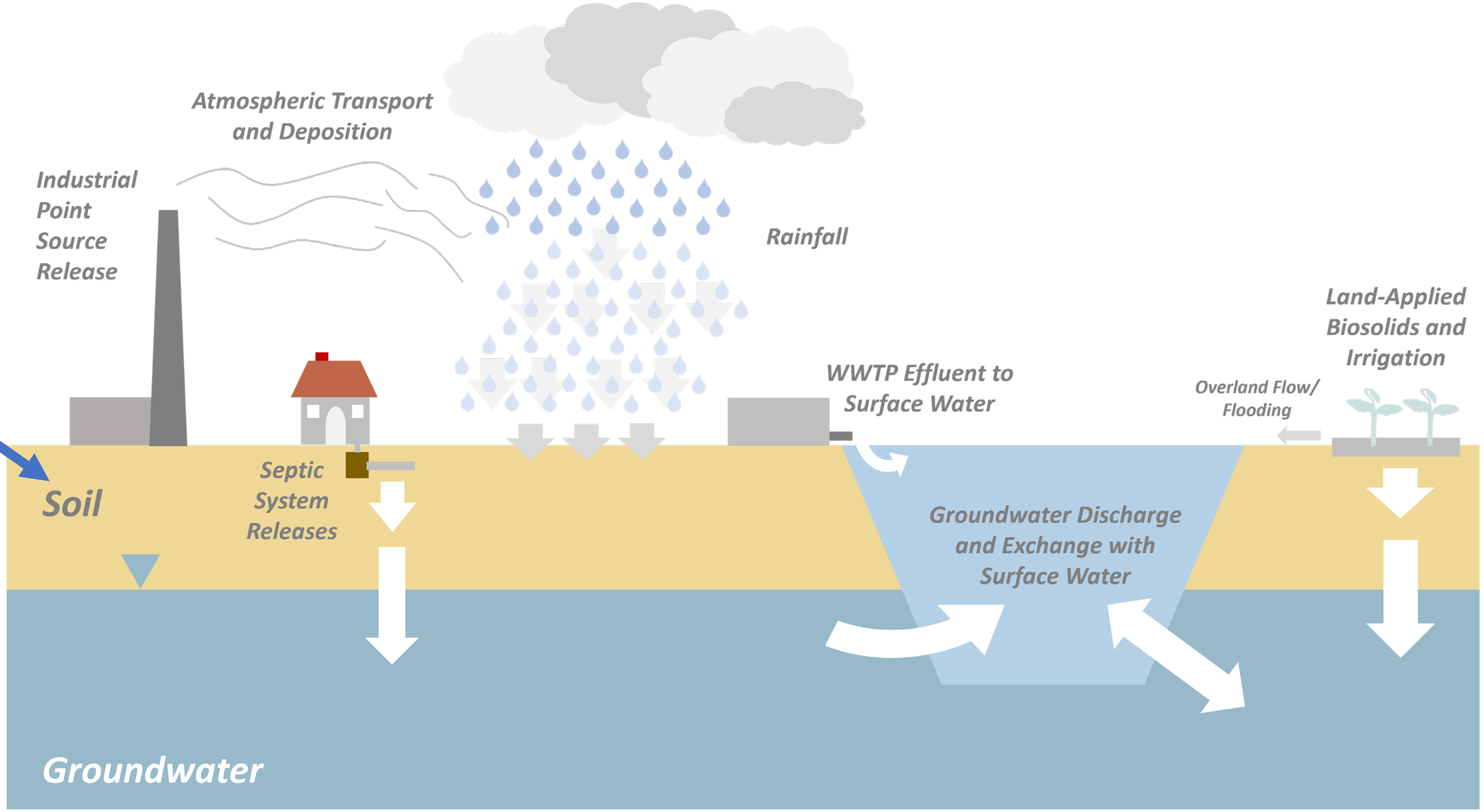
KEY POINT

PFAS in precipitation may exceed MCLs.

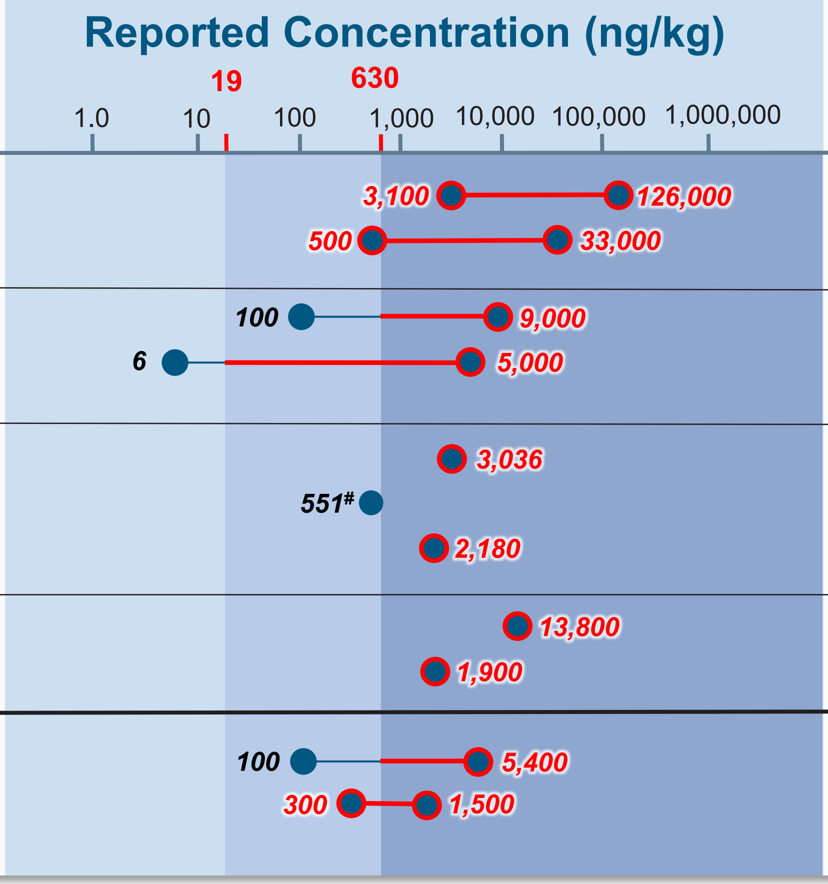
(Image from Microsoft Office)

Background PFAS in Soil

- Soil can be affected by background PFAS



Summary of Select Soil Background Studies



Reference	Detected Compound	Reported Concentration (ng/kg)	Location	Range or Threshold Value
Brusseau et al. (2020)	**PFOS** **PFOA**	3,100 – 126,000 500 – 33,000	United States (5 locations)	Range of Max C's for PFOS & PFOA
Zhu et al. (2022)	**PFOS** **PFOA**	100 – 9,000 6 – 5,000	Vermont	Range >40% detection frequency at 66 locations
Sanborn, Head & Assoc. (2022)	**PFOS** (urban) **PFOS** (non-urban) **PFOA**	3,036 551# 2,180	Maine	Threshold 95% Upper Tolerance Limit with 95% Coverage UTL90-95#
Anderson and Modiri (2024)	**PFOS** **PFOA**	13,800 1,900	DoD Study	Threshold (Max) Threshold (Min)
Brousseau et al. (2020)	**PFOS** **PFOA**	100 – 5,400 300 – 1,500	Tierra Del Fuego, & Antarctica (1), Nepal (1)	Range of Max C's for PFOS & PFOA

EPA November 2024 Residential Soil RSL: PFOA = 19 ng/kg, PFOS = 630 ng/kg

Red Font = Background Exceeds RSL

ng/kg: nanogram(s) per kilogram

RSL: regional screening level

PFAS in Soil

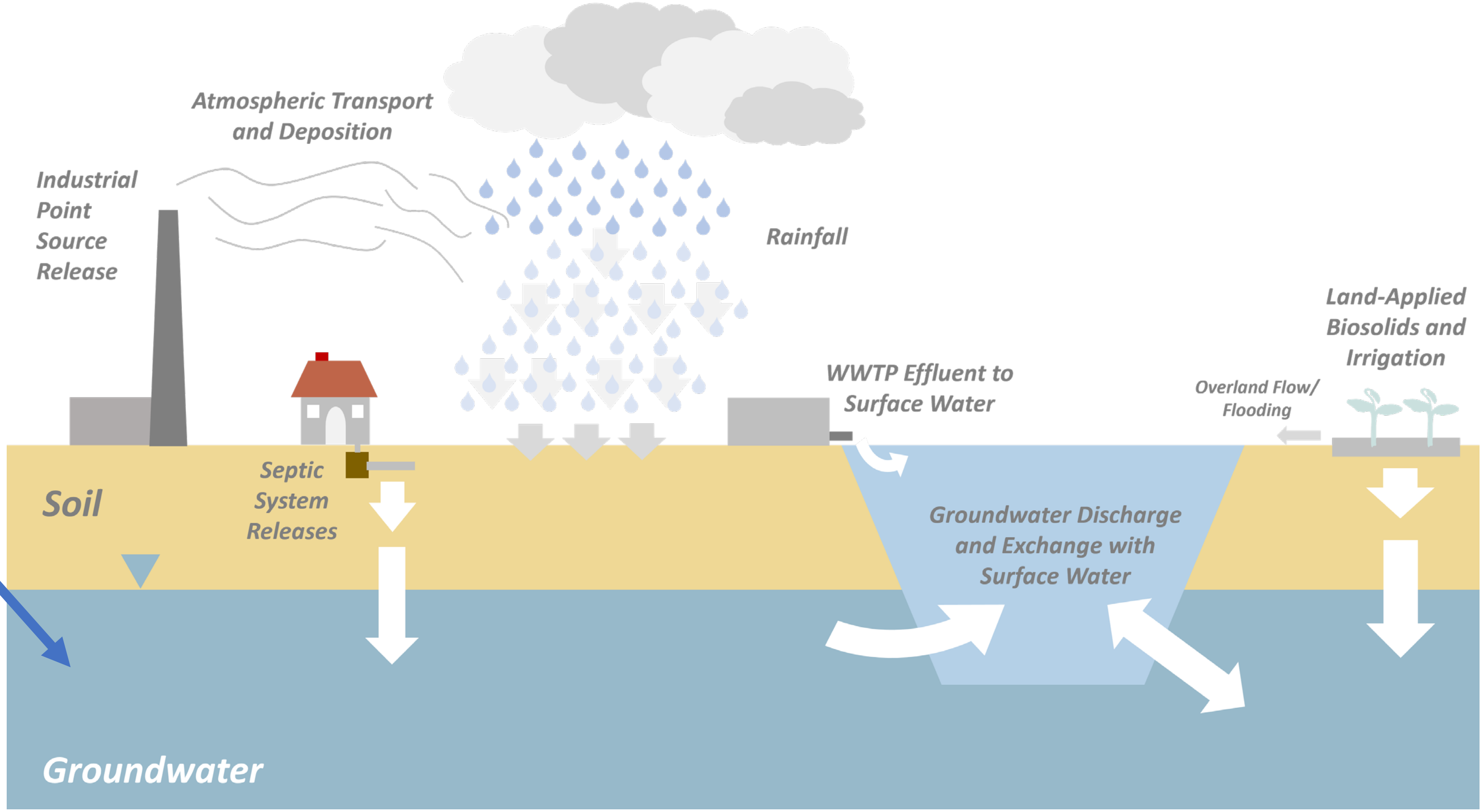
KEY POINT

Background PFAS in soil may exceed RSLs.

