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PFAS: Beyond the Basics Training



Sampling

Analytical Methods

Qualitative Analyses

Data Evaluation

PFAS Occurrence in Air



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Today's PFAS Trainers



Kristi Herzer
Vermont
Department of
Environmental
Conservation



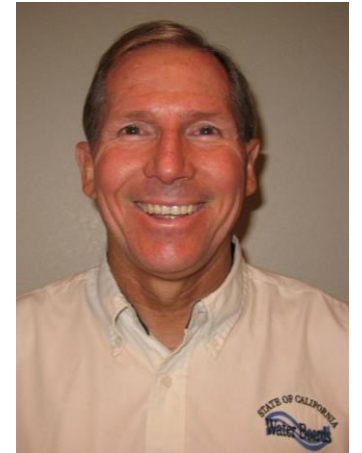
Elizabeth Denly
TRC



Chris Zevitas
US DOT



Jamie Fox
SGS



Alex MacDonald
Retired

ITRC PFAS Resources

- ITRC PFAS: <https://pfas-1.itrcweb.org/>
- Guidance Document
- 13 Fact Sheets
- External Tables

PFAS Introductory Training

- Archive on Clu-In: <https://www.clu-in.org/conf/itrc/PFAS-Introductory/>

Other video resources – available through links on: <https://pfas-1.itrcweb.org>

- Quick Explainer Videos
- Longer PFAS Training Modules
- Archived Round Table Sessions

ITRC PFAS Team: 2025 “Beyond the Basics” Training Modules



Learning Objectives – To Understand:

Key elements that make **PFAS sampling** different from other sampling events

Best practices for preparing for and **conducting a PFAS sampling event**
Focus on Surface Water/Foam Sampling

Current state of **PFAS analytical methods**

Basics of **compound-specific PFAS analysis**

Alternative analytical techniques and how they can be useful

Occurrence of **PFAS in air**



Sampling

Analytical Methods

Qualitative Analyses

Data Evaluation

PFAS Occurrence in Air

Section 11.1



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Sampling and Analysis, Section 11

Final web document PFAS-1: <https://pfas-1.itrcweb.org>

Section 11.1: Sampling

Section 11.2: Analytical Methods/Techniques

Section 11.3: Data Evaluation

Section 11.4: Source Identification (covered in separate training module)

External files

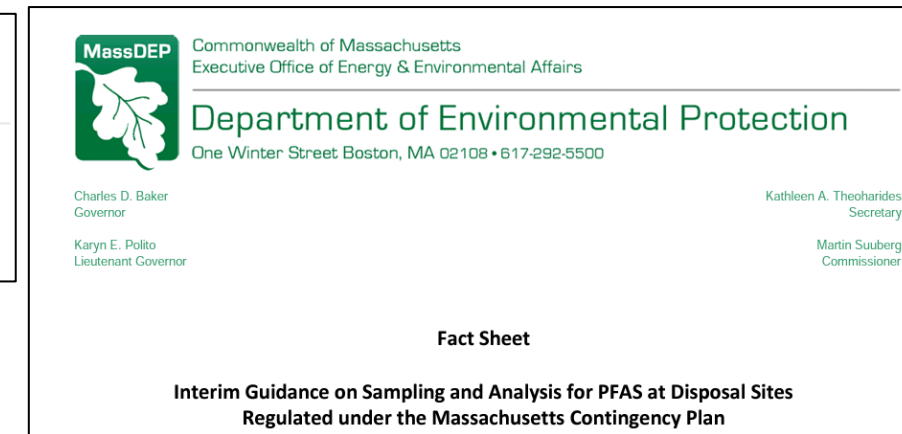
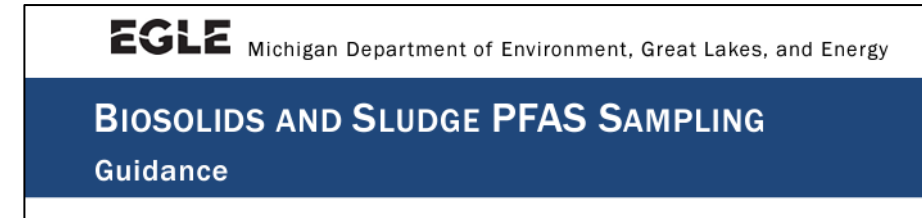
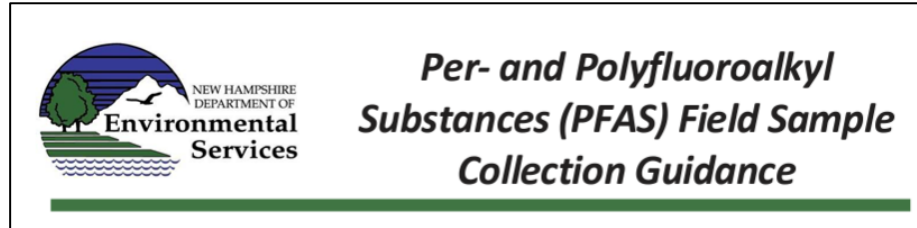
- **Table 11-2**, Finalized published methods basics
- **Table 11-3**, Finalized published methods specifics
- **Table 11-4**, Published methods analyte lists
- **Table 11-5**, Draft published methods
- **Table 11-6**, PFAS analytical data usability table

Section 16.4: Surface Water, Sampling & Analysis

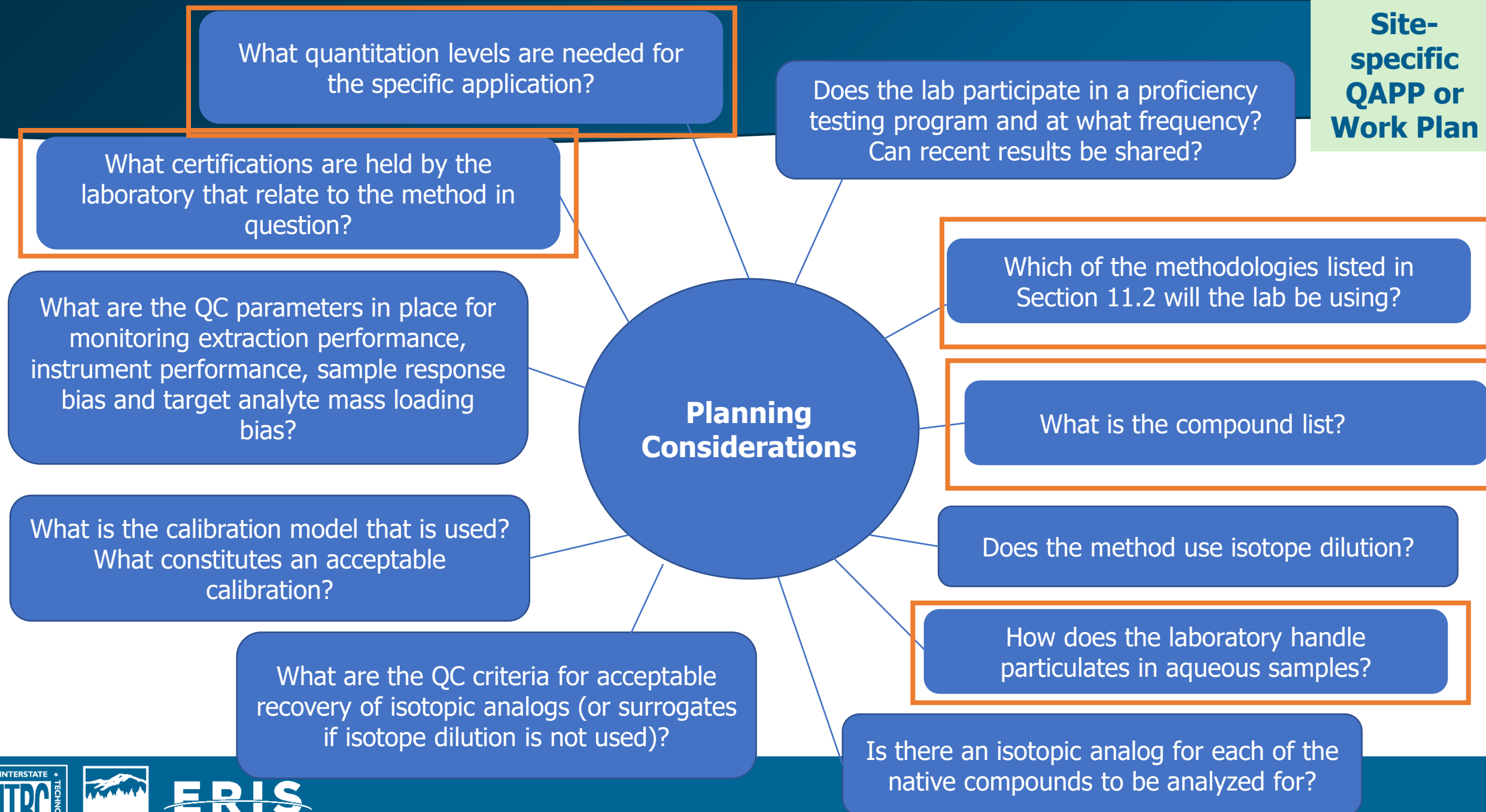
Section 16.5: Surface Water Foam

Published Sampling Guidance

- USEPA 2019
- DoD AFFF01
- State Guidance
 - MA DEP 2022
 - MI EGLE 2021
 - MPCA 2022
 - NH DES 2022
 - Washington Department of Ecology 2017



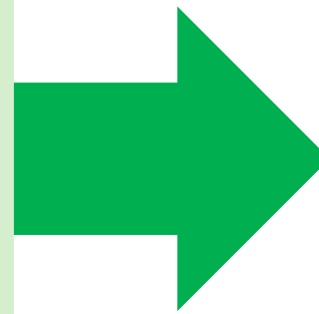
Links provided within technical regulatory guidance document



Sampling Event Preparation

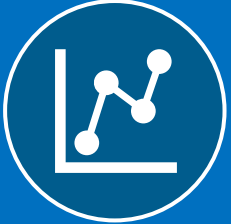
Objectives of project and conceptual site model influence the sampling and analysis program

- Site history (e.g., potential sources, quantities used) as indicator of potential level of PFAS
- Project Action Levels



Develop **project-specific quality assurance project plan (QAPP) or work plan** which addresses increased risk of contamination and project-specific considerations

Planning Laboratory Analysis



Project team must discuss with the laboratory

- *PFAS to be analyzed and project reporting levels
- *Volume of sample to achieve lab reporting levels
- *Sample preparation requirements, and # of bottles needed



Provide laboratory information on high concentration samples or aqueous samples with elevated particulate levels



For EPA 1633, may need to request laboratory screen all samples prior to sample preparation, (additional containers for aqueous samples needed)

Reasons Why Potential for PFAS Contamination Higher During Sampling

1. Low PFAS screening or regulatory criteria
parts per trillion (ppt) for aqueous
parts per billion (ppb) for soil/sediment
2. Inefficient decontamination procedures in source areas
3. Sampling equipment and materials may contain PFAS

Equipment & Supplies

There are some materials that should be avoided due to contamination and possible sorption issues that if used and contacted sample may introduce bias

Ethylene tetrafluoroethylene
(ETFE)

Low-density polyethylene
(LDPE)

Fluorinated ethylene-
propylene (FEP)

Polyvinylidene fluoride
(PVDF)

Polytetrafluoroethylene
(PTFE)

Waterproof coatings
containing PFAS

Pipe thread compounds and
tape

Equipment & Supplies

Review Safety Data Sheets (SDS);
if PFAS, “fluoro”, or “halo” listed,
recommendation to not use

- Exclusion from SDS does not assure PFAS are not present in equipment/material

Conservative Sampling Approach is Best

- Collect extra QC samples
- Test materials prior to sampling

Tiered Approach

- **1st:** Restrictions on sampling materials in direct contact with samples
- **2nd:** Restrictions on materials allowed on personnel and staging area

Sample Container Selection: Based on Analytical Method

USEPA 537.1 250 mL Polypropylene containers and caps/lids for drinking water

USEPA 533 250 mL Polypropylene or polyethylene containers and caps/lids for drinking water

USEPA SW-846
Method 8327 Polypropylene containers for groundwater, surface water, wastewater; other types of containers such as HDPE may be used if the needs of the project can be met with their use

USEPA 1633 Recommends use of 500 mL HDPE containers for wastewater, groundwater, and surface water, 125 mL HDPE containers for landfill leachate, wide-mouth HDPE for biosolids, soil, sediment, tissue; requires second container for screening aqueous samples

DoD AFFF-01 HDPE bottle with liner-less polypropylene cap for AFFF

Aqueous samples: fill two containers for PFAS for each sample

Laboratory Supplied Sampling Materials

Sample containers (polypropylene or HDPE), solvents (such as methanol), and water used for blanks in the field and for final rinse of equipment should:

- be supplied by the lab performing the analysis, and
- be verified as being PFAS-free (as defined by the project) prior to use

If site water is used in the field for any blanks or final rinse, a sample of this water should be sent to the laboratory for analysis.

Holding Time/Preservation Differences

Method	Preservative	Holding Time
EPA Method 537.1 Drinking water	Trizma®; ship at $\leq 10^{\circ}\text{C}$; store at lab $\leq 6^{\circ}\text{C}$	Extraction: within 14 days of collection Analysis: within 28 days of extraction
EPA Method 533 Drinking water	Ammonium acetate; ship at $\leq 10^{\circ}\text{C}$; store at lab $\leq 6^{\circ}\text{C}$	Extraction: within 28 days of collection Analysis: within 28 days of extraction
SW-846 8327 SW, GW, WW	$\leq 6^{\circ}\text{C}$	Extraction: within 14 days of collection Analysis: within 30 days of extraction
DoD AFFF01 AFFF Concentrate	None	Extraction: within 90 days of collection Analysis: within 30 days of extraction

EPA Method 1633 Preservation & Holding Times

Matrix	Preservation/Extraction	Analysis
<p>Aqueous Landfill leachate: 100 mL Other: 500 mL</p>	<ul style="list-style-type: none"> • If stored $\leq -20^{\circ}\text{C}$, 90 days from collection • If stored $0-6^{\circ}\text{C}$, 28 days from collection if perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids of concern, 7 days from collection 	<ul style="list-style-type: none"> • 90 days from extraction* <p>*issues observed for 11-Cl-PF3OUdS and 9Cl-PF3ONS after 28 days</p>
<p>Soil/Sediment 5 grams</p>	<ul style="list-style-type: none"> • If stored $\leq -20^{\circ}\text{C}$ or $0-6^{\circ}\text{C}$, 90 days from collection 	
<p>Biosolids 0.5 grams</p>	<ul style="list-style-type: none"> • If stored $\leq -20^{\circ}\text{C}$ or $0-6^{\circ}\text{C}$, 90 days from collection $\leq -20^{\circ}\text{C}$ recommended if storing more than few days due to production of gases from microbiological activity at $0-6^{\circ}\text{C}$ 	
<p>Tissue 2 grams</p>	<ul style="list-style-type: none"> • If stored $\leq -20^{\circ}\text{C}$ or $0-6^{\circ}\text{C}$, 90 days from collection $\leq -20^{\circ}\text{C}$ required for fish if sample will not be received by lab within 24 hours 	

If NFHDA of concern in soil/sediment/tissue, extract within 3 days of collection

Field Decontamination

- Reusable field equipment cleaned between samples
- The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluorosurfactants are not listed as ingredients
- Heavy equipment best cleaned at decontamination facility or other containment method
- Use laboratory-verified PFAS-free water in final rinse of decontamination of sampling equipment

Sampling Methods/Different Matrices



Drinking Water Sampling

537.1 or 533 preservation/bottle requirements

Collect from cold tap or spigot at or near wellhead or pump house

Flush water 3-5 minutes before collecting sample

Shake sample after filling to dissolve preservative



Groundwater Sampling

No chemical preservation required.

Low-flow sampling preferred
(keep turbidity down)

Bailers: use with caution: due to PFAS accumulating at air/water interface

No purge grab/passive samplers acceptable to use

Filtering should not be performed



Surface Water Sampling

Sampling guided by beneficial uses
Consider where in water column to sample due to PFAS accumulating at air/water interface

Be mindful of enrichment in PFAS containing foam and bioaccumulation in biota

Passive samplers acceptable to use

Sampling Methods/Different Matrices



Porewater Sampling

Peristaltic pumps: silicon and HDPE tubing
Push-point samplers/drive-point piezometers: stainless steel
Porewater observation devices (PODs): slotted PVC pipe and silicon tubing
PODs/piezometers for permanent sampling points; push-point samplers for temporary locations



Sediment Sampling

Most core and grab devices made of stainless steel. Can have HDPE sleeve in core barrel.
If using waders or personal flotation devices, be careful of water-resistant coatings contacting sample



Wastewater Sampling

Composite sampling for compliance not recommended. Grab sampling preferred.



Fish Sampling

Species of fish and portion of fish sampled depends on project objectives. NOTE: majority of PFAS in fish stored in organs, not flesh.
Wrap in aluminum foil or food-grade polyethylene wrap.
Homogenized tissue should go in HDPE containers.

Filtering of Water Samples: Potential Issues

Evidence that PFAS may sorb onto various filters (e.g., glass fiber filters)



Data may be misinterpreted as PFAS sorbed to soil/sediment in water sample when reduction may actually reflect PFAS sorbed onto filter



Consider use of low flow sampling



Laboratory centrifugation is a good alternative

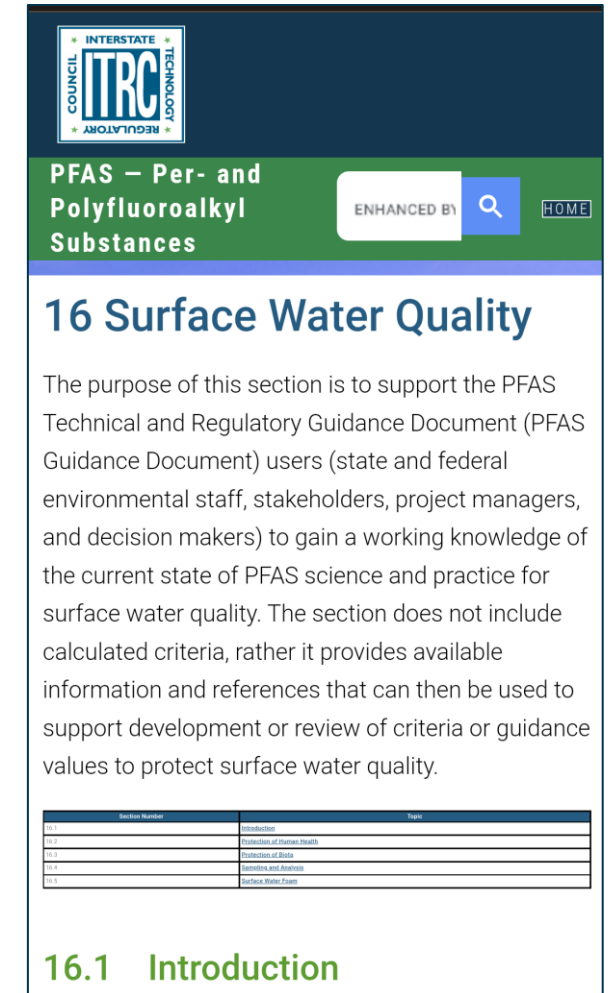


Case Study




Surface Water Sampling Outline

1. Beneficial Uses that need protecting
2. Sampling Considerations – Where, What, Purpose
3. Minnesota Case Study
 - a. PFAS-Containing Foam
 - b. Groundwater/Surface Water



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PFAS – Per- and Polyfluoroalkyl Substances

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16 Surface Water Quality

The purpose of this section is to support the PFAS Technical and Regulatory Guidance Document (PFAS Guidance Document) users (state and federal environmental staff, stakeholders, project managers, and decision makers) to gain a working knowledge of the current state of PFAS science and practice for surface water quality. The section does not include calculated criteria, rather it provides available information and references that can then be used to support development or review of criteria or guidance values to protect surface water quality.

Section Number	Topic
16.1	Introduction
16.2	Protection of Human Health
16.3	Protection of Benthos
16.4	Domestic and Livestock
16.5	Surface Water Fauna

16.1 Introduction

Beneficial Uses

Key Potential Beneficial Uses

- Drinking water source
- Habitat for aquatic life and wildlife
- Human consumption of aquatic organisms
- Human contact with water during recreation
- Agricultural supply – horticulture, dairy operations, ranching
- Groundwater recharge



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Sampling Considerations

Assigned **beneficial use**

- Determine what samples to collect

Potential PFAS **sources**

- Stormwater runoff
- Wastewater discharges
- Biosolids application

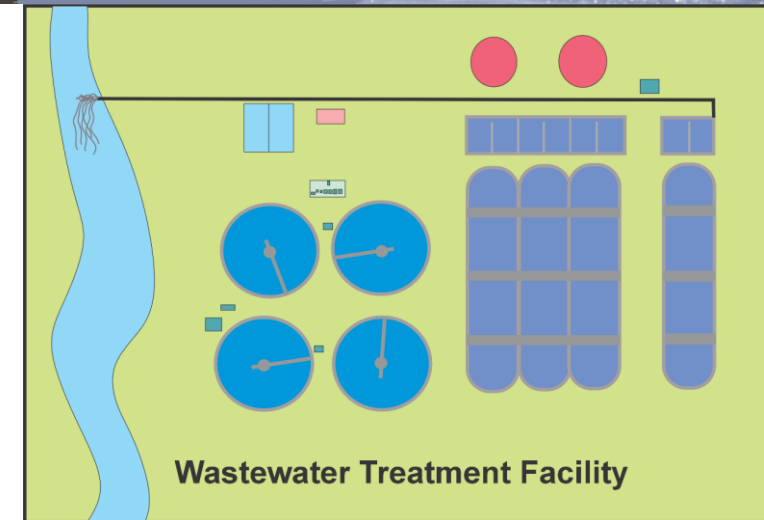
Stormwater Runoff



Biosolids Application to Land



Figures by A. MacDonald.
Used with permission.



Sampling Considerations

- **Location** within water body
Upstream and/or downstream of sources
- **Groundwater/surface water** interactions
To support site characterization and/or identification of sources
Minnesota case study
- Accumulate at **water-air interface**

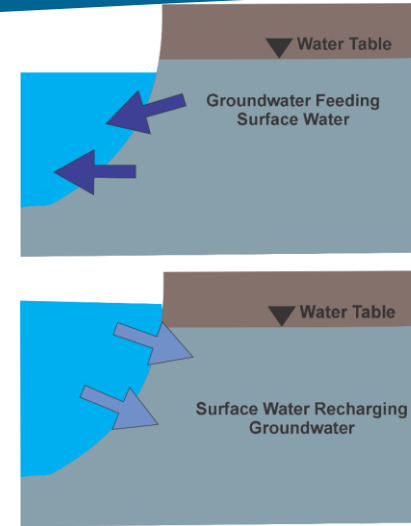


Figure by A. MacDonald. Used with permission.



Photo by Linda Logan

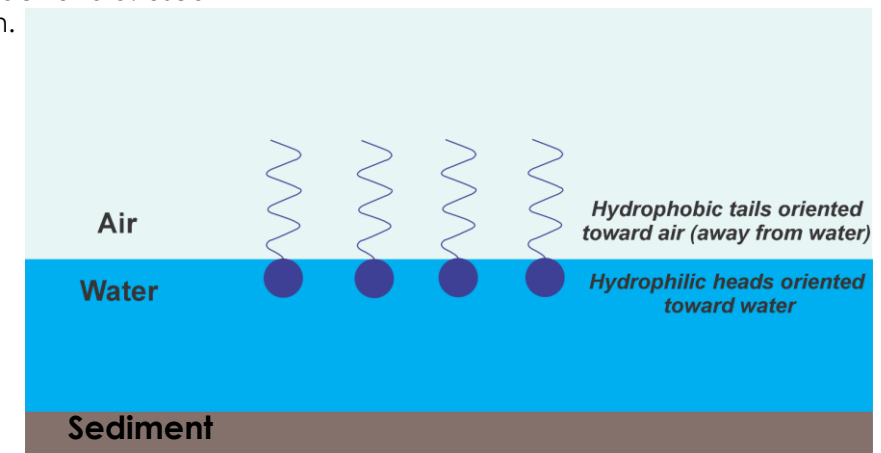


Figure by A. MacDonald, adapted from, Figure 4.1, ITRC 2023, PFAS-1

Sampling Considerations

PFAS-Containing Foam (not AFFF)

- Foam – contains **higher concentrations of PFAS than the underlying layers**; as foam is formed, it removes PFAS from the water column.
- Surface micro layer (about 50 µm thick) - includes the air-water interface. Likely **highest concentration of PFAS in water column**
- Neuston Layer – zone directly below surface micro layer. Rich in aquatic organisms
- Underlying water column
- Minnesota – Guidance under development
- Surface Water Foam PFAS Sampling Guidance – Michigan Dept. of Environment, Great Lakes and Energy, July 2019

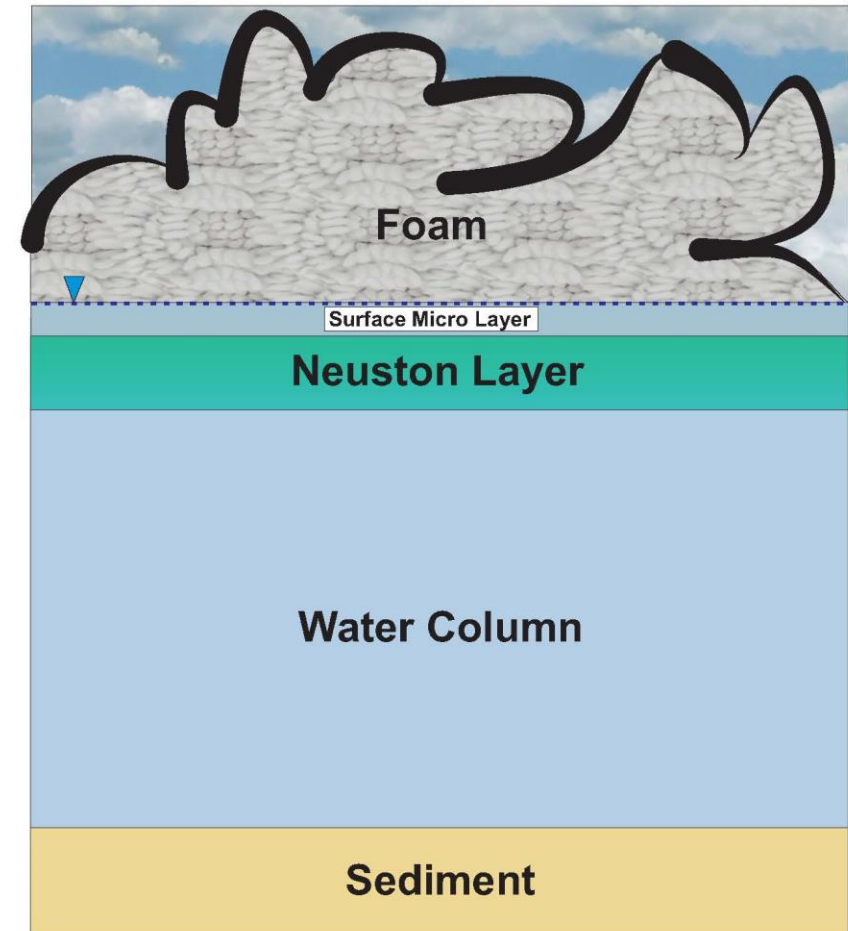


Figure 16-2, PFAS -1

not to scale

Sampling Considerations

PFAS-Containing Foam Considerations

- **Transport** as “foam islands” to a new location
- Collapse of foam and **dissolution of PFAS** back into water column
- PFAS in foam potentially leads to **additional exposure pathways** – both human and ecological receptors



Photographs courtesy of Rebecca Higgins,
State of Minnesota



Sampling Considerations

Biota

- Species of concern
- Size range gathered for human consumption
- Species targeted by birds and mammals
- Tissue types
- Fish Tissue



Photo courtesy of State of Minnesota, Used with permission.