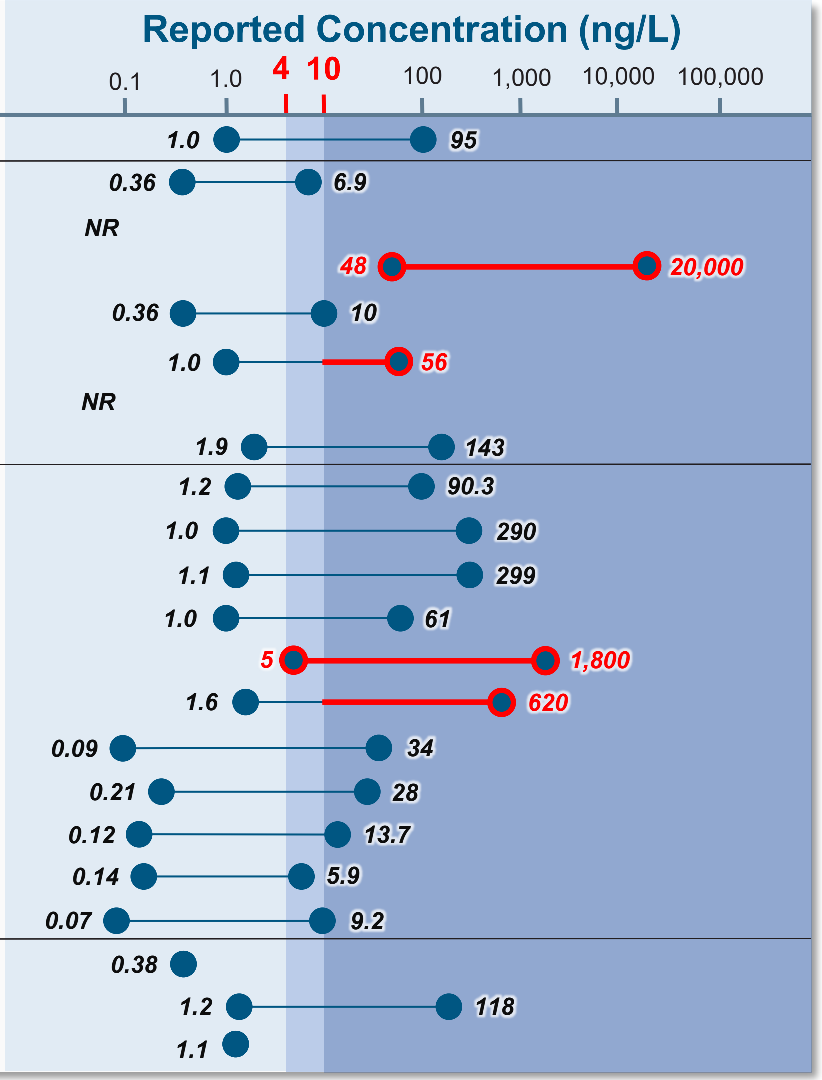
(Image from Microsoft Office)

Background PFAS in Groundwater

- Groundwater can be affected by background PFAS



Global Groundwater Background Study



Reference	Detected Compound	Reported Concentration (ng/L)	
Johnson et al. (2022) (Global Study) Range = 95% CI (min) to max n = 5,990 locations* **No known PFAS sources*	FOSA	1.0	95
	PFDS	0.36	6.9
	PFNS	NR	
	PFOS	48	20,000
	PFHpS	0.36	10
	PFHxS	1.0	56
	PFPeS	NR	
	PFBS	1.9	143
	PFBA	1.2	90.3
	PFPeA	1.0	290
	PFHxA	1.1	299
	PFHpA	1.0	61
	PFOA	5	1,800
	PFNA	1.6	620
	PFDA	0.09	34
	PFUnA	0.21	28
	PFDoA	0.12	13.7
	PFTrDA	0.14	5.9
	PFTeDA	0.07	9.2
	4:2 FTS	0.38	
	6:2 FTS	1.2	118
	8:2 FTS	1.1	

EPA MCL:
PFOS, PFOA = 4 ng/L
PFHxS, PFNA = 10 ng/L
Red Font = Background Exceeds MCL

CI: Confidence Interval

PFAS in Groundwater

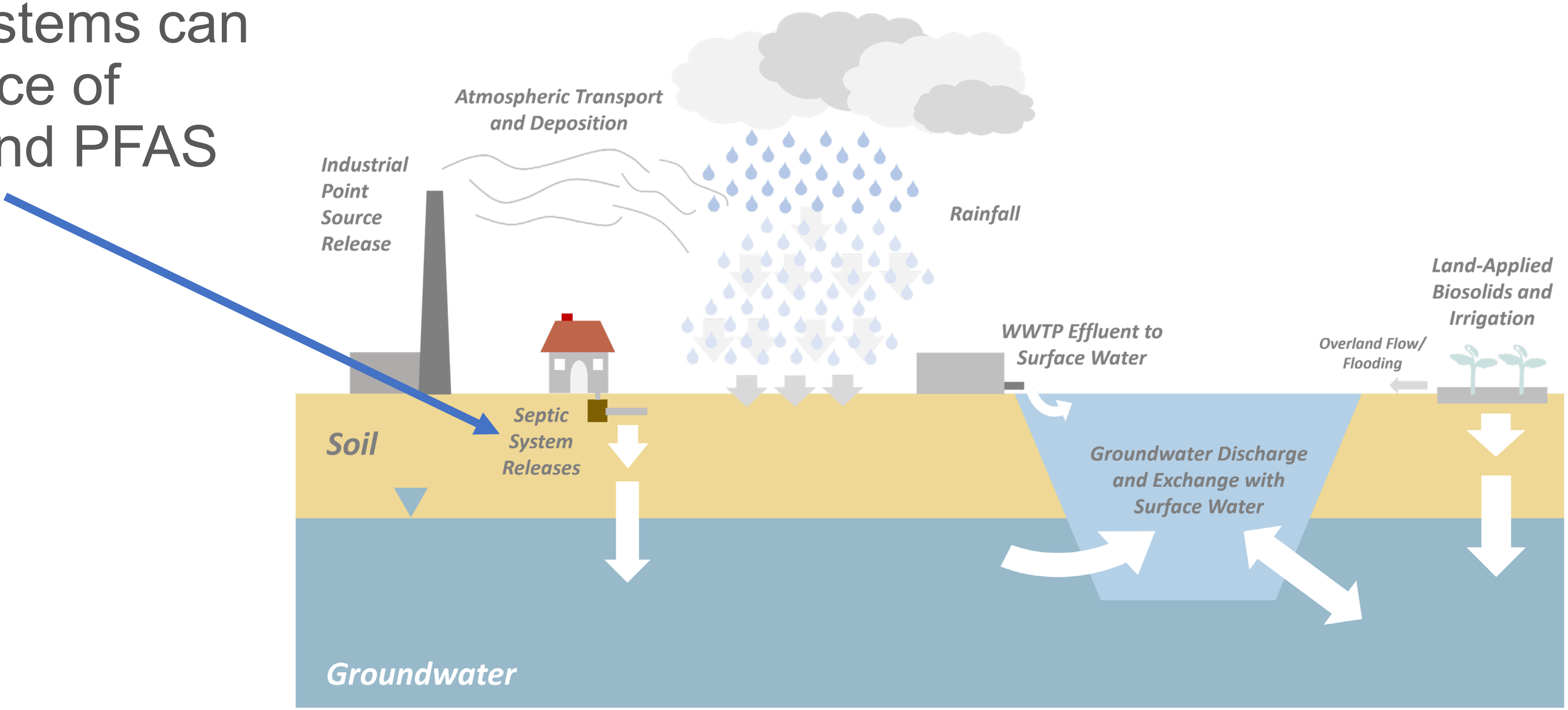
KEY POINT

Background PFAS in groundwater may exceed MCLs.


(Image from Microsoft Office)

Example of Background PFAS Source

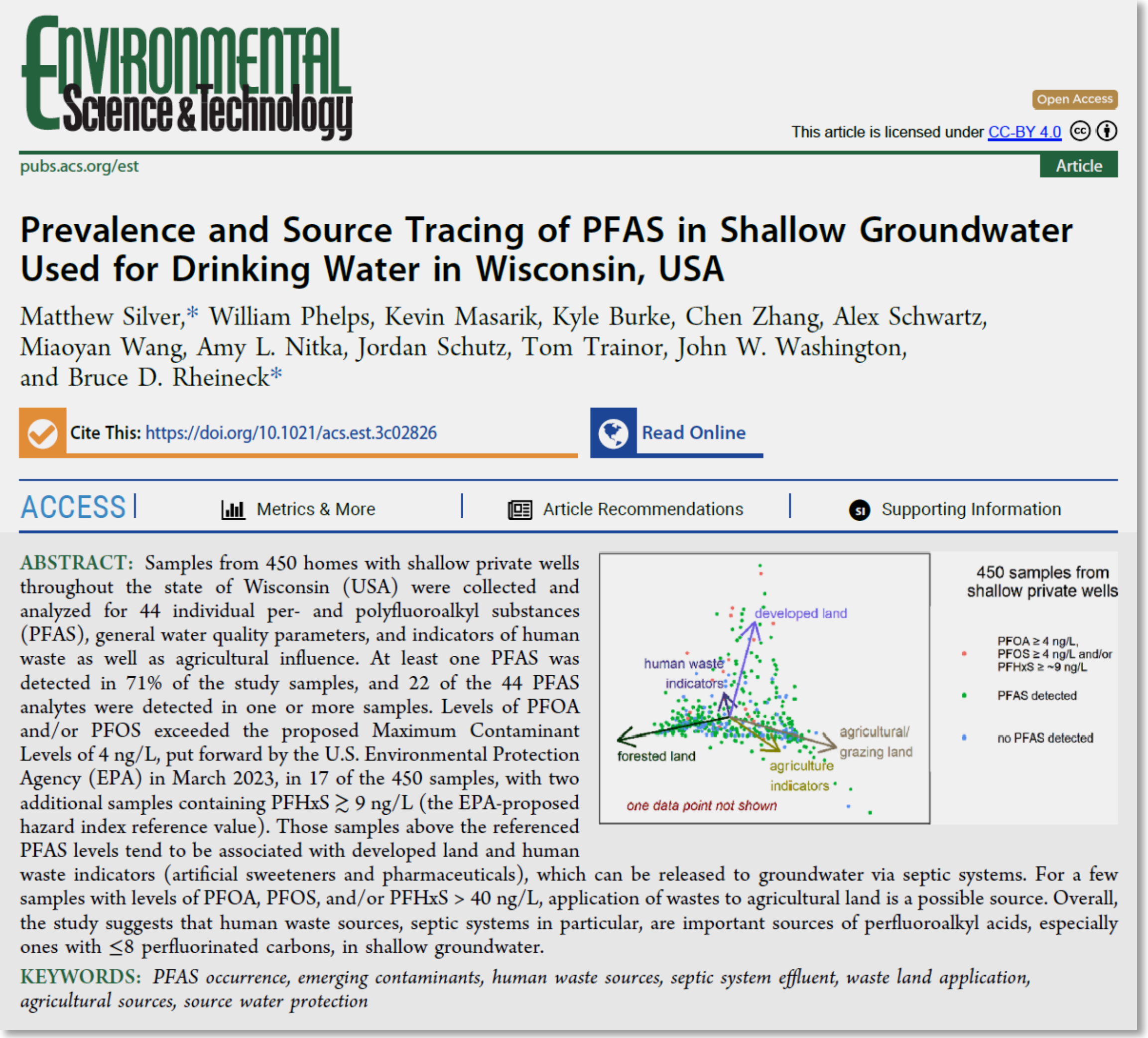
- Septic systems can be a source of background PFAS



Example of PFAS from Septic Tanks

- Samples from 450 private wells **more than 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

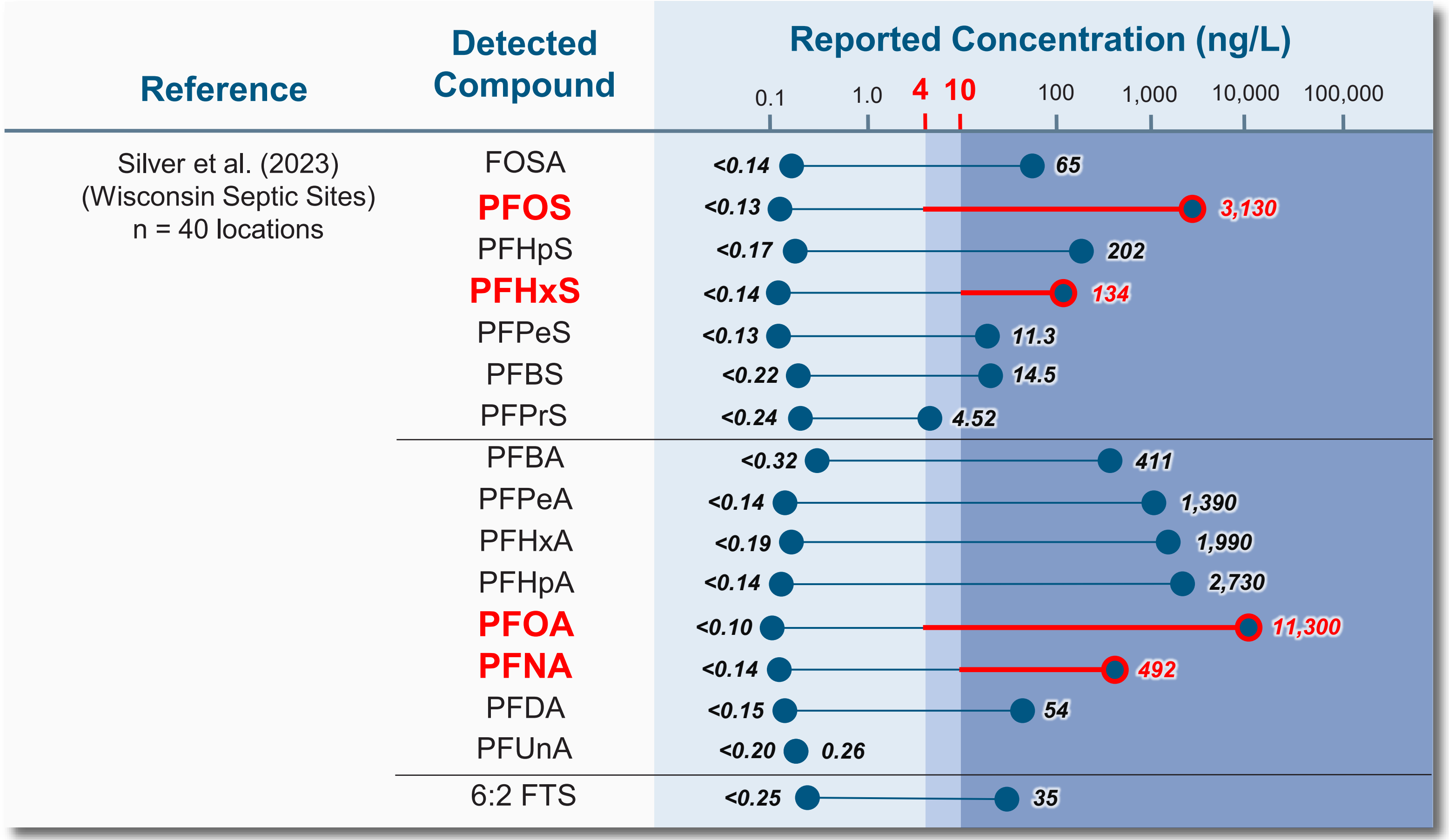
ABSTRACT: Samples from 450 homes with shallow private wells throughout the state of Wisconsin (USA) were collected and analyzed for 44 individual per- and polyfluoroalkyl substances (PFAS), general water quality parameters, and indicators of human waste as well as agricultural influence. At least one 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*

(Silver et al. 2023)

DNR: Department of Natural Resources

PFAS in Groundwater near Septic Sources



EPA MCL:
PFOS, PFOA = 4 ng/L
PFHxS, PFNA = 10 ng/L
Red Font = Background Exceeds MCL

PFAS From Septic Sources

KEY POINT

Septic sources can contribute to background.