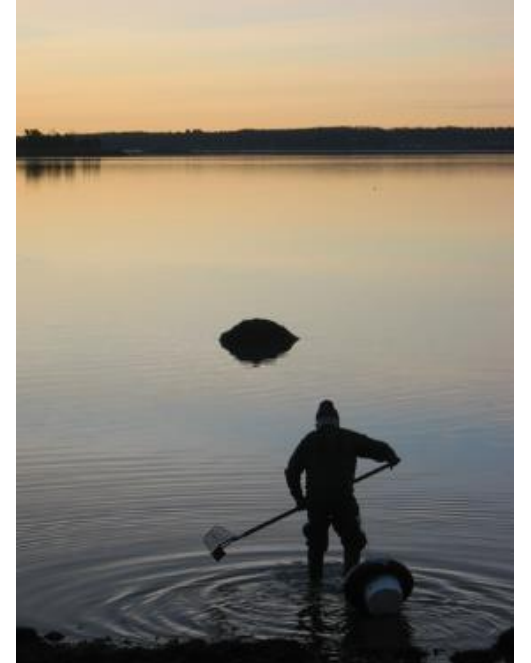
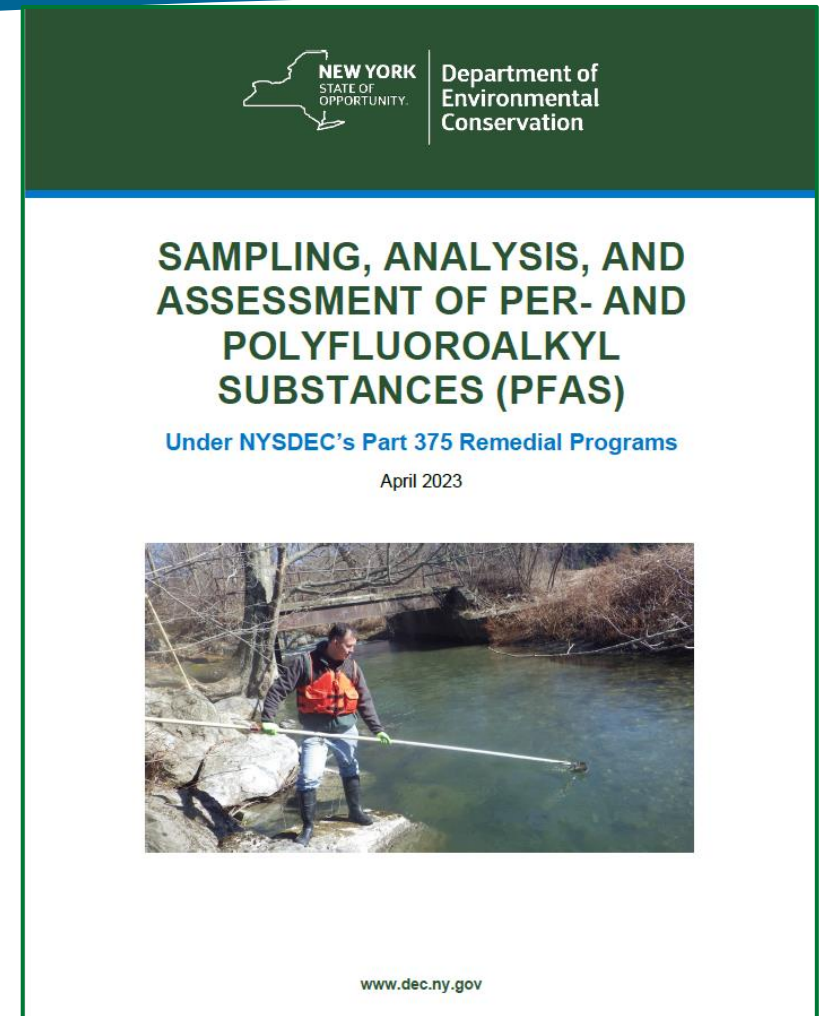


Photo courtesy of J. Petali, NH Department of Environmental Services. Used with permission.

REMINDER! Sampling Guidance

Examples of Other Sampling Guidance

- USEPA's *Compendium of Superfund Field Operations Methods* (USEPA 1987)
- Surface Water PFAS Sampling Guidance by Michigan Department of the Environment, Great Lakes and Energy, 2022
- Fish Tissue PFAS Sampling Guidance, Michigan Department of Environmental Quality, 2019
- Surface Water Foam PFAS Sampling Guidance – Michigan Dept. of Environment, Great Lakes and Energy, July 2019
- PFAS-specific sampling guidance by New York State Department of Environmental Conservation, 2023



Case Study

PFAS-Containing Foam

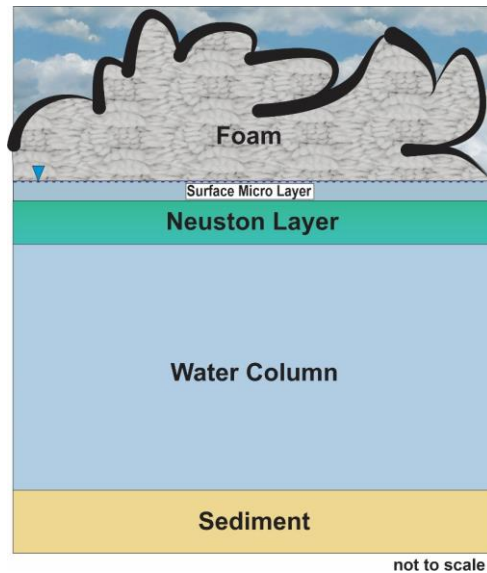
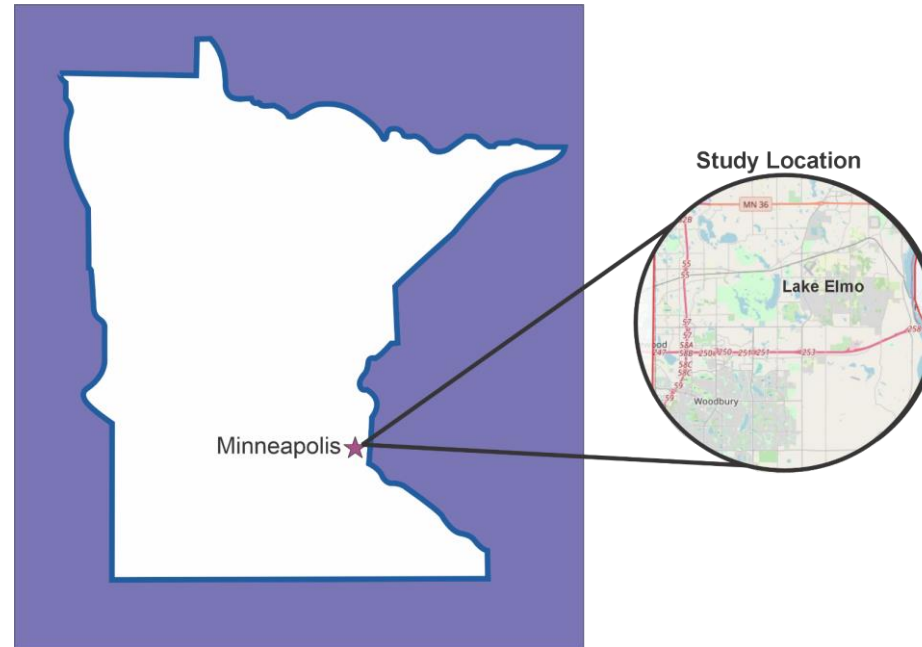
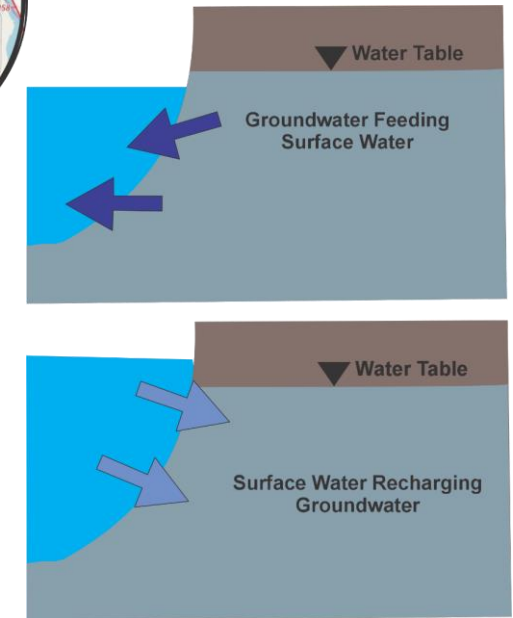


Figure 16-2, PFAS-1



Figures by A. MacDonald.
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Groundwater/Surface Water Interaction

Case Study

Minnesota Project 1007 – located in an area of known PFAS contamination in the Tri-Cities area

Initial samples found PFAS in the creeks, ponds and lakes downstream of the suspected source areas

How did the PFAS get from the source areas to surface water?

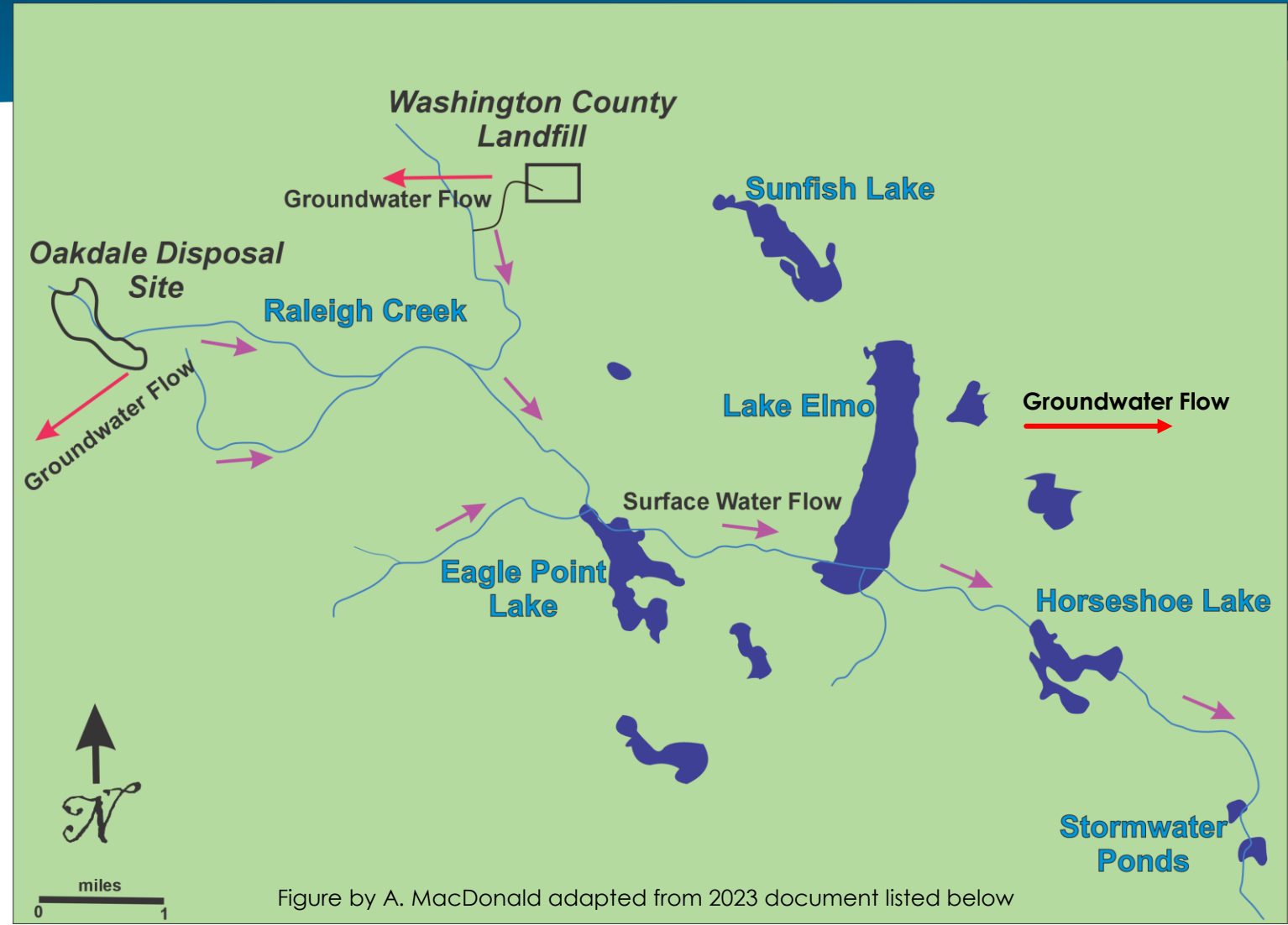


Figure by A. MacDonald adapted from 2023 document listed below

Case Study

- Occurrence of foam on surface water – related to PFAS or not?
- Samples for PFAS collected from surface water foam during 2019-2020
- Samples collected from flowing surface water, stormwater ponds and Lake Elmo.