(Image from Microsoft Office)

Poll Questions 4–6 (Answers)

- Can PFAS in precipitation exceed EPA MCLs?

  A) Yes B) No

- What sources of PFAS may contribute to background?

  A) Septic Tanks B) Biosolids C) Precipitation **D) All of the above**

- Will every PFAS background assessment rely on the same approach?

  A) Yes **B) No**

Objective

- We will review key factors for assessing background PFAS

(Image from Microsoft Office)

Knowledge Pre-Check: Questions 7–9

- Adjacent land use should be considered when evaluating background PFAS?

  A) Yes B) No

- Non-PFAS markers may help identify background PFAS?

  A) Yes B) No

- Site-specific factors should be considered when selecting the Background Reference Area(s)?

  A) Yes B) No

Adjacent Land Use

Increased Potential for Background PFAS

- Adjacent land use with known or suspected PFAS use
- For example, biosolids application, septic tanks, AFFF use, wastewater treatment, landfills, metal plating, etc.

Information presented is not all inclusive and site-specific factors should be assessed.

(Image from Microsoft Office)

AFFF: Aqueous Film Forming Foam

Local and Regional Transport Mechanisms

Increased Potential for Background PFAS

- Potential PFAS migration pathways from precipitation, air deposition, upstream surface water, and/or upgradient groundwater

Information presented is not all inclusive and site-specific factors should be assessed.

(Image from Microsoft Office)

Vadose Zone Retention

Increased Potential for Background PFAS

- Increased soil retention increases likelihood of background soil PFAS and potentially decreases likelihood of background PFAS for groundwater and surface water
- PFAS soil retention increases with organic carbon, NAPL, multivalent cations, salinity, decreased saturation, etc.

Information presented is not all inclusive and site-specific factors should be assessed.

(Image from Microsoft Office)

NAPL: nonaqueous phase liquid

Surface Water/Groundwater Connectivity

Increased Potential for Background PFAS

- Long-range surface water transport through PFAS-susceptible environments (e.g., biosolids areas, urban/suburban runoff)
- Discharge to groundwater via a losing stream or via artificial recharge to groundwater
- Enhanced migration due to pumping wells
- Potential retention and/or dispersion within floodplains and wetlands

Information presented is not all inclusive and site-specific factors should be assessed.

(Image from Microsoft Office)

Natural Hazard-Related Trends

Increased Potential for Background PFAS

- Flooding and/or rising water tables may mobilize PFAS from point or nonpoint sources
- Prolonged drought and blowing dust (e.g., from biosolids areas) could potentially mobilize PFAS

Information presented is not all inclusive and site-specific factors should be assessed.

(Image from Microsoft Office)

USGS Studies Predicting PFAS in Groundwater

- USGS correlated non-PFAS chemical markers to the occurrence of PFAS (McMahon et al. 2022 and Tokranov et al. 2024)
- Chemical markers may be helpful for assessing PFAS background
  - Higher concentrations of tritium (“age”), chloride, sulfate, DOC, Mn, and Fe
  - Higher percentage of urban land use within 500 meters of the wells
  - Higher VOC and pharmaceutical detection frequencies
  - Estimated nitrogen loading from septic systems
  - Higher average annual natural groundwater recharge
  - Decreased depth to water

DOC: dissolved organic carbon
Fe: iron
Mn: manganese
USGS: United States Geological Survey
VOC: volatile organic compound

Poll Questions 7–9 (Answers)

- Adjacent land use should be considered when evaluating background PFAS?

  A) Yes B) No

- Non-PFAS markers may help identify background PFAS?

  A) Yes B) No

- Site-specific factors should be considered when selecting the Background Reference Area(s)?

  A) Yes B) No

Presentation Overview

- Part 1: Introduction to the PFAS Analyte List
- Part 2: PFAS Forensics: Fate and Transport Considerations
- Part 3: PFAS Background Definitions
- Part 4: Key Considerations for Assessing Background PFAS
    - Lunch Break
- Part 5: Putting it All Together: Source Areas vs. Background
- Part 6: NAVFAC PFAS Background Case Study
- Wrap-Up

NAVFAC
Naval Facilities Engineering Systems Command
EXWC Engineering and Expeditionary Warfare Center

Lunch Break

Welcome Back

(Image from Microsoft Office)

Presentation Overview

- Part 1: Introduction to the PFAS Analyte List
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- Part 3: PFAS Background Definitions
- Part 4: Key Considerations for Assessing Background PFAS
  - Lunch Break
- Part 5: Putting it All Together: Source Areas vs. Background
- Part 6: PFAS Background at Navy Installations
- Wrap-Up

Objectives

- Explain how to identify PFAS data patterns that can be used to identify source areas
- Explain how PFAS fate and transport mechanisms can affect PFAS patterns over time/distance
- An example will be presented of how to
    - Identify PFAS source areas
    - Consider whether background PFAS may be contributing to observed PFAS concentrations

Knowledge Pre-Check: Questions 10–12

- Is AFFF the only source of PFAS?
  A) Yes B) No
- PFAS patterns in soil will be identical to PFAS patterns in groundwater?
  A) Yes B) No
- Retention and precursor transformation will affect PFAS patterns?
  A) Yes B) No

Source Area Identification vs. Background

- It is important to understand **patterns associated with PFAS source areas versus those from background PFAS**
  - Is the observed PFAS from a site release or from background?
  - What PFAS-specific trends are expected to be observed as PFAS migrates through environmental media?
  - **What PFAS patterns may be useful to identify when an additional PFAS source is present?**

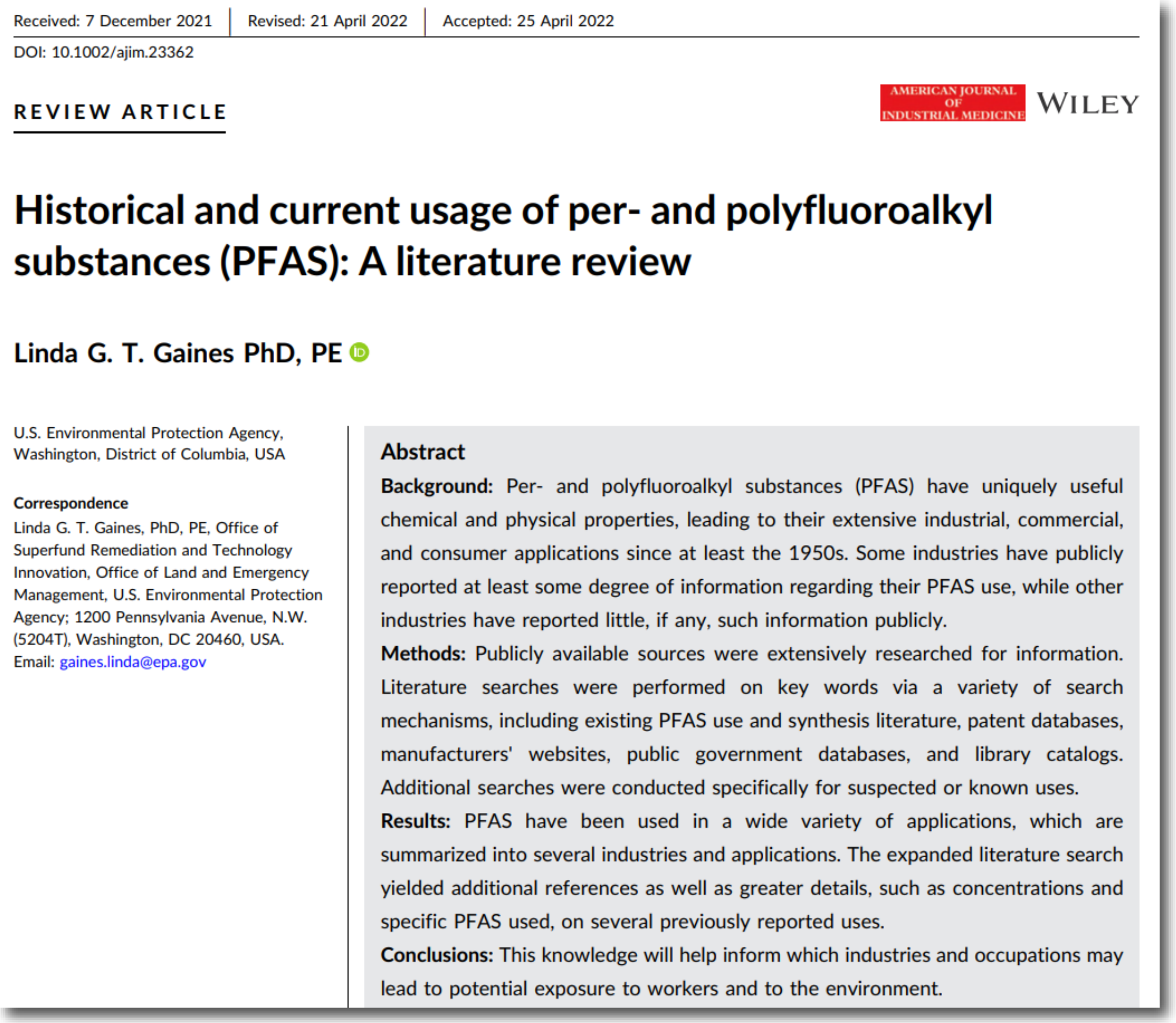
KEY POINT

General principles of source area identification for other chemicals can apply to PFAS—we just need to know what to look for.

What are Potential Sources of PFAS?

- It is important to be aware of all potential sources of PFAS when conducting investigation and remediation activities
- Potential for background PFAS sources may exist near DoD facilities
  - Literature indicates there are numerous potential PFAS sources that could contribute to background
  - Adjacent land use and other factors should be considered during the site-specific sampling design prior to assessing Background PFAS

(Gaines 2022)



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AMERICAN JOURNAL OF INDUSTRIAL MEDICINE WILEY

REVIEW ARTICLE

Historical and current usage of per- and polyfluoroalkyl substances (PFAS): A literature review

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Abstract

Background: Per- and polyfluoroalkyl substances (PFAS) have uniquely useful chemical and physical properties, leading to their extensive industrial, commercial, and consumer applications since at least the 1950s. Some industries have publicly reported at least some degree of information regarding their PFAS use, while other industries have reported little, if any, such information publicly.

Methods: Publicly available sources were extensively researched for information. Literature searches were performed on key words via a variety of search mechanisms, including existing PFAS use and synthesis literature, patent databases, manufacturers' websites, public government databases, and library catalogs. Additional searches were conducted specifically for suspected or known uses.

Results: PFAS have been used in a wide variety of applications, which are summarized into several industries and applications. The expanded literature search yielded additional references as well as greater details, such as concentrations and specific PFAS used, on several previously reported uses.

Conclusions: This knowledge will help inform which industries and occupations may lead to potential exposure to workers and to the environment.