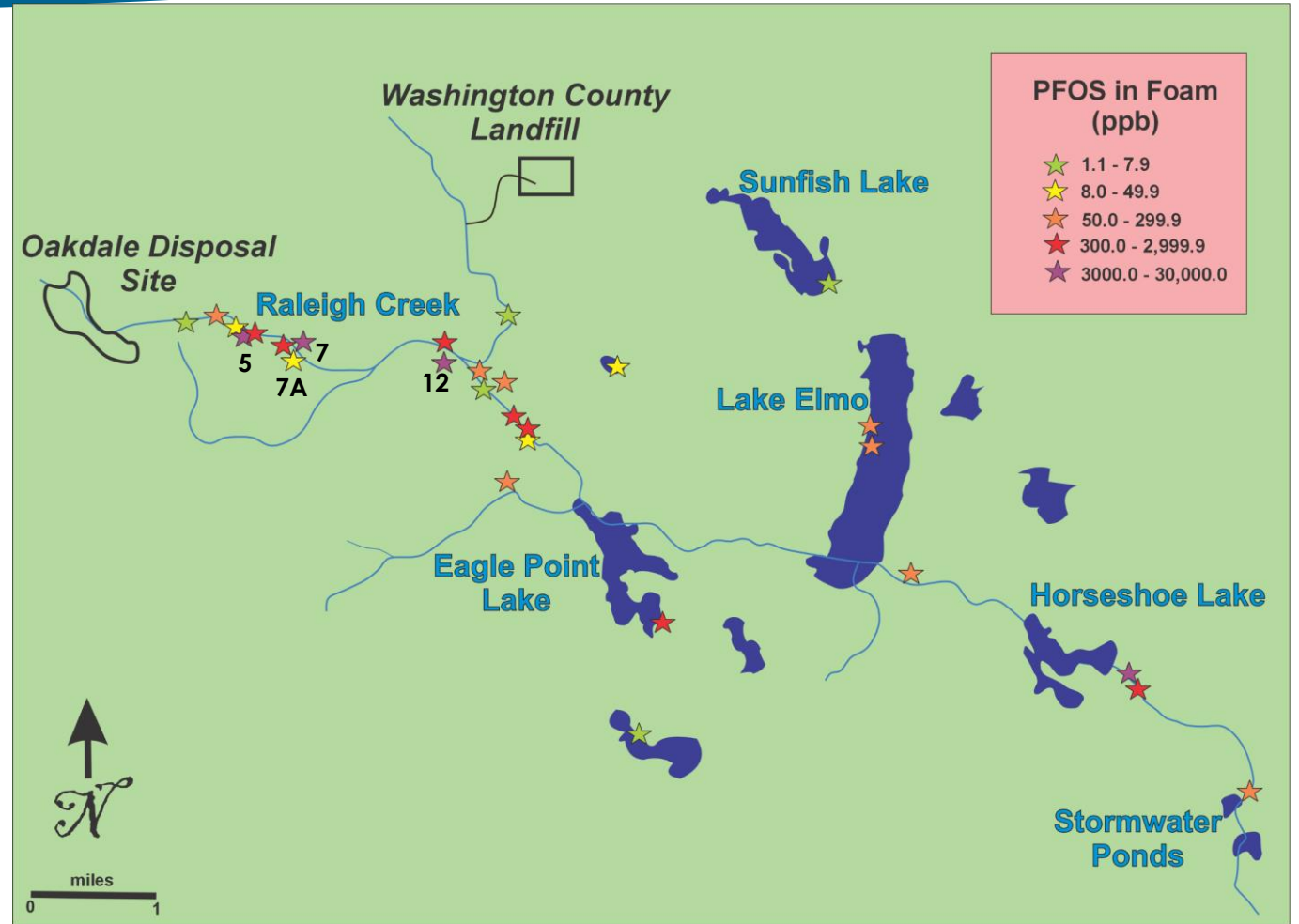
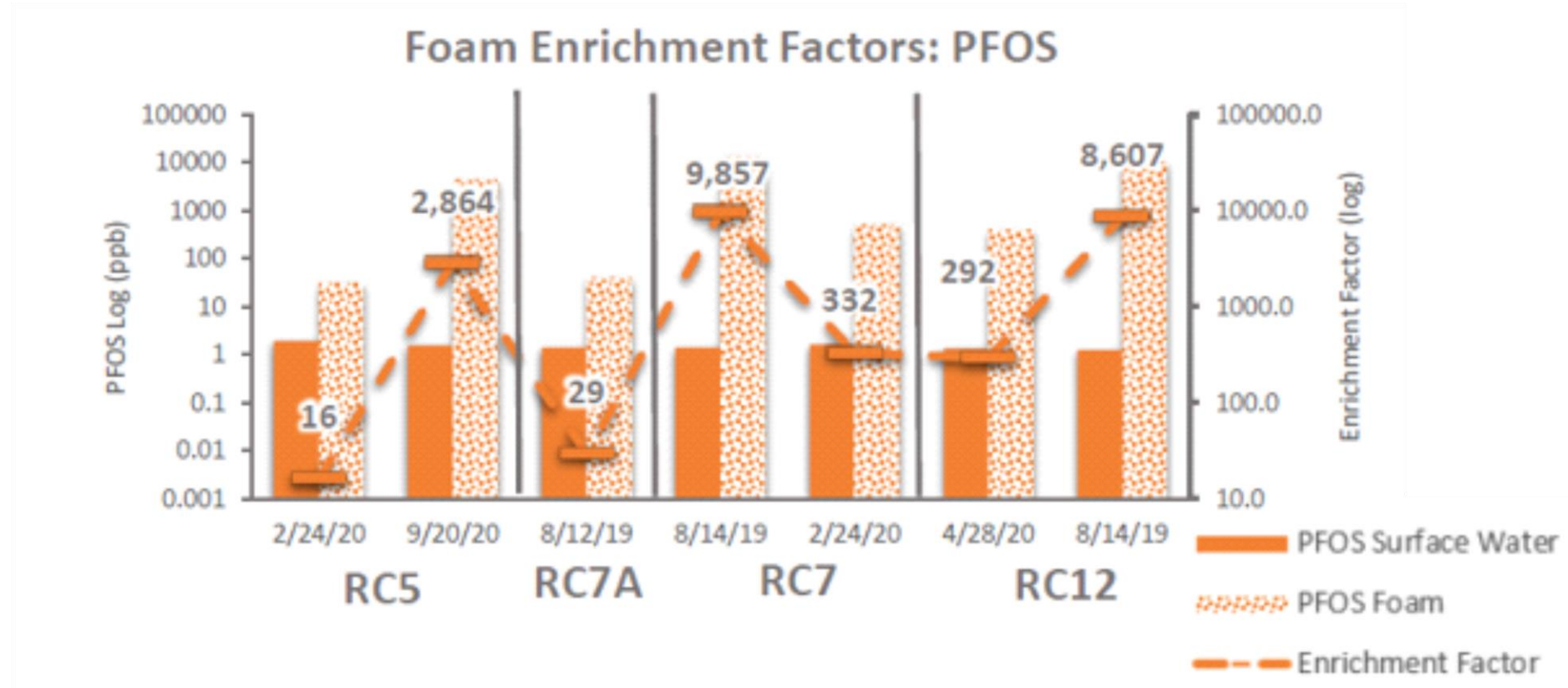


Figure by A. MacDonald adapted from 2023 document listed below

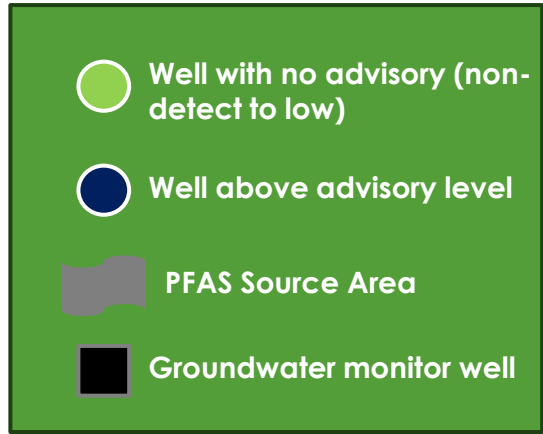
ITRC 2023, PFAS-1, Section 16.5, Surface Water Foam, Section 15.5.1, PFAS-Containing Foam Case Study, Sources: Project 1007 Six-Month Investigation Progress Report, Minnesota Pollution Control Agency, October 13, 2020 and Project 1007 Minnesota Pollution Control, Agency 2023

Case Study

- Enrichment factor
– ratio of concentration in foam to water
- Enrichment factors varied by over an order of magnitude across the study area

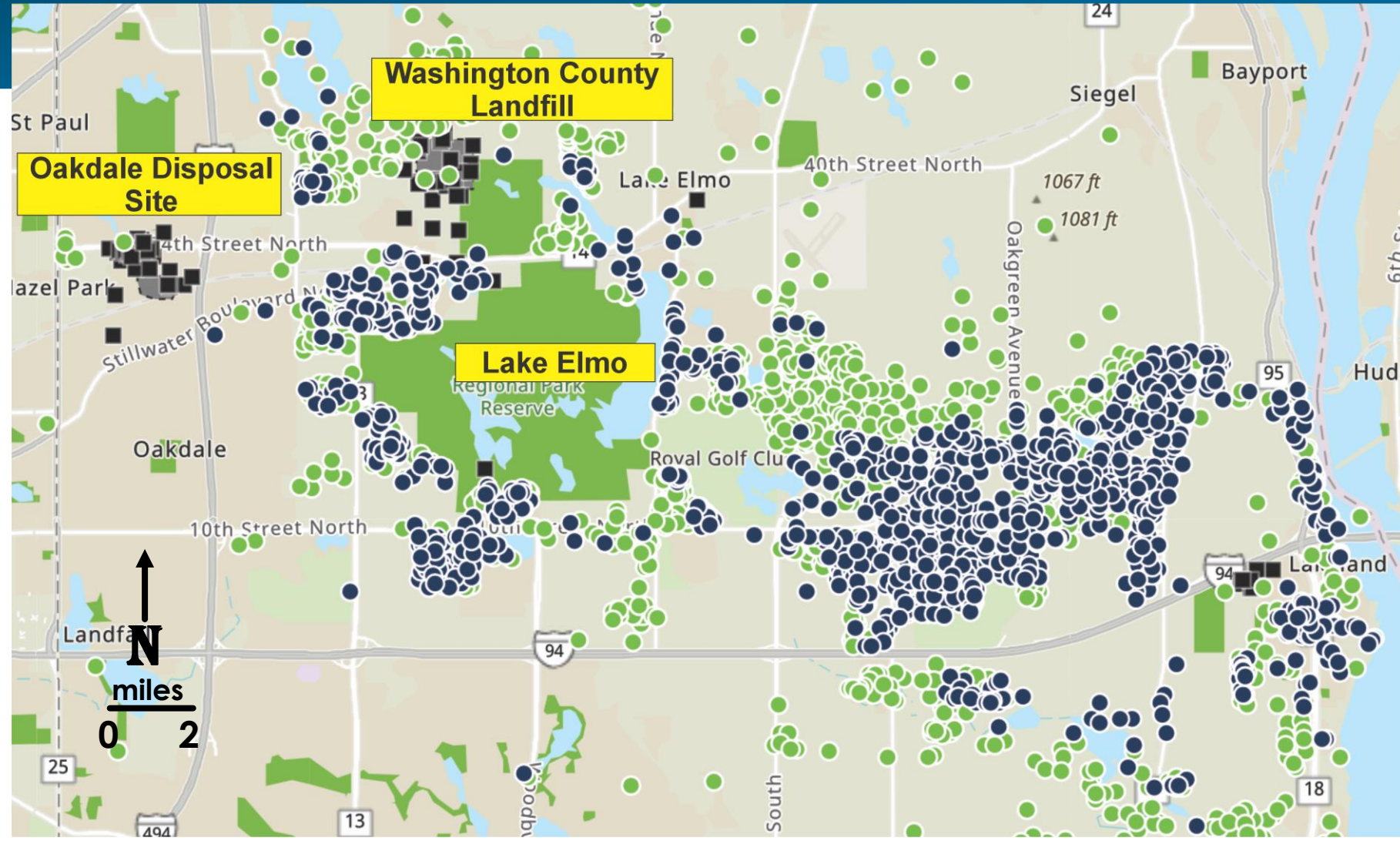


Case Study



Advisory:
PFOS/15
+ PFOA/35
+ PFBS/100
+ PFBA/7000
+ PFHxS/47
+ PFHxA/200
is greater or equal to 1.
(Concentrations in ng/L)

Figure by A. MacDonald with [map](#) from Minnesota Dept. of Health.