Literature Review of Potential PFAS "Sources"

Priority

- **AFFF**

Common Sources

- **Metal Plating and Machining**
- **Landfills**
- **Septage and Wastewater**
  - **Personal Care Products and Cosmetics**
- **Paper and Packaging Products**
- **Textiles and Carpets**

Other Sources

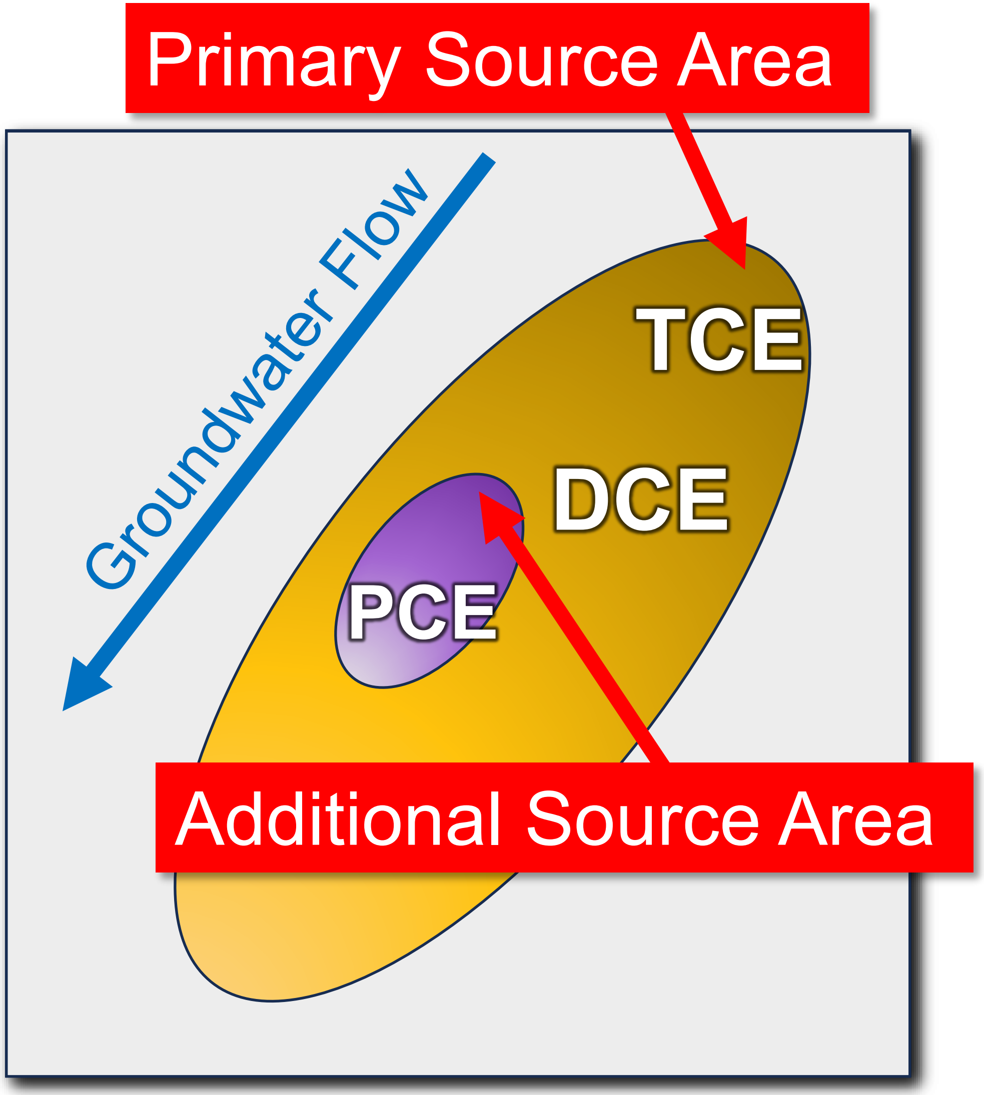
- Pesticides and Herbicides
- Dry Cleaning
- Coatings and Adhesives
- Cleaning Agents and Waxes
- Transportation Industry
- Plastics and Rubbers
- Printing, Etching, and Photography
- Medical Sector
- Electronics and Energy Sector
- Building and Construction Industry
- Mining, Oil, and Gas

Modified from Glüge et al. (2020) and Gaines (2022) – this list is not intended to be all inclusive and may not be applicable in some cases

Lessons Learned from Chlorinated Solvents

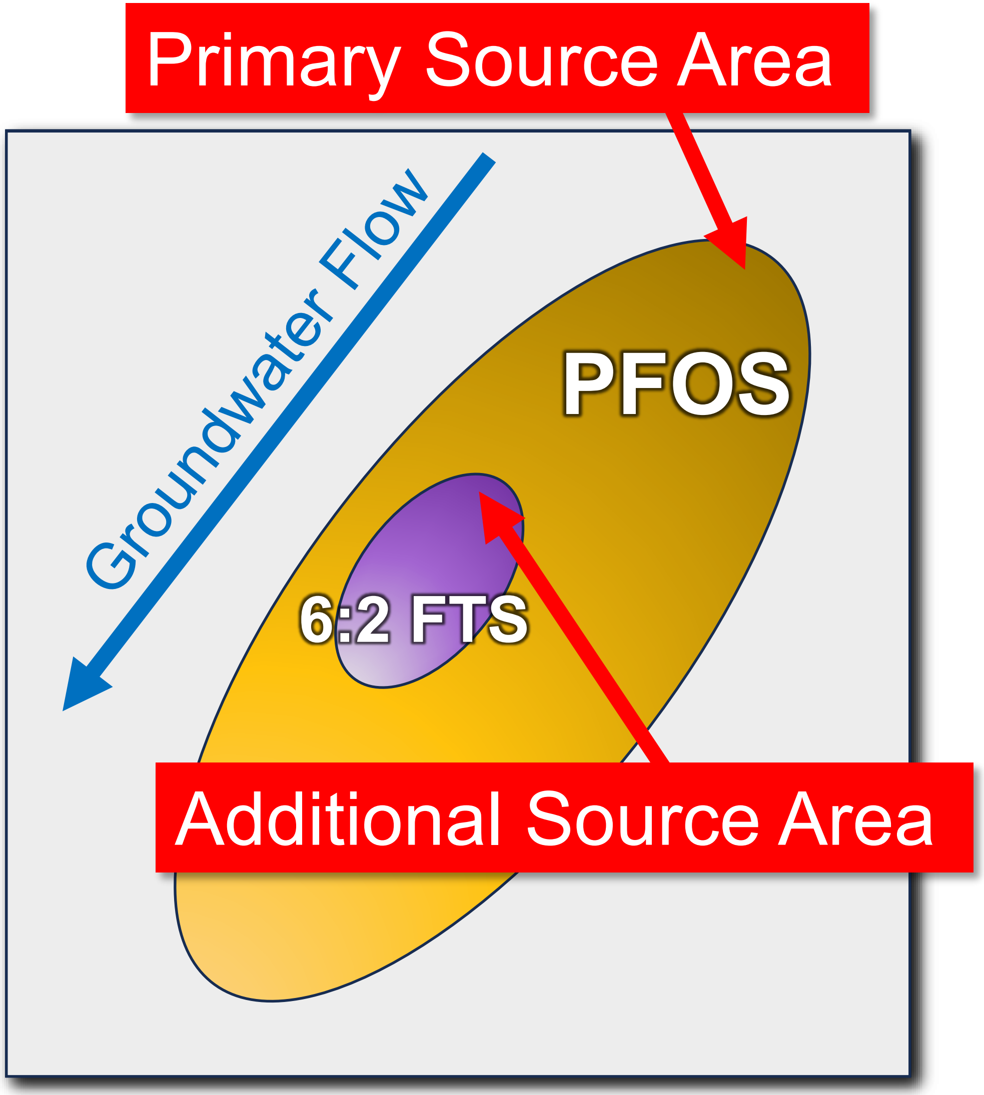
- **Imagine a TCE source area where PCE is subsequently detected downgradient of the primary TCE source area**
  - We know the transformation pathway follows this logic:
    PCE → TCE → DCE → vinyl chloride
  - Based on expected chemical patterns, the downgradient PCE area is likely a separate source (assuming no preferential pathways, etc.)

DCE: dichloroethylene (e.g., cis-1,2-DCE)
PCE: tetrachloroethylene
TCE: trichloroethylene



ECF-based vs. FT-based AFFF Source Areas

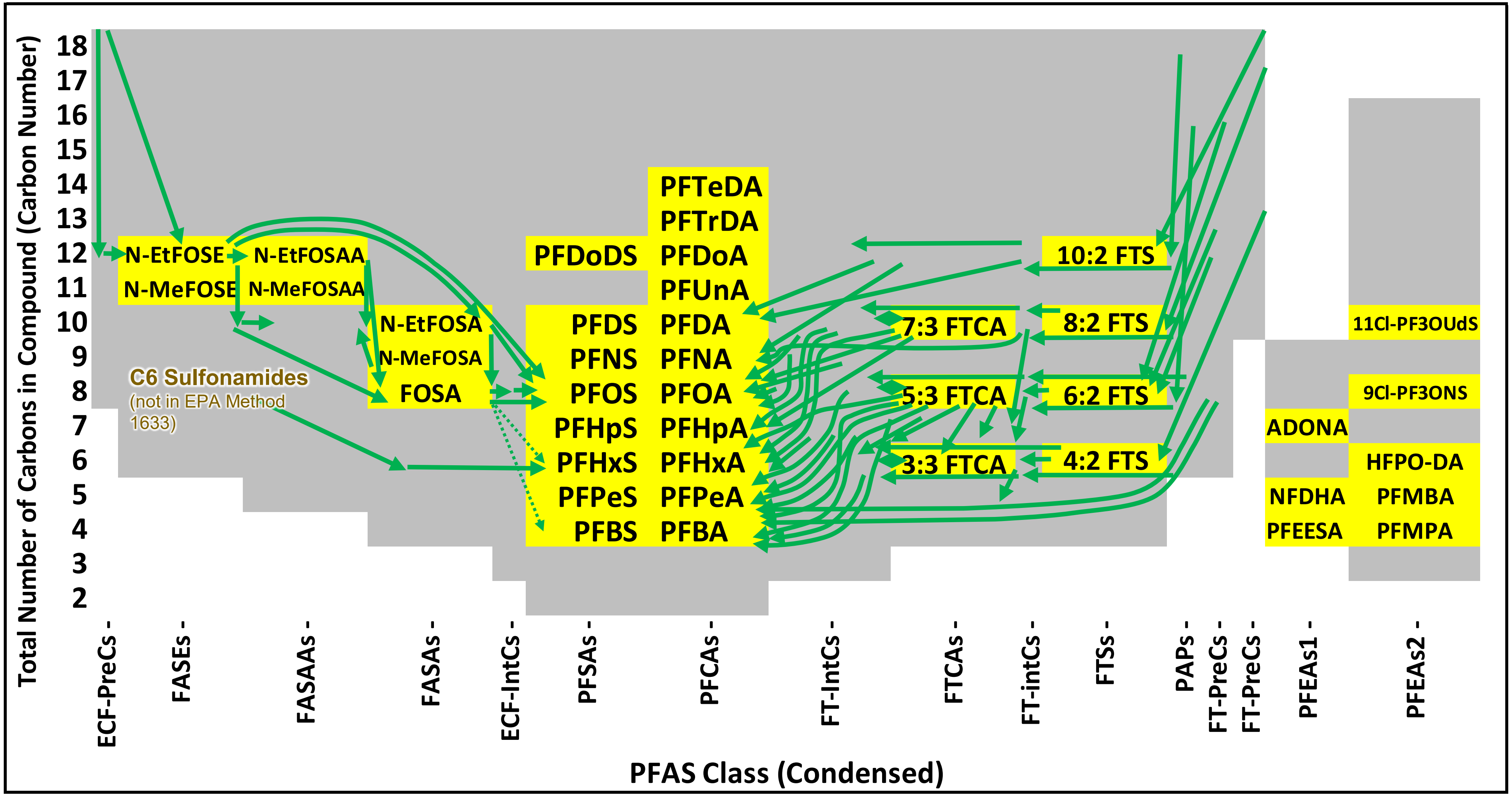
- **Some PFAS-containing products have chemical patterns that can be used in a similar way**
  - For example, ECF-based products (with PFOS) can have different PFAS signatures compared to FT-based products (with identifiable compounds such as 6:2 FTS)
  - We will explore this in more detail in subsequent slides



Primary Source Area

Additional Source Area

Precursor Transformation and Retention

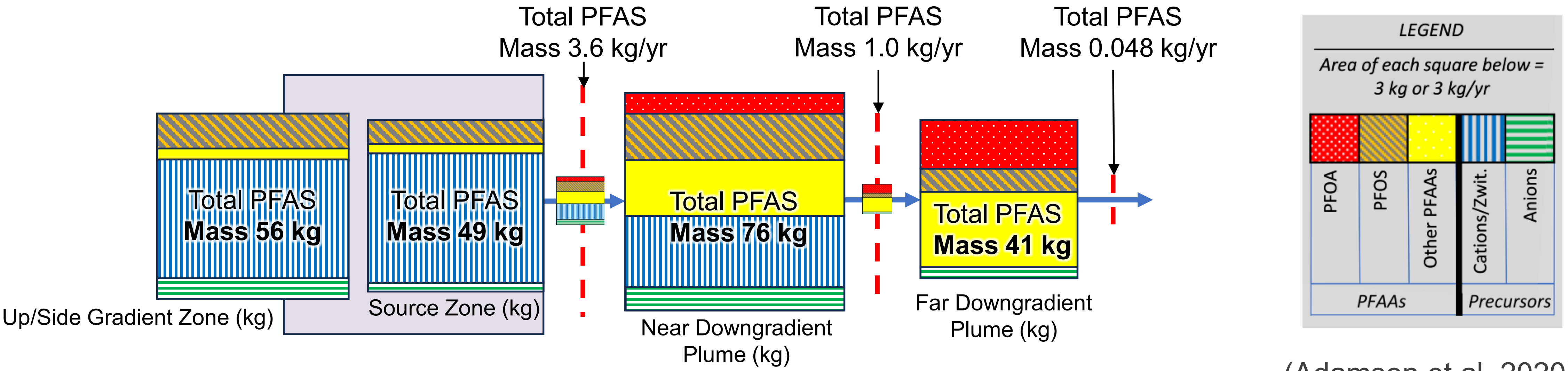


Greater Retention

Less Retention

Spatial Distribution of PFAS

- Precursors & long-chain PFAAs tend to stay closer to source area
- Short-chain PFAAs tend to migrate farther from the source area
- PFCAs tend to migrate farther than PFSAs of similar chain length



Total PFAS
Mass 3.6 kg/yr

Total PFAS
Mass 1.0 kg/yr

Total PFAS
Mass 0.048 kg/yr

Total PFAS
Mass 56 kg

Up/Side Gradient Zone (kg)

Total PFAS
Mass 49 kg

Source Zone (kg)

Total PFAS
Mass 76 kg

Near Downgradient
Plume (kg)

Total PFAS
Mass 41 kg

Far Downgradient
Plume (kg)

LEGEND

Area of each square below =
3 kg or 3 kg/yr

PFOA
PFOS
Other PFAAs
Cations/Zwit.
Anions

PFAAs
Precursors

(Adamson et al. 2020)

Soil vs. Groundwater PFAS Patterns

- Observed soil PFAS patterns are often different than underlying groundwater patterns from same source area
  - **Longer-chain PFAS and precursors** (i.e., PFAS with higher carbon numbers) **tend to be preferentially retained in soil compared to groundwater**, which may lead to different soil vs. groundwater patterns
  - PFAS patterns should be evaluated using multiple lines of evidence with consideration for expected compound-specific fate and transport effects

KEY POINT

PFAS patterns being different in soil versus groundwater does not exclude the PFAS being from the same source.