PFAS-1, Section 15.5.2, Surface Water/Groundwater Interaction Case Study



Air Sampling



Draft Other Test Method 45 (OTM-45): Air Emissions



USEPA 2021 *Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources*

July 2024: *Revisions issued by USEPA*



Sample and analyze PFAS targets from stationary sources



Additional field QC measures such as field blanks, isotopically labeled PFAS field spikes

Draft OTM-45: Air Sampling for PFAS from Stationary Sources

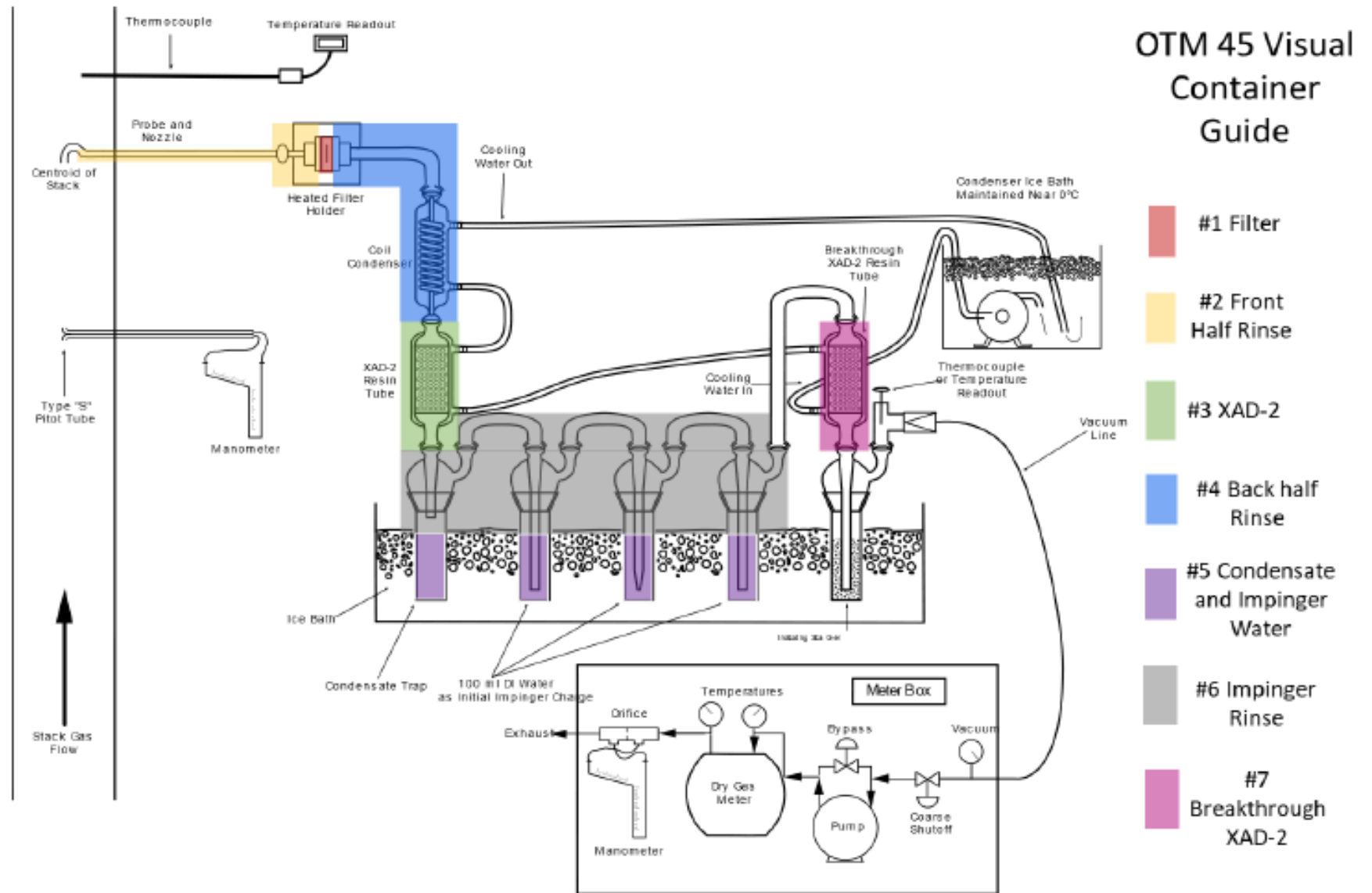


Figure OTM-45-1. Sampling Train

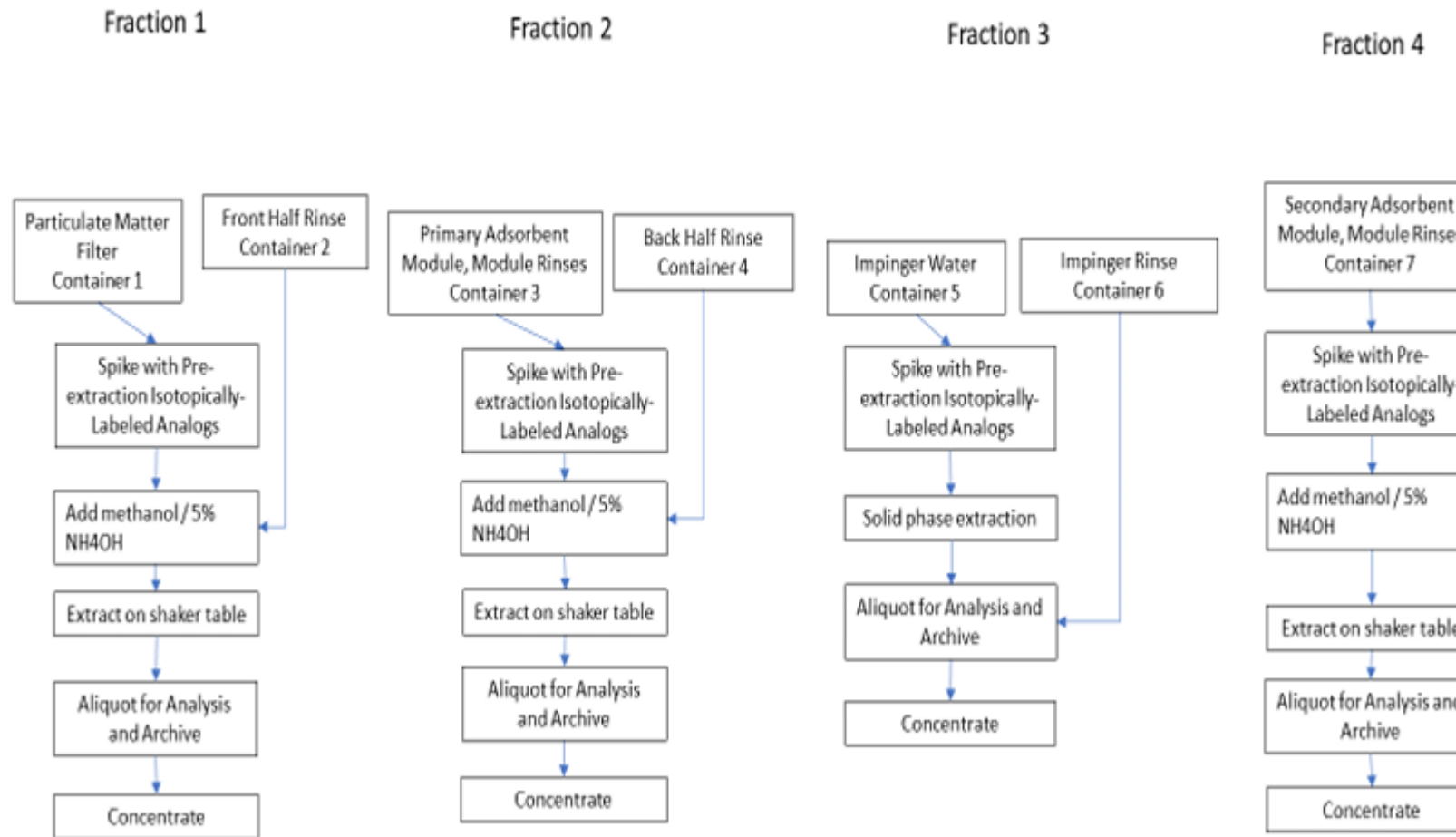
Figures Source: Draft OTM-45 method.

https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

PFAS-1, Section 11.1.7 Sampling Procedures

41

Draft OTM-45: Air Sampling for PFAS from Stationary Sources



- Measures 50 PFAS
- Based on modified EPA Method 5 sampling train
- PFAS collected in 4 fractions
 - Filter
 - Primary XAD-2
 - Impingers
 - Secondary XAD-2 (breakthrough)
- Requires field blank and field spikes

Figures Source: Draft OTM-45 method.

[https://www.epa.gov/sites/default/files/2021-](https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf)

[01/documents/otm_45_semivolatile_pfas_1-13-21.pdf](https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf) PFAS-1, Section 11.1.7 Sampling Procedures



Field Quality Control



Field Quality Control



Table 11-1 lists typical field QC samples



USEPA 537.1
and 533 have
additional
requirements

Minimum 1 field reagent blank/ set of samples / site
and field duplicates

Both methods specify frequency of field duplicate in
terms of extraction batch (1 per extraction batch, not
to exceed 20 field samples), not collection frequency



Additional quality control samples may be needed based on site-specific
work plan and data quality objectives

Collection of Blanks in the Field

Using blanks to evaluate composition or suitable nature of equipment/supplies for sampling, and to assess possibility of cross-contamination during sampling/transport/storage

- **Pre-investigation equipment blanks** (decon water, methanol, new equipment, plastic bags as sample containers, anything you are unsure of)
- **Equipment blanks** to assess adequacy of decontamination process and/or evaluate potential contamination from equipment.
- **Field blanks** to assess contamination from field conditions.
 - Recommended frequency: one blank/day/matrix or one blank/20 samples/matrix, whichever more frequent.
 - **Field reagent blanks** (USEPA Method 537.1, 533) should originate from the laboratory for all drinking-water programs (minimum of 1/event).

Takeaway Messages



Special considerations for PFAS sampling – what matters is what comes into contact with sample; have a practical approach to contamination concerns



PFAS-specific sampling protocols are recommended – general guidelines exist



Method specific requirements for sampling, sample preservation, shipping & holding times vary



Sample event planning/upfront work is key

Questions





Sampling & Analysis

Analytical Methods

Qualitative Analyses

Data Evaluation

PFAS Occurrence in Air

Section 11.2



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Learning Objectives – Reminder

Key elements that make **PFAS sampling** different from other sampling events

Best practices for preparing for and **conducting a PFAS sampling event**

Focus on Surface Water/Foam Sampling

Current state of **PFAS analytical methods**

Basics of **compound-specific PFAS analysis**

Alternative analytical techniques and how they can be useful

Occurrence of **PFAS in air**

USEPA PFAS Drinking Water Methods



USEPA 537.1

Finalized Method (Version 2.0 published 2020)
Compound-Specific Analyses (18 PFAS)



USEPA Method 533

Finalized Method (published 2019)
Compound-Specific Analyses (25 PFAS)
Addresses some compounds that were not included
in Method 537.1 due to poor performance

USEPA 537.1 & 533 PFAS Drinking Water Methods

Similarities

- ▶ Sample preparation via Solid Phase Extraction (SPE)
- ▶ Compound-Specific Analysis by LC-MS/MS
- ▶ Laboratories allowed some modifications, but not:
 - Sample collection/preservation
 - Extraction
 - Quality control
- ▶ Multi-laboratory validated method

Differences

- ▶ Sample collection – chemical preservation
- ▶ Analysis
 - Quantification scheme
 - Analyte Lists
 - Holding time

USEPA PFAS Analytical Methods

Method 537.1 Only		Both Methods 537.1 and 533			Method 533 Only		
NEtFOSAA	NMeFOSAA	PFOA	PFOS	11Cl-PF3OUdS	4:2 FTS	6:2 FTS	8:2 FTS
PFTA	PFTrDA	PFDA	PFDoA	9Cl-PF3ONS	PFBA	PFHpS	PFPeS
		PFHxA	PFUnA	ADONA	PFPeA	PFMBA	PFMPA
		PFBS	PFHpA	HFPO-DA	PFEESA	NFDHA	
		PFHxS	PFNA				

Table 2-5, separate PDF, categorizes the PFAS analytes according to the family tree hierarchy.

USEPA Method 1633

USEPA Method 1633A (December 2024)

- Multi-lab validated for Wastewater, Surface Water, Groundwater, Soils, Sediments, Landfill Leachates, Biosolids, and Tissue

Isotope dilution method

- Compound-Specific Analyses (targeting 40 PFAS)
- GW, SW, WW, Leachate, Biosolid, Tissue, Sediment, Soil

Considerations When Samples Are at the Laboratory



USEPA Methods 537.1 and 533, and USEPA Method 1633 require laboratories to prepare **entire sample** collected, **including sample container rinsate(s)**

DoD AFFF01 requires container holding diluted AFFF concentrate be prepared in its entirety, including a rinse of container

SW-846 Method 8327

July 2021

Compound-Specific Analyses by LC-MS/MS (24 PFAS analytes)

- Does not include all PFAS included in USEPA Method 537.1 or 533

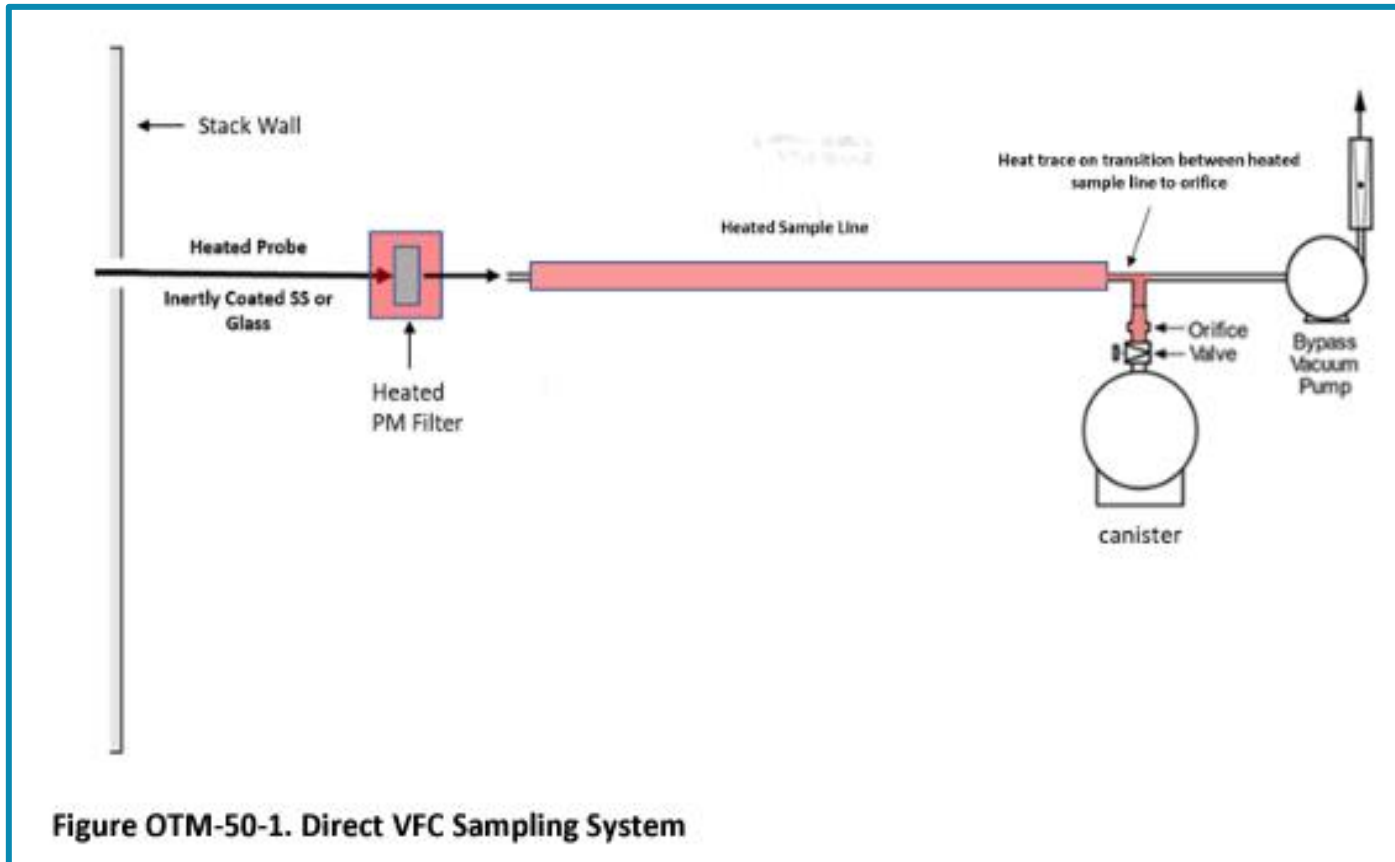
GW, SW, and
WW

No extraction or cleanup

USEPA Draft Other Test Method 45 (OTM-45): Air Emissions

- January 2021
 - Single-laboratory validated
 - July 2024: *Revisions issued by USEPA*
- Compound-Specific Analyses by LC-MS/MS (50 PFAS analytes)
- Semivolatile and nonvolatile polar PFAS in air emissions (stationary sources)
- Includes sampling, sample preparation, and analytical procedures

Draft OTM-50: Sampling for Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters



Compound Name	CAS #	Chemical Formula
Carbon tetrafluoride	75-73-0	CF ₄
Hexafluoroethane (FC-116)	76-16-4	C ₂ F ₆
Tetrafluoroethene	116-14-3	C ₂ F ₄
Trifluoromethane (HFC-23)	75-46-7	CHF ₃
Octafluoropropane	76-19-7	C ₃ F ₈
Difluoromethane (HFC-32)	75-10-5	CH ₂ F ₂
Fluoromethane (HFC-41)	593-53-3	CH ₃ F
Pentafluoroethane (HFC-125)	354-33-6	C ₂ HF ₅
Hexafluoropropene	116-15-4	C ₃ F ₆
Hexafluoropropene oxide (HFPO)	428-59-1	C ₃ F ₆ O
Decafluorobutane	355-25-9	C ₄ F ₁₀
Dodecafluoropentane	678-26-2	C ₅ F ₁₂
Tetradecafluorohexane	355-42-0	C ₆ F ₁₄
1H-Perfluoropentane	375-61-1	C ₅ HF ₁₁
Hexadecafluoroheptane	335-57-9	C ₇ F ₁₆
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1)	3330-15-2	C ₅ HF ₁₁ O
1H-Perfluorohexane	355-37-3	C ₆ HF ₁₃
1H-Perfluoroheptane	375-83-7	C ₇ HF ₁₅
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	3330-14-1	C ₈ HF ₁₇ O ₂
1H-Perfluorooctane	335-65-9	C ₈ HF ₁₇
Octadecafluorooctane	307-34-6	C ₈ F ₁₈
1H-Nonafluorobutane	375-17-7	C ₄ HF ₉
1H-Heptafluoropropane	2252-84-8	C ₃ HF ₇
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	C ₂ H ₂ F ₄
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	C ₂ H ₃ F ₃
Chlorodifluoromethane (HCFC-22)	75-45-6	CHClF ₂
Chlorotrifluoromethane (CFC-13)	75-72-9	CF ₃ Cl
Octafluorocyclobutane (FC-C318)	115-25-3	C ₄ F ₈
Octafluorocyclopentene (FC-C1418)	559-40-0	C ₅ F ₈
Trichloromonofluoromethane (CFC-11)	75-69-4	CCl ₃ F

December 2021

- Multi-laboratory validated

**LC-MS/MS
(PFOA and PFOS
only)**

AFFF Concentrates

- Compliance for military specifications MIL-PRF-24385

Other Published Methods

Finalized Methods

- ISO Method 25101 (ISO 2009): water
- ASTM D7979-20 (ASTM 2020): water
- ASTM D7968-17a (ASTM 2017): soil
- ASTM D8421-22 (ASTM 2022): water
- ASTM D8535-23 (ASTM 2023): soil/biosolids
- FDA C-010.01 Version 2019: food
- CDC:6304.09: blood serum
- ISO/CD 21675:2019 (E): water

Key Quantitation Differences

External Standard (SW-846 8327)

- Surrogates added prior to sample preparation
- Quantitation does not account for bias associated with sample preparation or instrumentation
- Data review must include evaluation of surrogate recoveries

Internal Standard (EPA 537.1)

- Surrogates added before sample preparation and internal standards added to aliquot of extract prior to analysis
- Quantitation does not account for bias associated with sample preparation but DOES account for instrumentation bias
- Internal standard recoveries matter

Isotope Dilution (EPA 533, EPA 1633, DoD AFFF01)

Key Quantitation Differences

Isotope Dilution Quantitation

Isotopically labeled standards added before sample preparation

Quantitation accounts for bias associated with sample preparation AND instrumentation

Isotopically labeled standard recoveries matter

Isotope Dilution: What is It?

- Sample spiked with KNOWN amount of extracted internal standards (EIS) (aka labeled surrogates) prior to centrifuging/extraction
- EIS match target analytes
 - $^{13}\text{C}_4\text{PFBA}$ is EIS associated with PFBA
 - $^{13}\text{C}_4\text{PFOS}$ is EIS associated with PFOS
- Target result corrected by proportional amount based on isotope
- BENEFITS:
 - Corrects for analytical error associated with matrix
 - Corrects for matrix interferences

**EPA 537 does NOT
utilize isotope dilution**

**DoD QSM/1633/EPA
533 require isotope
dilution**

$$\text{Concentration Target} = \frac{\text{Target Area} * \text{True Concentration Isotope}}{\text{Area EIS} * \text{Calibration Factor}}$$



Key Method Consistencies

Methods use liquid chromatography tandem mass spectrometry (LC-MS/MS)

Methods do not address neutral/volatile PFAS
(e.g., fluorotelomer alcohols and derivatized PFCAs)

Standards must be analyzed in order to identify and quantify individual PFAS

Same equipment and supply concerns associated with field
sampling apply to sample preparation and analysis in the lab

Key Method Differences

Method Scope

- Media
- Limit of Detection & Quantitation
- Analytes
(individual and isomeric profile)
- Holding Times

Sample Preparation Processes

- Whole sample vs Aliquot
- Solid Phase Extraction vs solvent dilution
- Clean-up vs no clean-up

Analytical Method Differences

Method	Sample Preparation	Quantitation Scheme	Evaluation of Confirmation Ion Required?	# PFAS Analytes	Quantitation Limits (analyte dependent)
EPA Method 537.1	SPE	Internal Standard	No	18	0.53 to 6.3 ng/L
EPA Method 533	SPE	Isotope Dilution/EIS	No	25	1.4 to 13 ng/L
SW-846 8327	Solvent Dilution	External Standard	Yes	24	SPE = Solid Phase Extraction EIS = Extracted Internal Standard LC/MS/MS = Liquid Chromatography/Dual Mass Spectrometry ng/L = nanograms per liter (ppt) ug/kg = micrograms per kilogram (ppb)
DoD AFFF01	SPE	Isotope Dilution	Yes	2 PFOA/PFOS	
EPA 1633A-Aqueous	SPE	Isotope Dilution/EIS	Yes	40	Landfill leachate: 10-250 ng/L Other: 2-50 ng/L
EPA 1633A-Solid	Solvent Extraction	Isotope Dilution/EIS	Yes	40	Soil/Sediment: 0.2-5 ug/kg Biosolids: 2-50 ug/kg Tissue: 0.5-12.5 ug/kg

Aqueous Samples with Particulates

Issue: Sorption of PFAS to particulates or solids. Longer-chain PFAS and PFASs tend to absorb more to solids.



Labs not consistently handling aqueous samples with suspended solids.

- *Centrifuge sample and decant off water portion for extraction.*
- *Centrifuge sample, decant off water portion for extraction, extract remaining solids, and combine extract with aqueous extract.*
- *Some labs filter the samples, if requested by client.*
- *Centrifuge sample, decant off water portion for extraction, rinse remaining particulates with solvent and add to aqueous portion for extraction.*

Sometimes above procedures not performed and particulates clog the SPE cartridge.

- *Some labs may re-extract sample on dilution.*
- *Some labs may start a new cartridge and attempt to continue extraction remaining sample.*

Aqueous Samples with Particulates

Are your PFAS results representative of total (with solids) or dissolved (water only) measurements?

- Depends on how your lab handled the sample.
- Do you want a total or dissolved measurement?
- Talk to your lab!