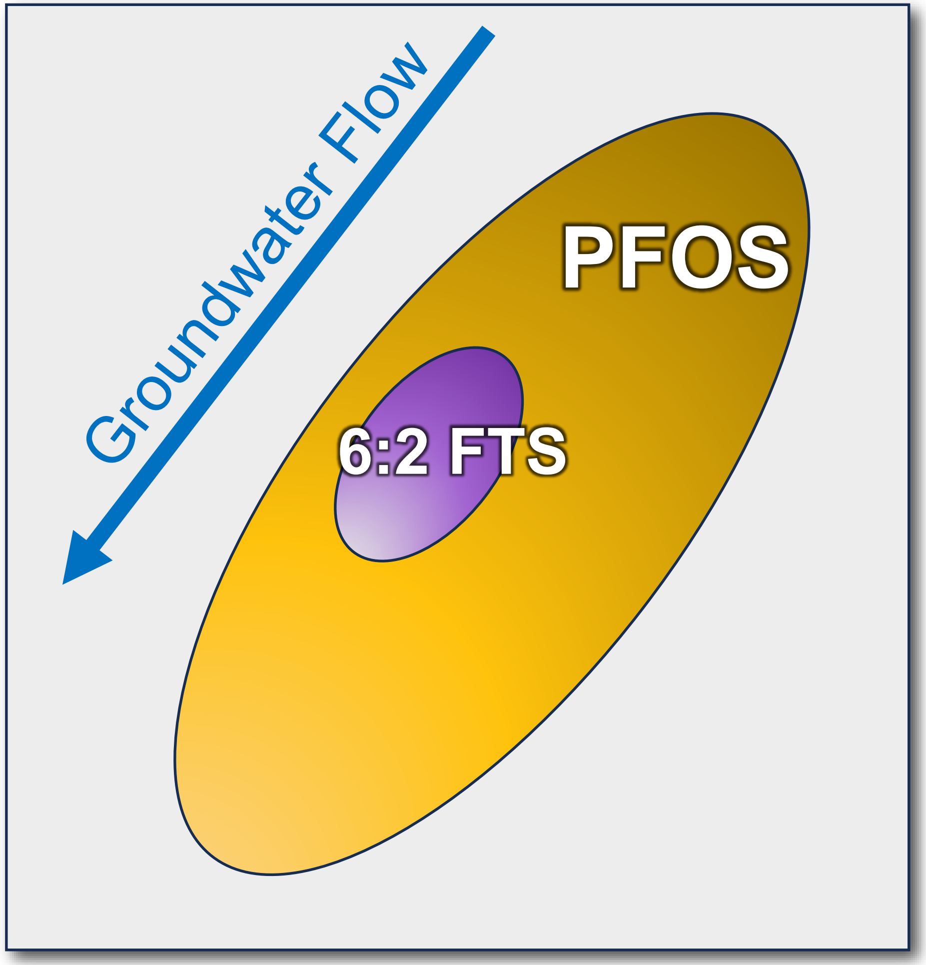
PFAS Forensics Considerations

- The ratios and metrics described in the subsequent slides are based on potentially relevant PFAS fate and transport mechanisms, as described in Gamlin et al. (2024)
- This approach may **aid in identifying potential PFAS source areas** and is based on the standard EPA Method 1633 analyte lists
- Some PFAS used in this approach may not have toxicity values, and **the ratios and metrics presented do not represent a quantification of risk**

PFAS Forensics Considerations

Example 1: Understanding PFAS Classes

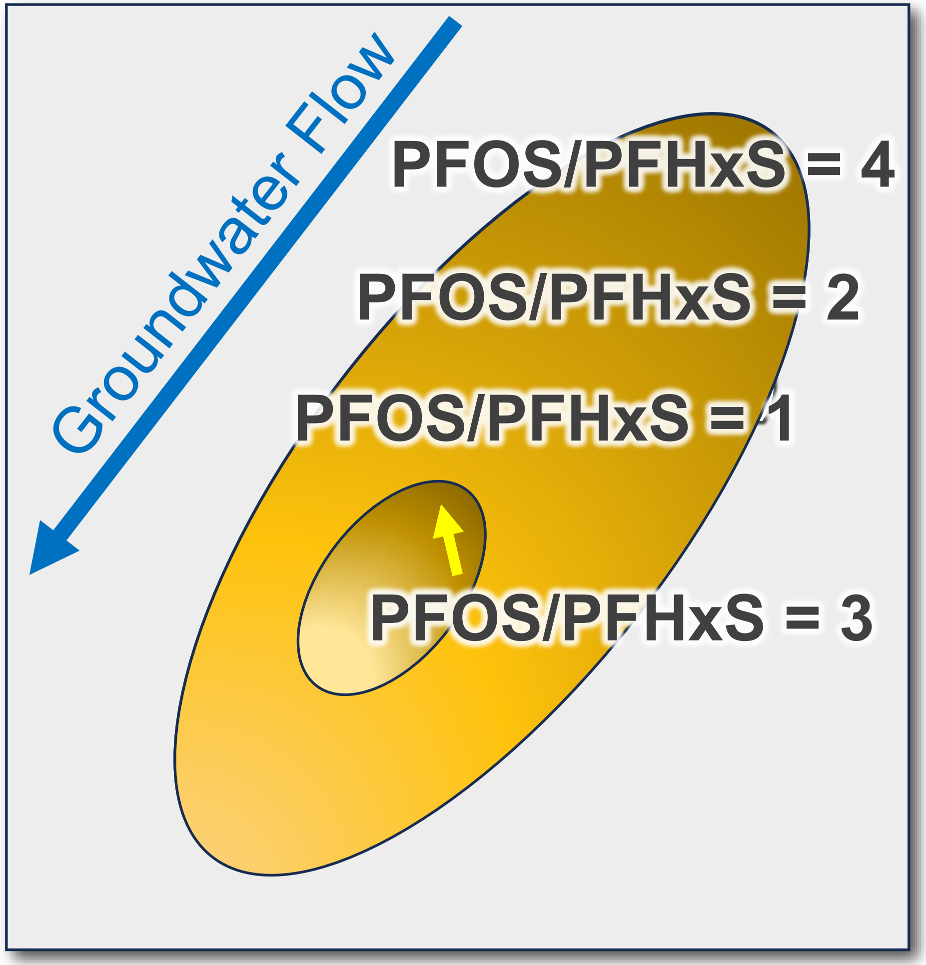
- Certain PFAS can be used to identify different AFFF products released within a mixed AFFF groundwater plume
- In this example, the upgradient plume is dominated by PFOS from an ECF AFFF source zone
- Assuming no preferential pathways, the downgradient detection of 6:2 FTS (not from ECF AFFF) in groundwater may indicate a separate AFFF release area (this should be confirmed with other lines of evidence)



PFAS Forensics Considerations

Example 2: Understanding PFAS Ratios

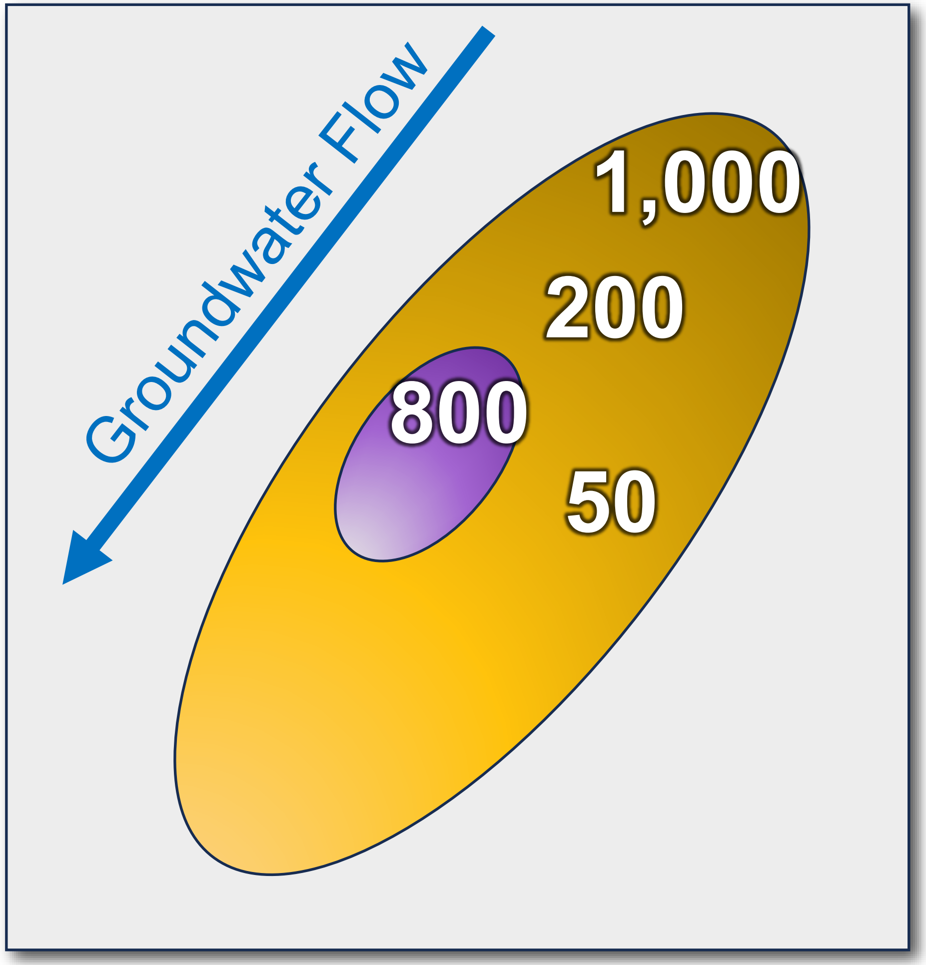
- The ratio of PFOS/PFHxS typically decreases along a flow path, as PFOS and its precursors are preferentially retained compared to PFHxS and its precursors (see Gamlin et al. 2024)
- In this example, the PFOS/PFHxS ratio decreases from 4 to 2 to 1, and then farther downgradient it increases to 3
- Assuming no preferential pathways, the downgradient increase in the PFOS/PFHxS ratio may indicate a separate downgradient source area (this should be confirmed with other lines of evidence, such as overall concentrations, etc.)



PFAS Forensics Considerations

Example 3: Understanding Sum of PFAS

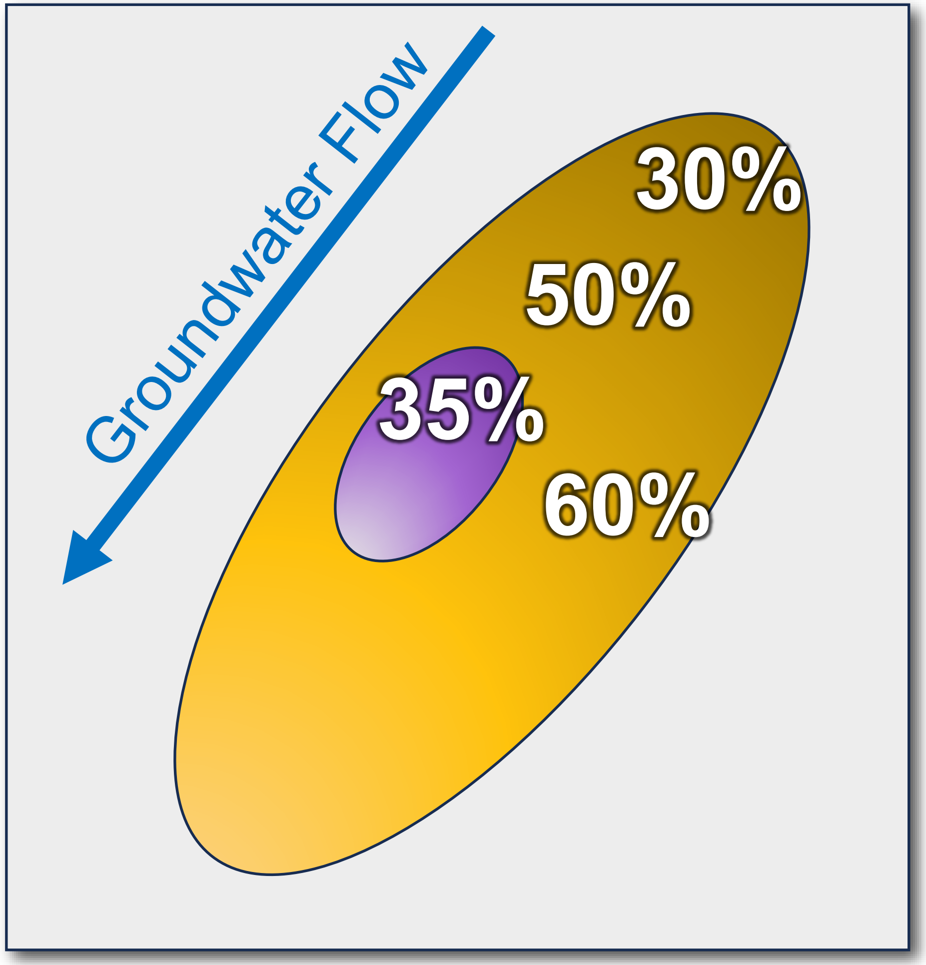
- Does not indicate risk, just a tool for helping to identify source areas
- The sum of PFAS may be useful for identifying additional source areas (assuming equivalent analyte lists are used)
- In this example, the upgradient portion of the plume decreases from 1,000 ng/L to 200 ng/L, before increasing to 800 ng/L
- Assuming no preferential pathways, the increase to 800 ng/L may indicate a separate source area (this should be confirmed with other lines of evidence)



PFAS Forensics Considerations

Example 4: Understanding PFAS Metrics

- The percent of PFAAs with 6 or less carbons, and their precursors (%≤C6) will generally increase along a flow path due to the preferential retention of longer-chain PFAS
- In this example, the %≤C6 in the upgradient portion of the plume increases from 30% to 50%, before decreasing to 35%
- Assuming no preferential pathways, the decrease to 35% may indicate a separate source area (this should be confirmed with other lines of evidence)



Poll Questions 10–12 (Answers)

- Is AFFF the only source of PFAS?

  A) Yes **B) No**

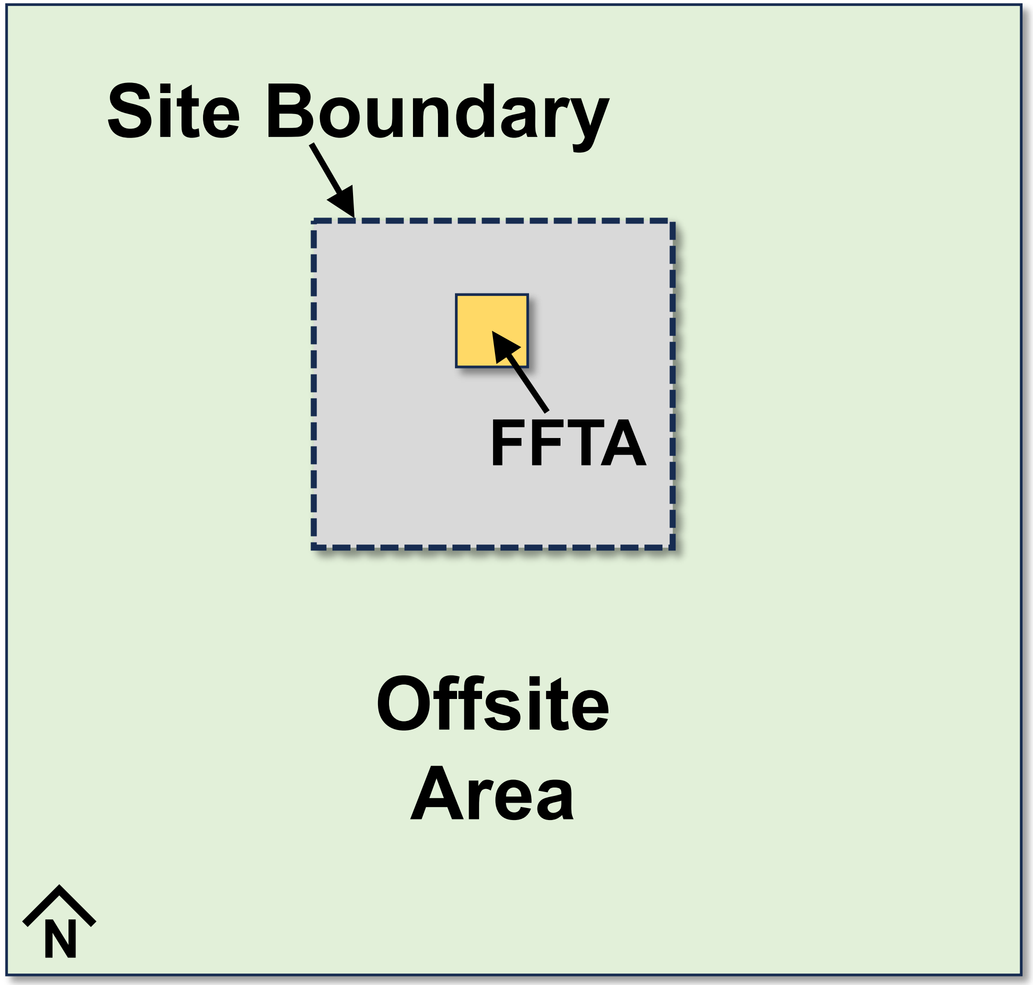
- PFAS patterns in soil will be identical to PFAS patterns in groundwater?

  A) Yes **B) No**

- Retention and precursor transformation will affect PFAS patterns?

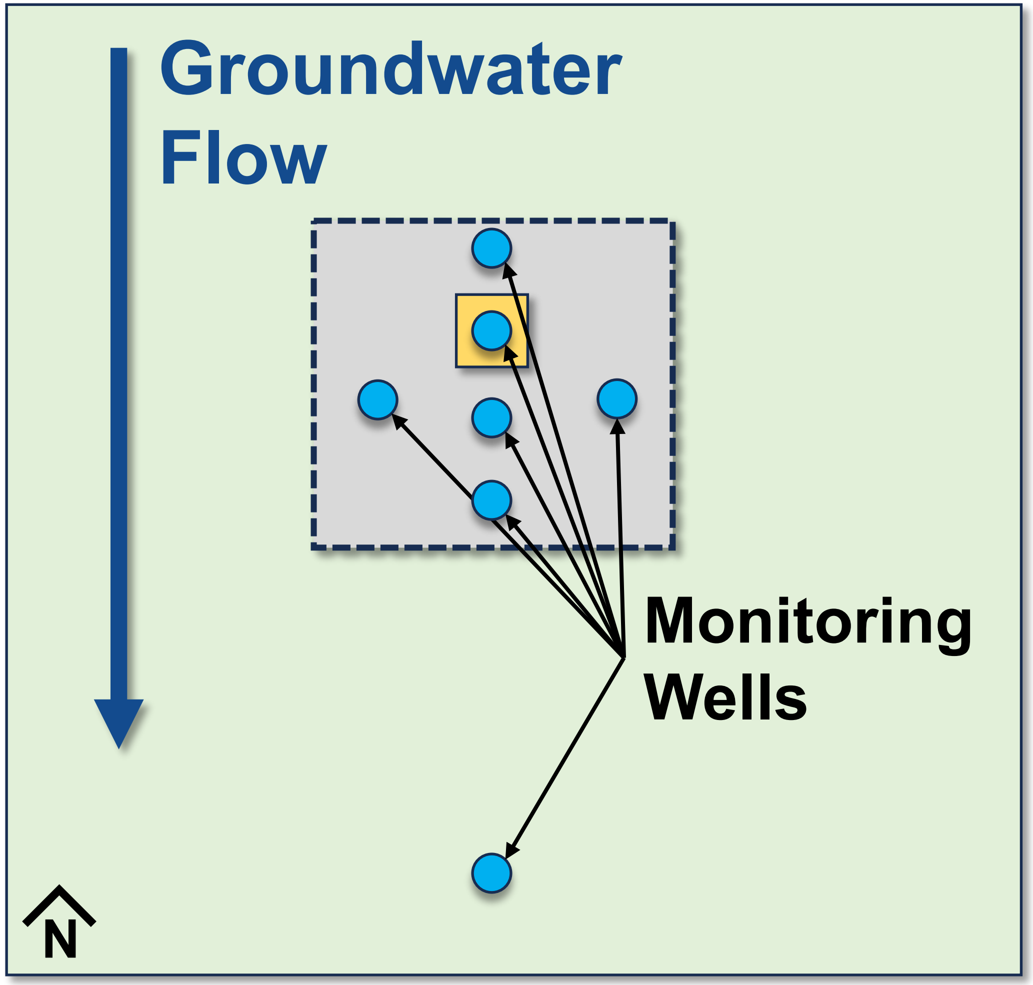
  A) Yes B) No

Hypothetical PFAS Background Assessment



- Next, we will use what we have learned and walk through a simplified, hypothetical example of PFAS patterns that may be present near a former fire training area (FFTA)

Hypothetical PFAS Background Assessment

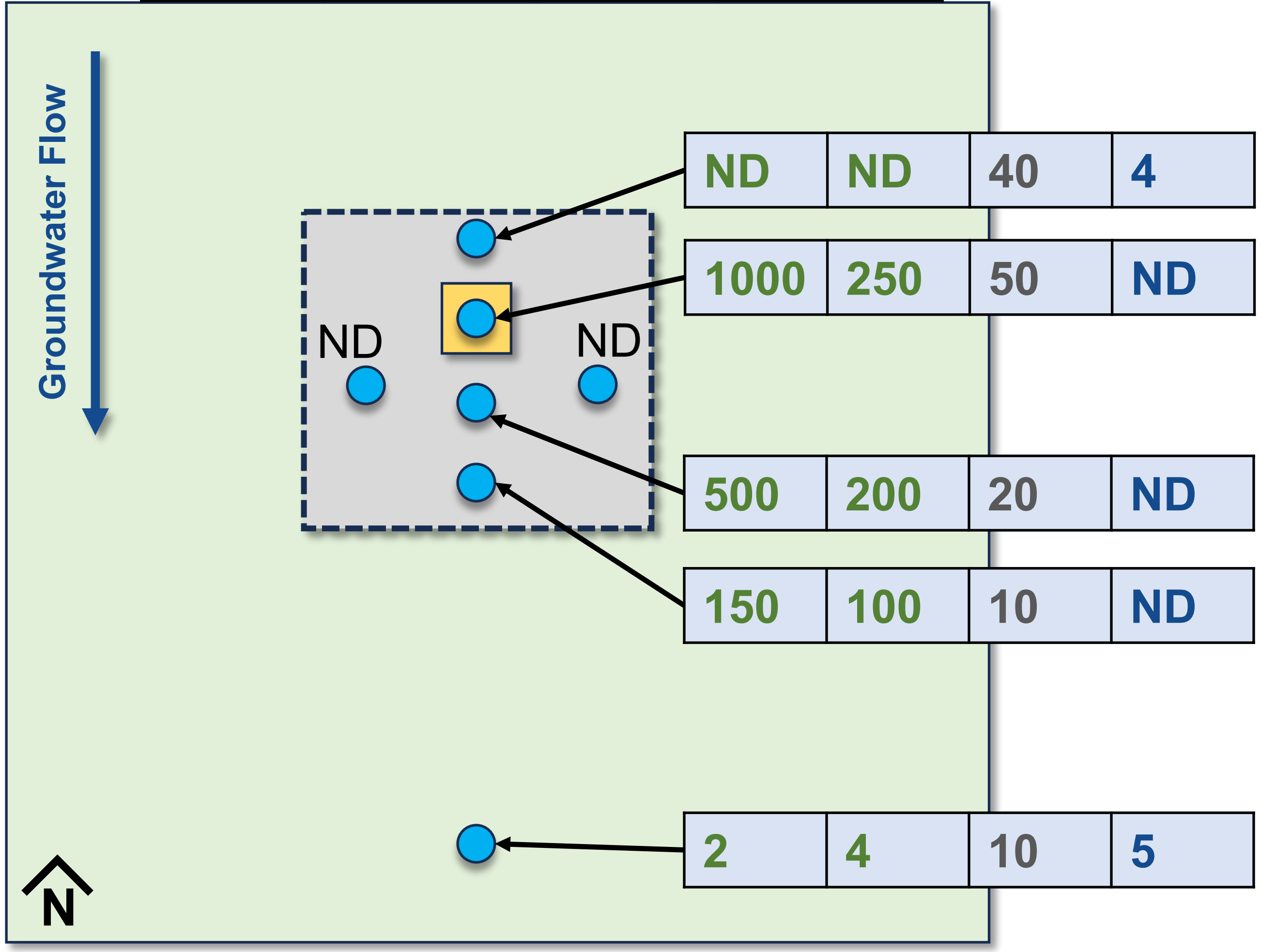


- Site Setting
  - Groundwater flow is to the south in a shallow, unconfined aquifer with stable water levels
  - No preferential pathways have been identified
  - Monitoring wells have been installed upgradient, downgradient and cross-gradient to the FFTA
  - The offsite area is a mix of commercial and industrial land use

Hypothetical PFAS Background Assessment

Key =	PFOS	PFHxS	PFOA	6:2 FTS

Color: ECF-based PFAS, ECF- or FT-based PFAS, FT-based PFAS



PFOS	PFHxS	PFOA	6:2 FTS
ND	ND	40	4
1000	250	50	ND
500	200	20	ND
150	100	10	ND
2	4	10	5

PFOA and 6:2 FTS detected upgradient?