Groundwater:

Turbidity >10 NTU: consider “total” measurement if for compliance, delineation, remedial design, risk assessment

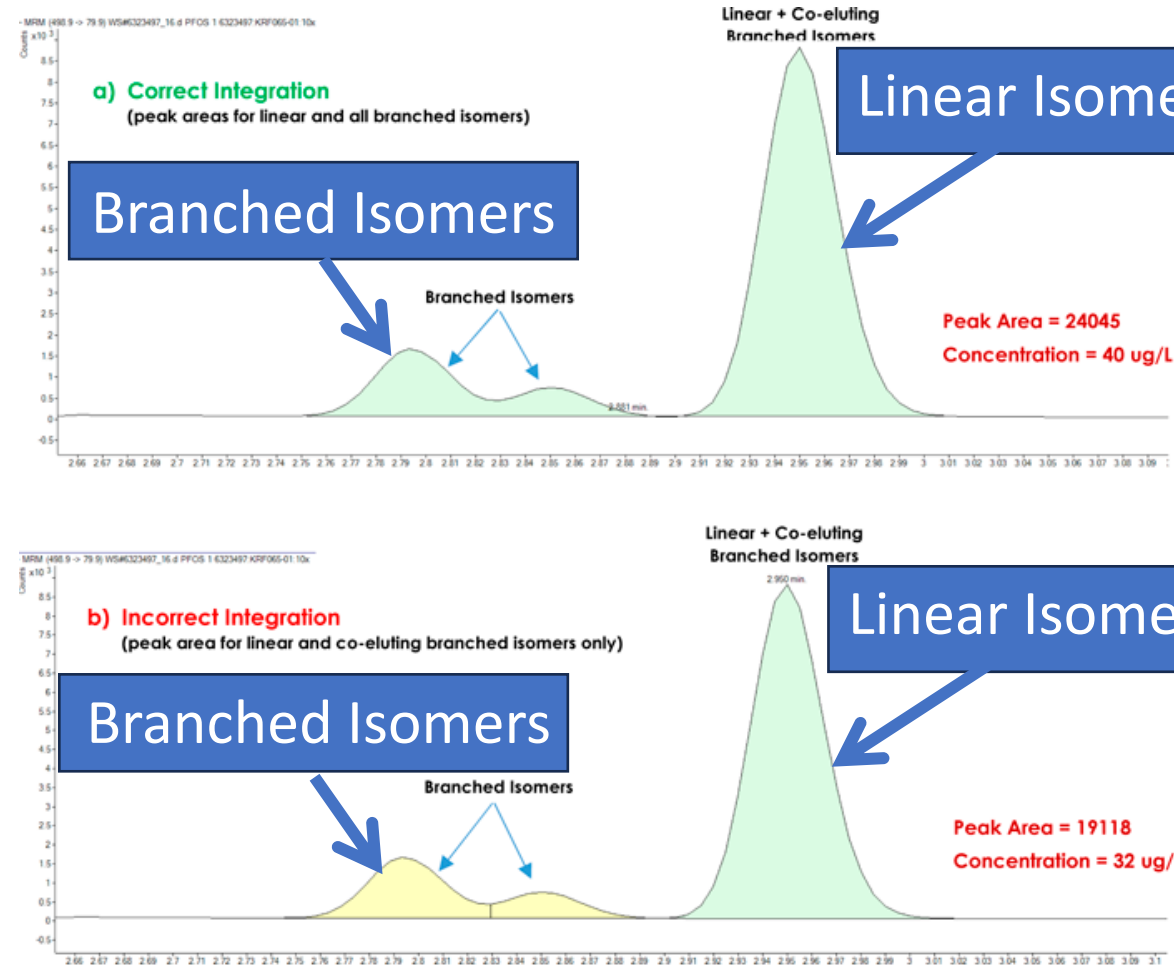
Surface Water:

Consider “total” measurement if for compliance, permitting, remedial design, risk assessment

Drinking water: always “total” measurements

Branched & Linear PFAS

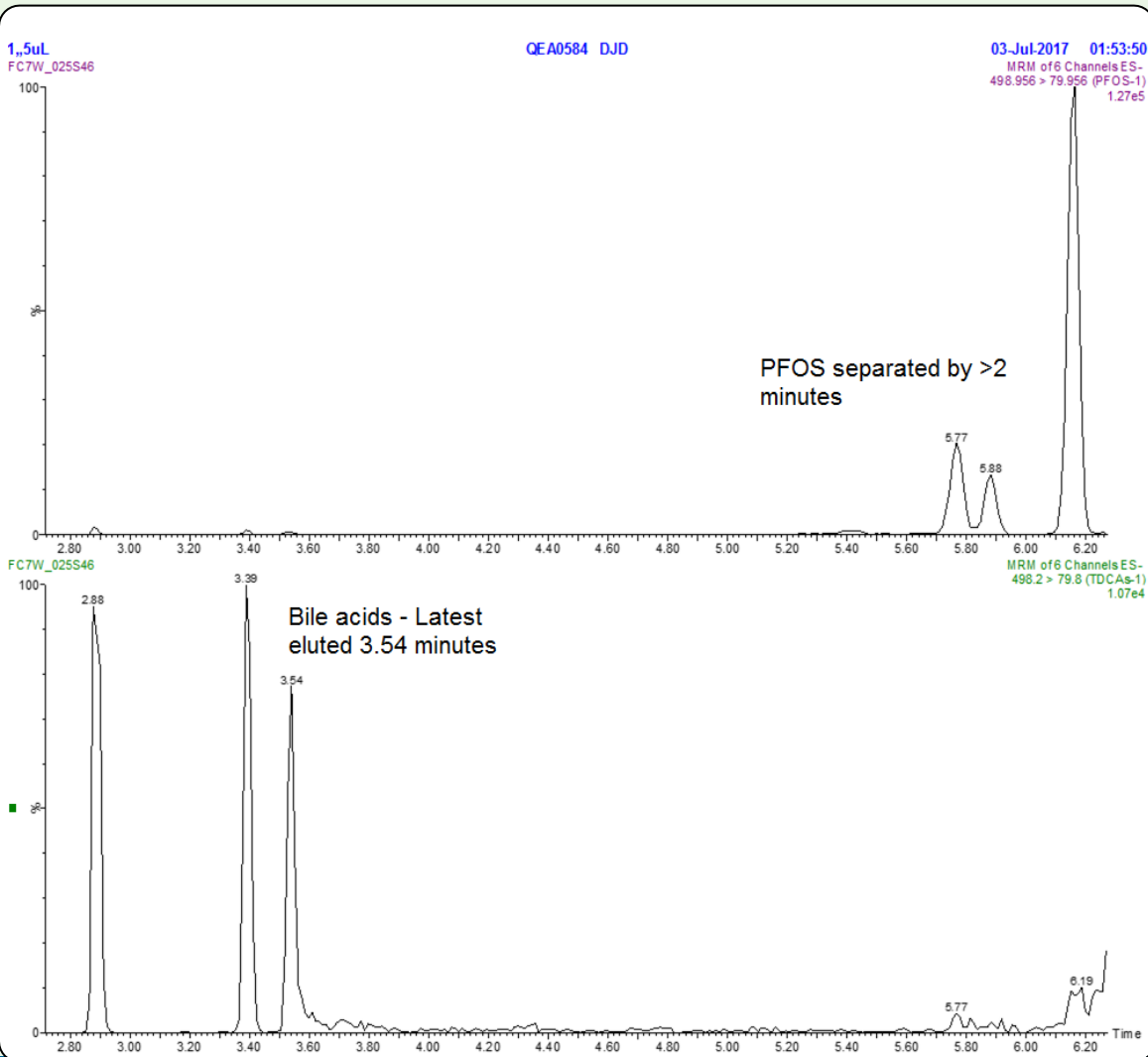
- Branched and linear isomers of PFAS (including PFCAs) produced by ECF seen in consumer products, groundwater, sediment, soil, wastewater, landfills
- Observing branched isomers depends on chromatography
- If ignoring the branched peak, concentrations may be biased low
- Telomer chemistry theoretically produces predominantly linear PFAS, however, final product may contain branched isomers



Currently labs reporting L&B consistently for: PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA

EPA 1633: also includes L&B for PFNA, PFOSA, NMeFOSA, NEtFOSA, NEtFOSE, NMeFOSE

TDCA Interference: Tissue and Wastewater Matrices



- Interferences caused by **co-extraction of bile salts** (taurodeoxycholic acid [TDCA], taurochenodeoxycholic acid, and tauroursodeoxycholic acid) **with PFOS** from **tissue and wastewater matrices**
- Bile salts can vary considerably from sample to sample and by species
- Use of carbon clean-up steps helps eliminate TDCA in most extracts
 - If excessive amounts present in extract, carbon cleanup may only reduce (not eliminate) the amount of these bile salts
- EPA Method 1633A requires chromatographic conditions be adjusted so bile salts elute at retention time > 1 minute from retention time window of PFOS.

Figure Source: <https://www.sgsaxys.com/2019/11/15/bile-acids-and-other-interferences-in-pfas-analysis/>. Used with permission B. Chandramouli. SGS.



Sampling & Analysis

Analytical Methods

Qualitative Analyses

Data Evaluation

PFAS Occurrence in Air



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TOP Assay (qualitative)

Analysis of PFAS using EPA 1633 can significantly underestimate PFAS mass

Total Oxidizable Precursor (TOP) Assay

Analyze sample normally and then after oxidation

Total precursors = $\text{PFAS}_{\text{treated}} - \text{PFAS}_{\text{untreated}}$

Reporting Limits: same as EPA 1633 (~2 ng/L)

- Estimate concentrations of oxidizable precursors in sample.
- Precursors can transform to measurable PFAAs. TOP Assay oxidation forces transformation.
- Predominant precursor transformation products are perfluorocarboxylic acids (PFCAs).
- Increased concentrations of PFCAs after oxidation provide estimate of oxidizable precursors.
- Potential low biases:
 - Incomplete oxidation
 - Lack of quantification of PFCAs < C4

Total Fluorine Screening (qualitative)

Adsorbable organic fluorine (AOF) or Extractable organic fluorine (EOF)

- Detection Limit ~1-2 ug F/L (ppb)
- EPA Method 1621 (AOF)
 - Aqueous samples through carbon sorbent
 - Inorganic fluoride removed prior to analysis
 - Samples combusted: decomposes organics into elemental constituents (i.e., F)
 - Followed by ion chromatography analysis of gaseous stream for F
- Limitations
 - How sample is extracted and treated can affect results
 - High TOC can affect results
 - Short chain PFAS may not sorb to carbon sorbent (negative bias)
 - May overestimate PFAS (e.g., fluorine-containing pharmaceuticals)

May be useful for determining presence/absence of PFAS, confirming a foam is "PFAS-free"



Particle-Induced Gamma Ray Emission: PIGE (qualitative)

Total organic
fluorine (analogous
to TPH)

No speciation

Screening tool; only
available from one
academic/research
lab

DLs: 2.2-15 ug/L
and 10 mg/kg
Fluorine

Looks at total
fluorine content of a
variety of materials
isolated on a thin
surface (0.22 mm)

Nontarget Analysis (NTA)

- Quadrupole Time-of-Flight (QTOF)
- Identify individual PFAS with an established chemical formula, name, and CAS number
- Qualitative results
- Academic labs and some commercial labs have their own libraries
- Lab report is interpretive

May be useful for determining exact PFAS structure when differentiating forensically between 2 different sources



Sampling & Analysis

Analytical Methods

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PFAS Occurrence in Air

Section 11.3



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Published Data Review and Validation Guidelines

- Drinking Water Data Validation Guidance (*Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537* (EPA 910-R-18-001, November 2018)
- Data Review Guidance (USEPA Technical Brief “Per-and Polyfluoroalkyl Substances (PFAS): Reviewing Analytical Methods Data for Environmental Samples.” April 2019)
- DOD Validation Guidance (*Data Validation Guidelines Module 6: Data Validation Procedure for Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-24*, 2022)

Data Review and Validation

PFAS data cannot be adequately evaluated using existing guidelines created for other technologies (for example GC/MS)

Review and validation of PFAS data needs to be performed by someone with a clear understanding of the technology utilized (LC-MS/MS)

Takeaway Messages

There are a number of PFAS analytical methods published

Significant differences between methods need to be evaluated when selecting a method in order to achieve project's DQOs.

Additional analytical methods are currently in development

Less-standardized analytical techniques can be helpful as a qualitative, or screening tool

What Else?

Released since September 2023 ITRC Tech Reg Publication

- Draft OTM-50: source emissions; 30 volatile PFAS
- EPA 1633 Method
- EPA 1621 Method

What to Watch Out For

- EPA OTM-55: non-polar semi-volatile and non-volatile PFAS compounds, including fluorotelomer alcohols (FTOHs) and PIC/Ds
- EPA 3512/8327 Updates
- EPA Aqueous Leaching Methods (LEAF)
- EPA Non-Targeted Analysis Method
- EPA Extractable Organic Fluorine (EOF) Method
- EPA TOP Assay Method
- GC-MS/MS Target Analysis of Semi-volatile PFAS Precursors
- ASTM Direct Injection Drinking Water Method
- ASTM PFAS Data Evaluation Guide



Sampling & Analysis

Analytical Methods

Qualitative Analyses

Data Evaluation

PFAS Occurrence in Air



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Learning Objectives – To Understand:

Key elements that make **PFAS sampling** different from other sampling events

Best practices for preparing for and **conducting a PFAS sampling event**

Focus on Surface Water/Foam Sampling

Current state of **PFAS analytical methods**

Basics of **compound-specific PFAS analysis**

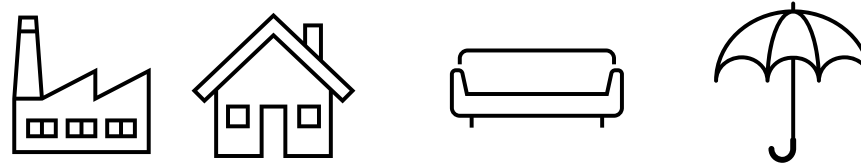
Alternative analytical techniques and how they can be useful

Occurrence of **PFAS in air**

Learning Objectives

Understand the relative concentrations of PFAS observed in air, including:

- Outdoor Air
- Indoor Air
- Settled Dust
- Precipitation



Section 6.1: Media-specific Occurrence: Air

Section 17.1: Additional Information for Media-specific Occurrence

Limitations

The media-specific tables in section 17 are intended to provide context to the reader and serve as a starting point for further study as new information on PFAS occurrence is constantly being added to the literature.