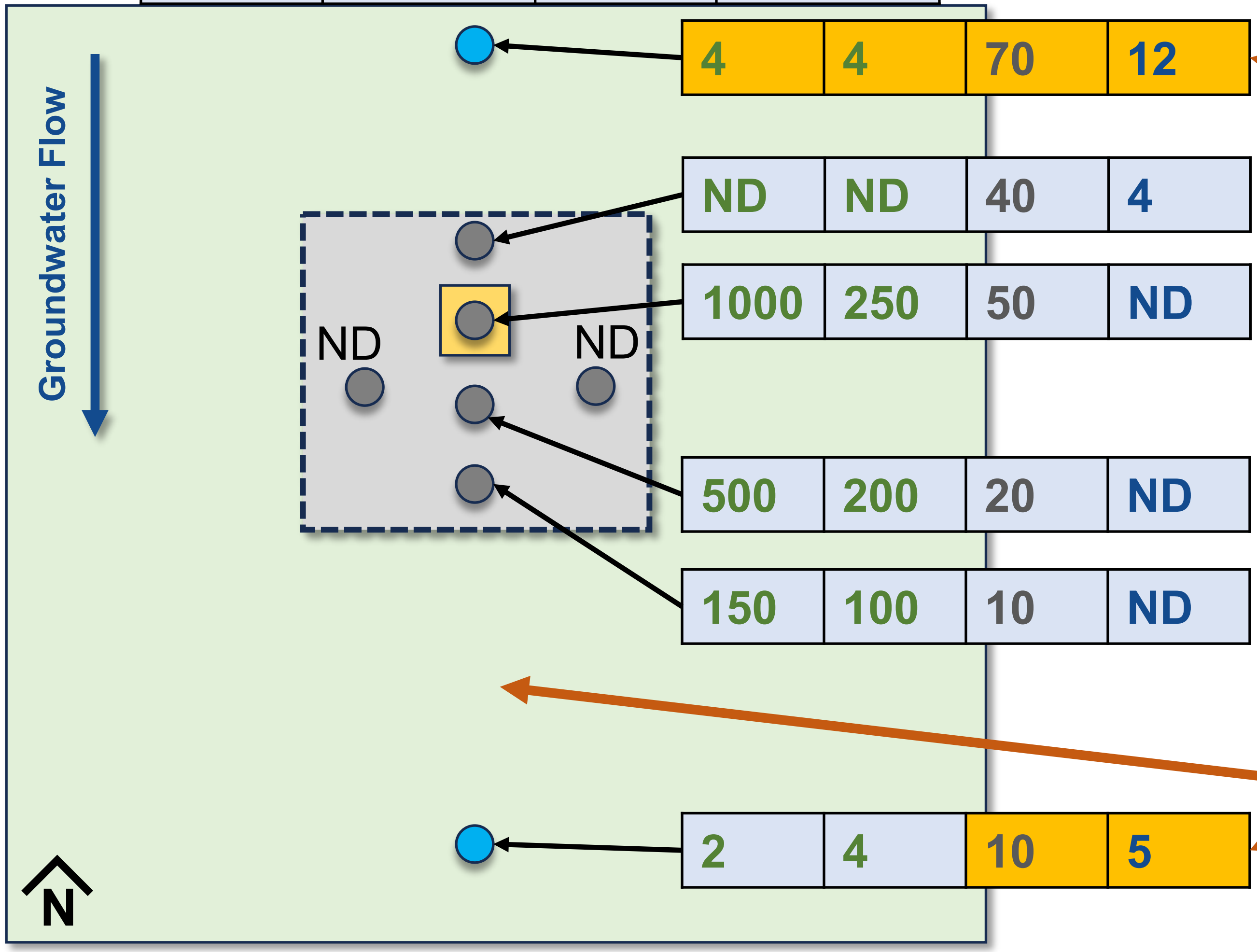
PFOS and PFHxS dominant with no 6:2 FTS, this indicates ECF AFFF may have been released

PFOA and 6:2 FTS are higher than expected?

Concentrations in ng/L

Hypothetical PFAS Background Assessment

Key = **PFOS** | **PFHxS** | **PFOA** | **6:2 FTS** Color: ECF-based PFAS, ECF- or FT-based PFAS, FT-based PFAS



4	4	70	12
ND	ND	40	4
1000	250	50	ND
500	200	20	ND
150	100	10	ND
2	4	10	5

Well installed for background assessment, indicates background PFAS

Downgradient well indicates background PFAS should be further evaluated to explain PFOA and 6:2 FTS detections

Concentrations in ng/L

PFAS Data Evaluation

KEY POINT

PFAS often behave in predictable ways along routes of migration, resulting in patterns that can be helpful during identification of sources versus background.

(Image from Microsoft Office)

Naval Facilities Engineering Systems Command

EXWC Engineering and Expeditionary Warfare Center

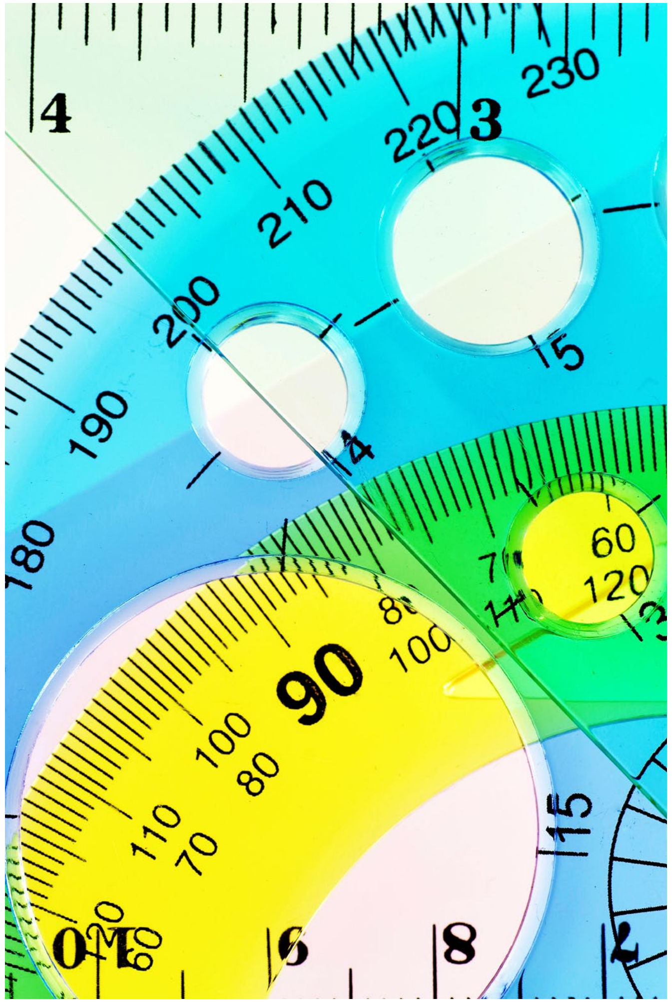
Break

Presentation Overview

- Part 1: Introduction to the PFAS Analyte List
- Part 2: PFAS Forensics: Fate and Transport Considerations
- Part 3: PFAS Background Definitions
- Part 4: Key Considerations for Assessing Background PFAS
  - Lunch Break
- Part 5: Putting it All Together: Source Areas vs. Background
- Part 6: PFAS Background at Navy Installations
- Wrap-Up

Background Study Reference Area(s)

- No specific guidance for selecting PFAS Background Study Reference Areas (yet)
- Scale Considerations
  - Will require review of site-specific conditions
  - Large Site: Sites with watershed-scale considerations may require sampling at greater distances away from site
  - Small Site: Will focus on selecting representative sampling areas outside of the PFAS release area

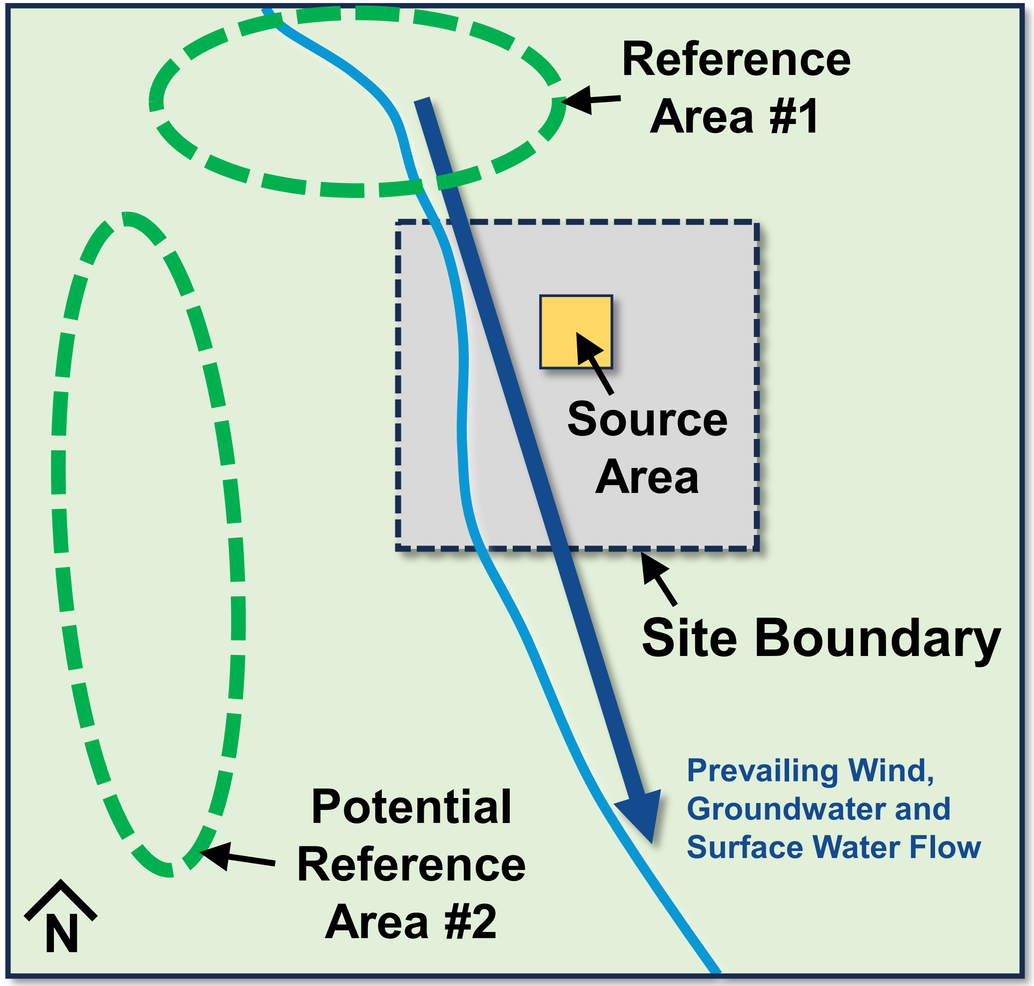


(Image from Microsoft Office)

Determining Background Reference Area(s)

- The **Background Reference Area(s)** should **have similar physical, chemical, geological, and biological characteristics of the site being investigated**, but should not be affected by site activities (CERCLA reference, but Navy uses this term)
    - Different areas may be required depending on the media affected by site activities (e.g., soil vs. surface water vs. groundwater)

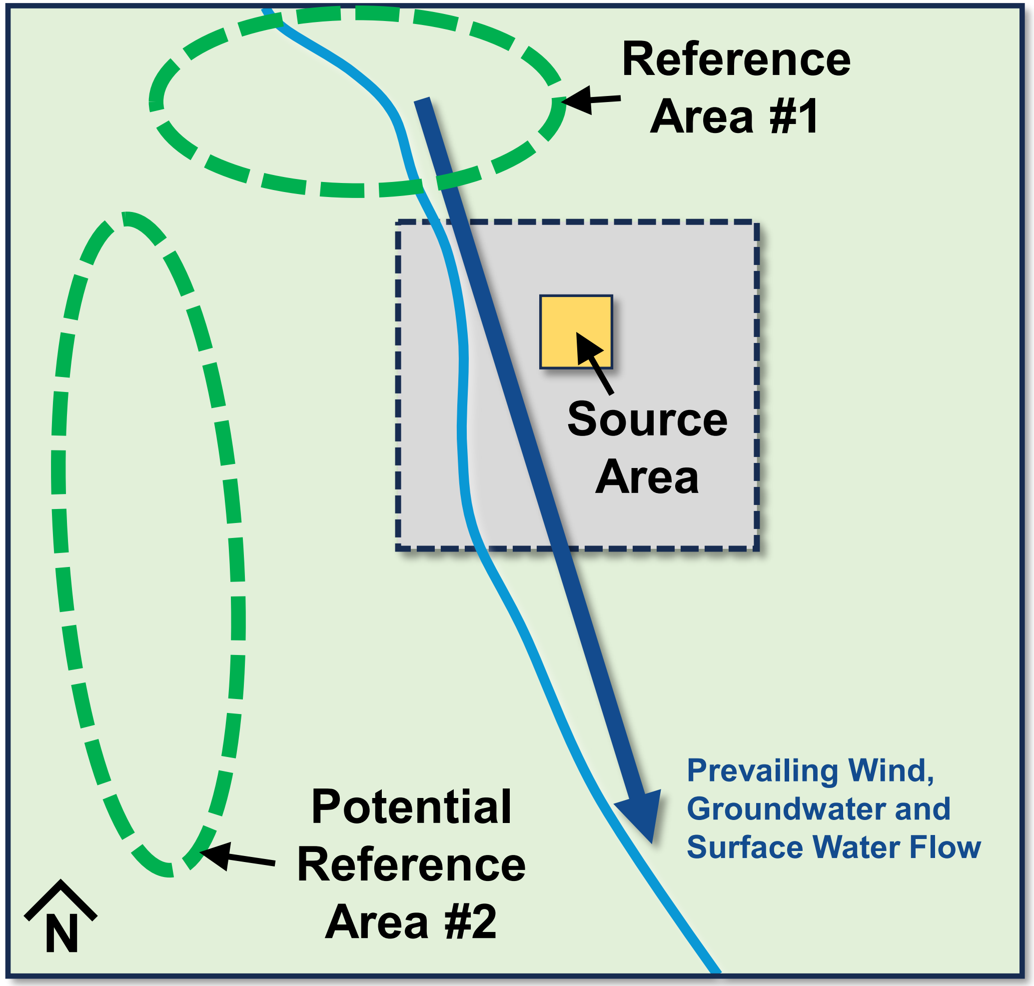
Generic Example: Requires Site-Specific Consideration



Selecting Background Sampling Locations

- Potential site-specific assessment may include
    - Precipitation (prevailing wind can vary)
    - Upstream/adjacent surface water
    - Upgradient/adjacent groundwater
    - Potential down/cross-gradient groundwater depending on offsite land use(s)
    - Soil (and potentially porewater) at appropriate distance(s) from release area(s)
    - Assessment of non-PFAS markers that may be indicative of background PFAS

Generic Example: Requires Site-Specific Consideration



Statistical Methods

- Due to inherent **variability in data**, background levels are **statistical calculations and incorporate uncertainty** (which may be large)
- Refer to EPA "Role of Background in the CERCLA Cleanup Program" (2002), or other required guidance, to determine appropriate statistical evaluation of the background data
- In some cases, multiple sampling events may be required

Selecting Background Sampling Locations

KEY POINT

The design of PFAS background studies will require consideration of site-specific factors.

(Image from Microsoft Office)

Background Case Study In Progress

PFAS Background at Navy Installations:

Precipitation and Ambient Soils Research

- NAVFAC EXWC
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  - Arun Gavaskar
- WSP
  - Usha Vedagiri, PhD, PI
  - Michael Fuerte
  - Dean Lay
  - Joshua Klein
  - Sean Gormley
  - Konrad Quast
  - Lansana Coulibaly

PI: principal investigator

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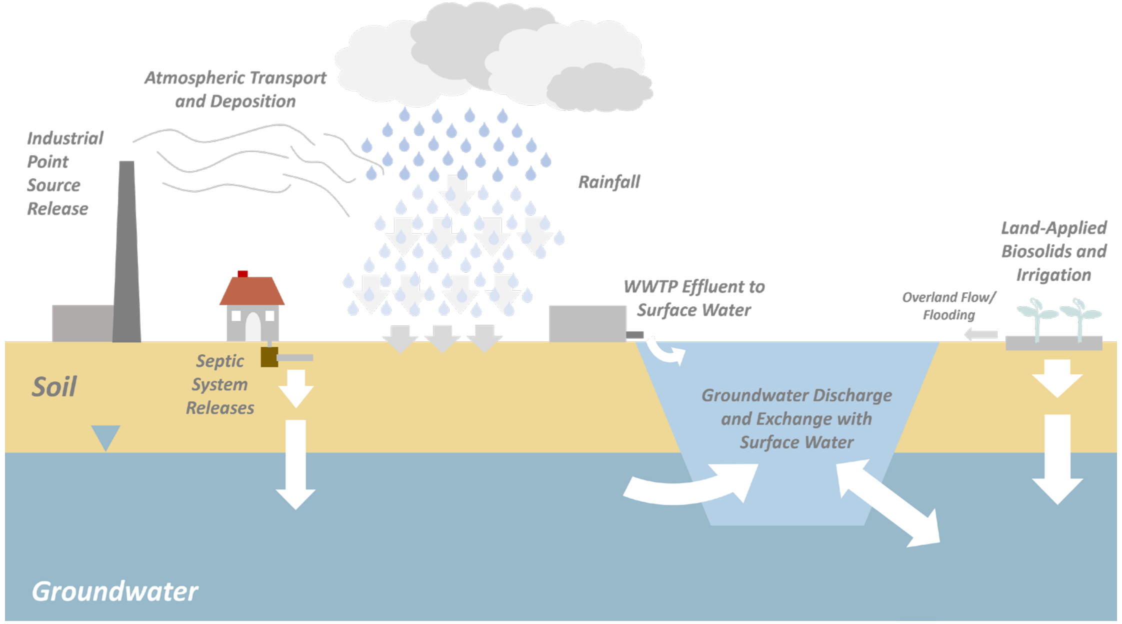
Wrap-Up #1

Background

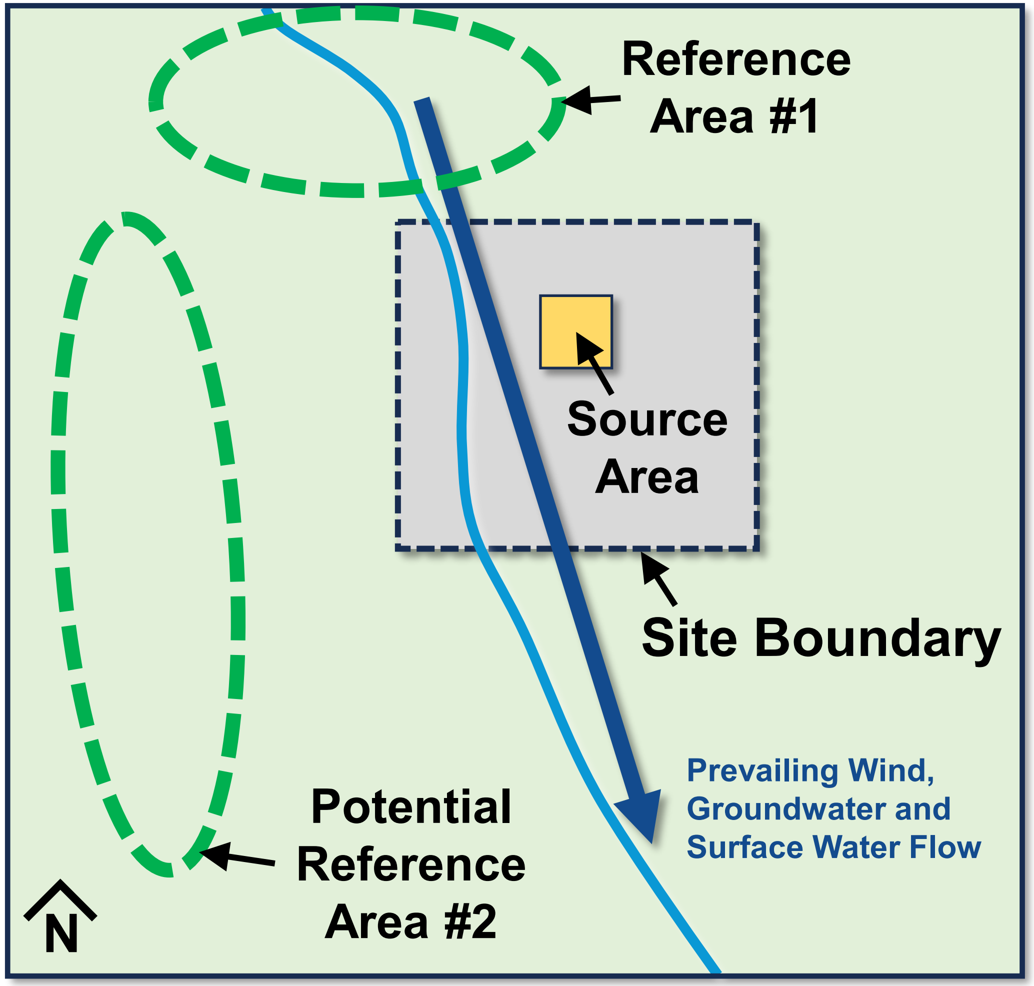
- Background PFAS assessments will be a component of PFAS Remedial Investigations
- Background guidance specific to PFAS is evolving (stay tuned for NAVFAC studies and ESTCP project ER25-8813)



Wrap-Up #2

Background

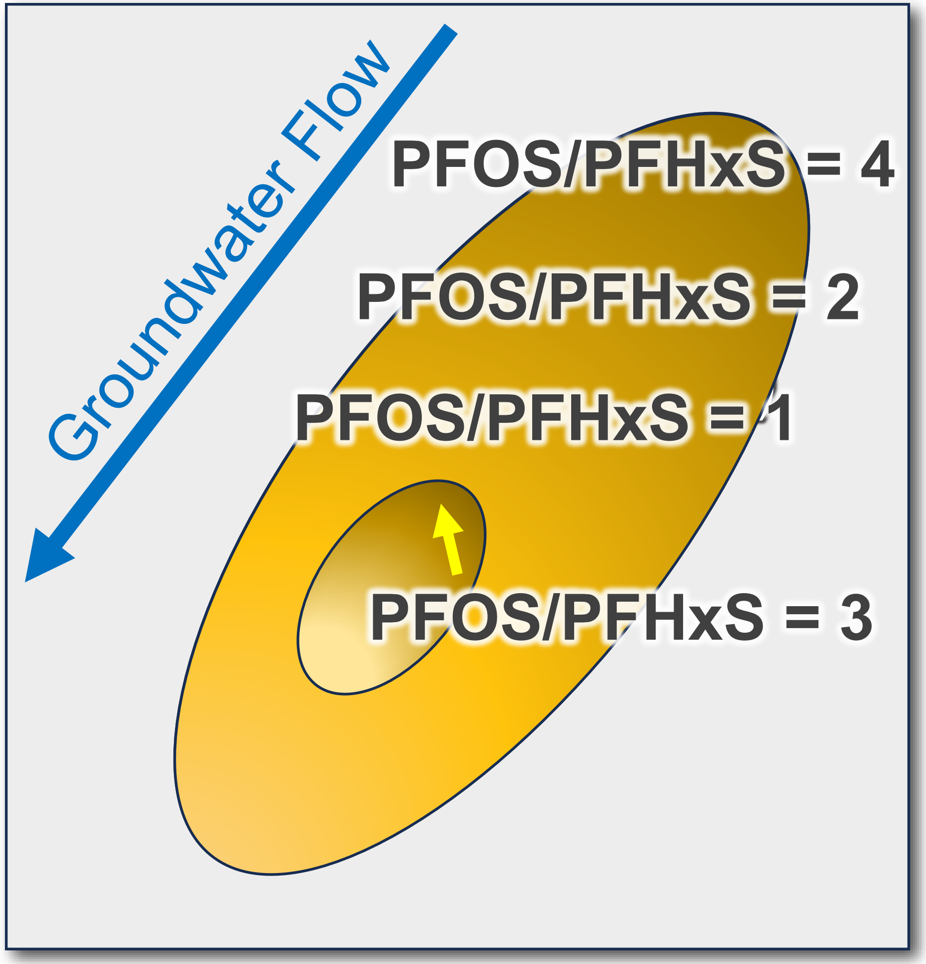
- Background PFAS concentrations can exceed regulatory standards in precipitation, soil, surface water, and groundwater
- Carefully plan your background investigation area based on site-specific considerations



Wrap-Up #3

Forensics

- Identification of PFAS source areas should include consideration of fate and transport effects along routes of migration
- Use multiple lines of evidence to confirm source areas have been properly identified



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Questions