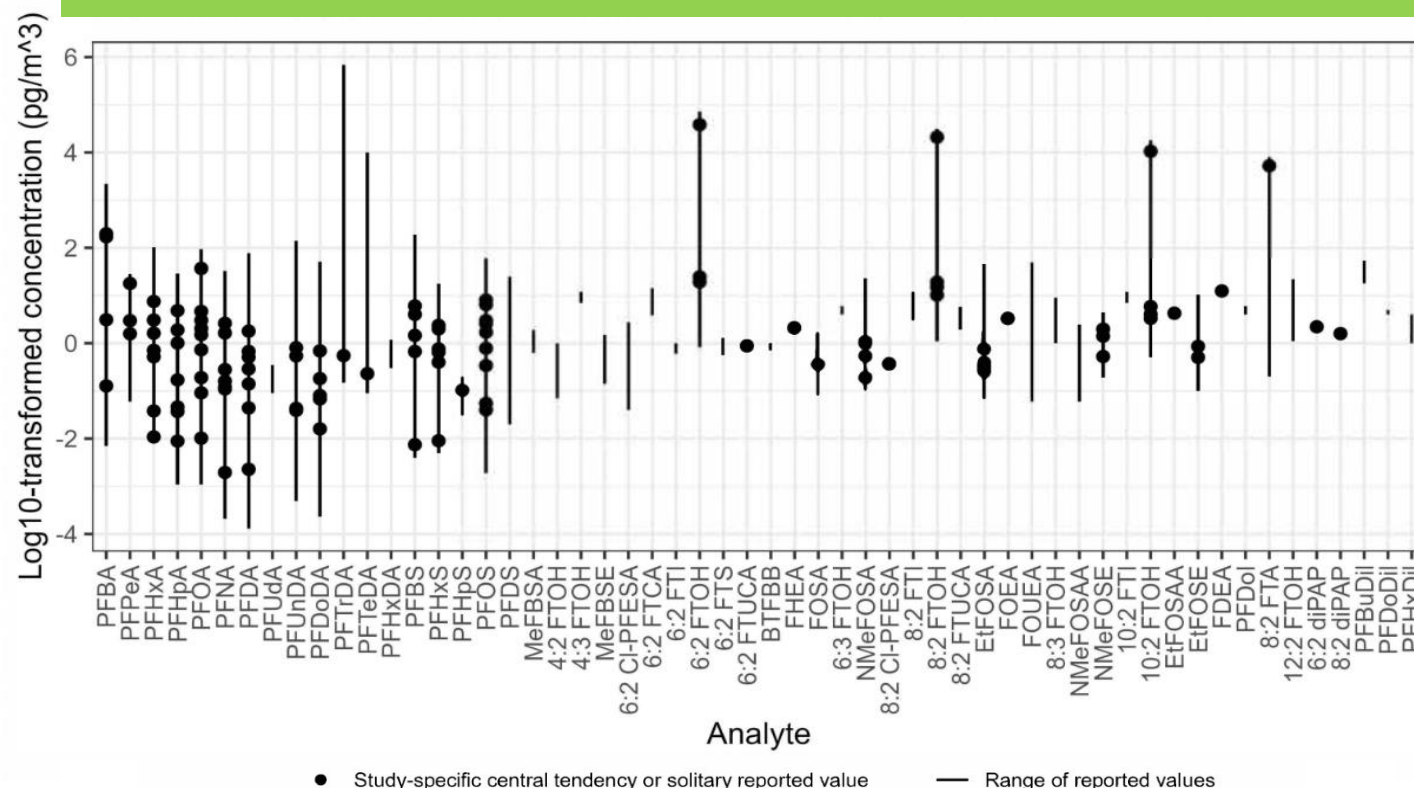
Outdoor Air

Based on review of recent literature (2017 – 2022):

- Typical range for **PFOA** and **PFOS** ~1-30 pg/m³
- **Near major industrial sources** (China and S. Korea)
 - **Max. PFOA** ~ 50-200 pg/m³
 - **PFOS** > 2,000 pg/m³
- **FTOHs** in the hundreds of pg/m³

Figure 6-1A and Table 17-1A

Figure 6-1A: Observed concentrations of PFAS in outdoor air



Sources: Casas et al. (2020), Casas et al. (2021), Lee et al. (2020), Lin et al. (2022), Morales-McDevitt et al. (2022), Rauert et al. (2018a), Rauert et al. (2018b), Seo et al. (2019), Sha et al. (2022), Wang Q. et al. (2022), Wang S. et al. (2022), Yamazaki et al. (2021), Zhao et al. (2017), Zao et al. (2020), Zhou et al. (2021)

Source: Figure developed using ggplot2 (Wickham 2016)

Indoor Air

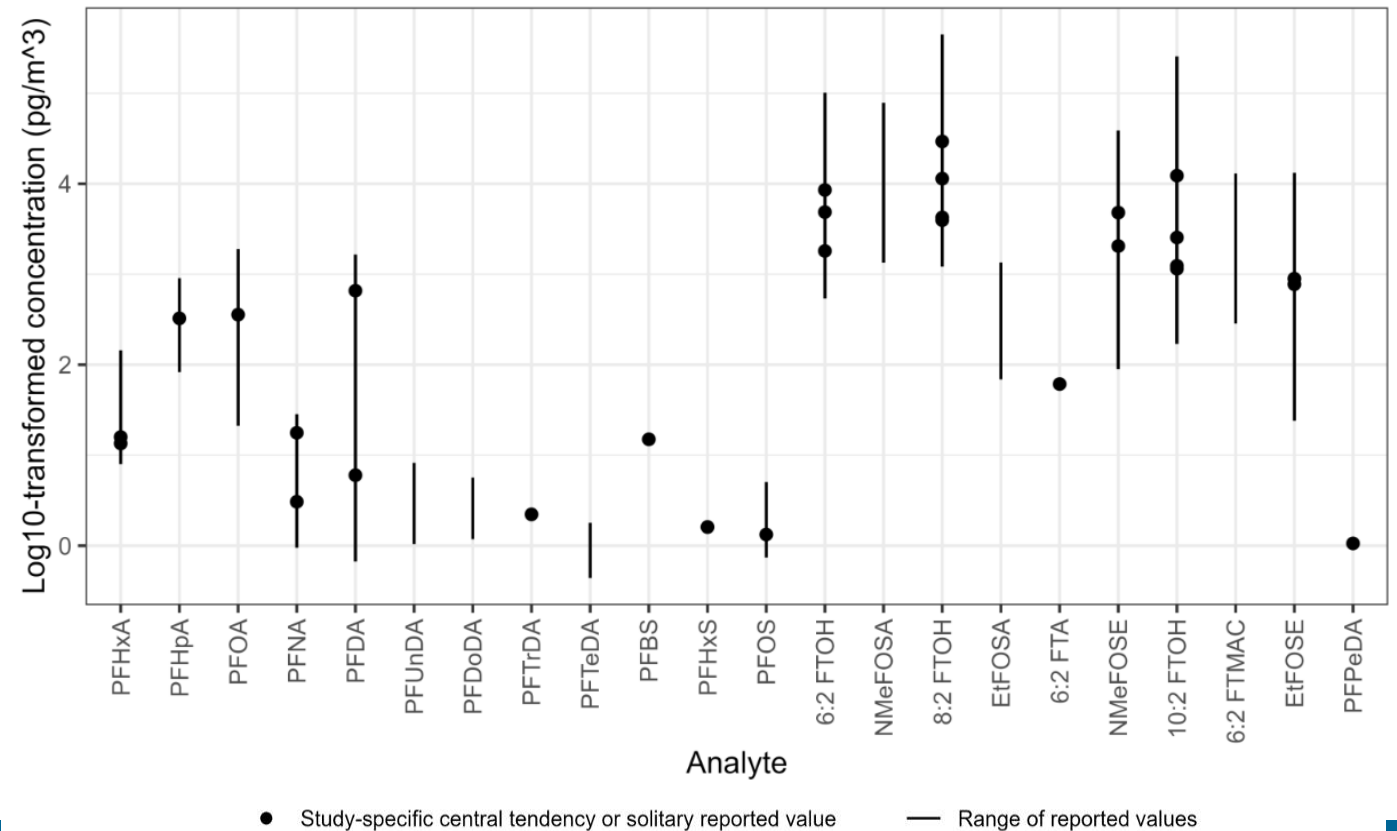
Concentrations can be higher than outdoors due to the presence of indoor sources

Based on review of recent literature (2017-2022):

- **PFOA** (in $PM_{2.5}$) ranged from ~ 200 - $1,900 \text{ pg/m}^3$ in **kindergartens** (Hong Kong)
- In Finnish **homes**, **max. PFOA and PFOS** $\sim 100 \text{ pg/m}^3$ and 7 pg/m^3 , respectively
- **FTOHs** observed in the **hundreds of thousands of pg/m^3** in **homes** (Finland)

Figure 6-1B and Table 17-1B

Figure 6-1B: Observed concentrations of PFAS in indoor air



Sources: Beesoon et al. (2012), Li et al. (2021), Padilla-Sanchez et al. (2017), Wilkens et al. (2017)

Source: Figure developed using ggplot2 (Wickham 2016)

Settled Dust

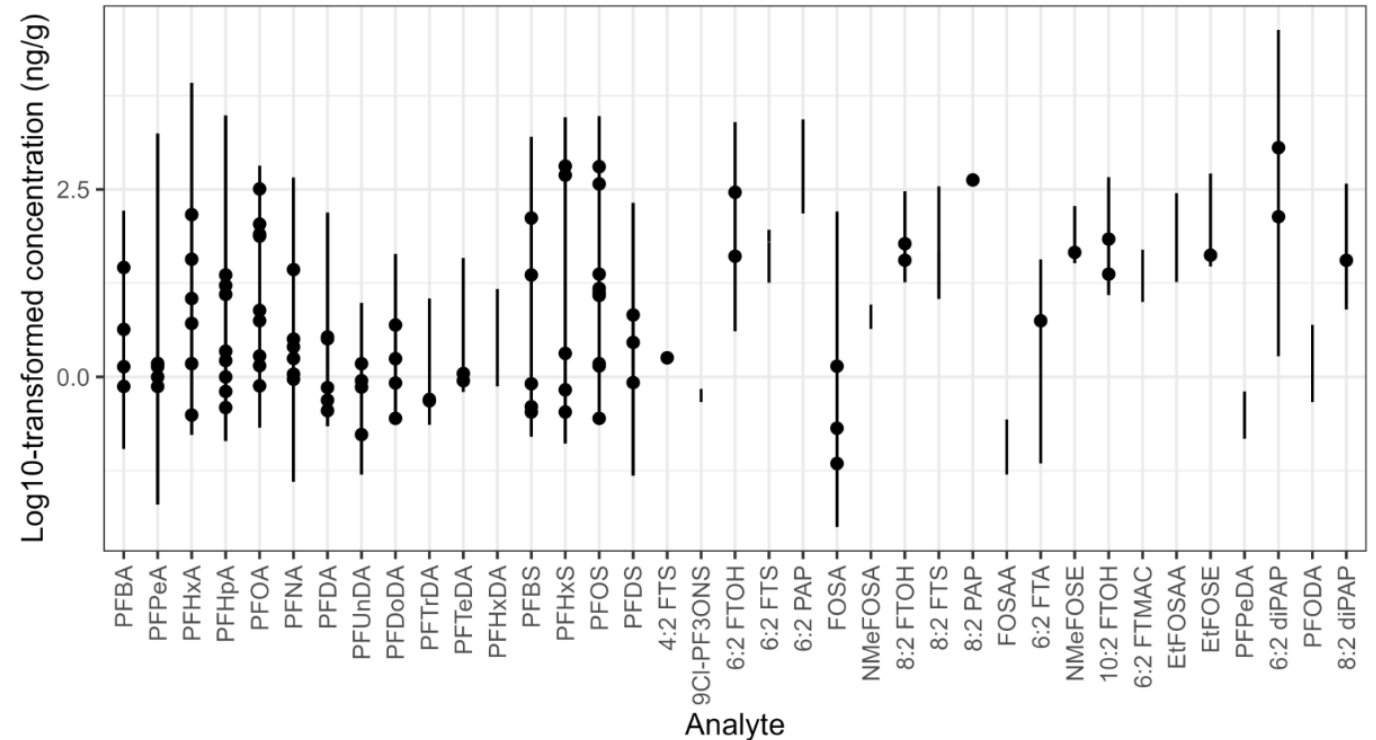
PFAS found in dust from floors, A/C filters, and carpets in schools, childcare facilities, homes, and workplaces

Based on review of recent literature (2017-2022):

- **PFOA and PFOS** range from nondetect to ~650 ng/g and 3,000 ng/g, respectively
- **FTOHs** range from nondetect to ~2,500 ng/g
- **diPAPs** observed in preschools from nondetect to > 42,000 ng/g (Stockholm, Sweden)

Figure 6-1C and Table 17-1B

Figure 6-1C: Observed concentrations of PFAS in settled dust



● Study-specific central tendency or solitary reported value — Range of reported values

Sources: Ao et al. (2019), Beesoon et al. (2012), Basis et al. (2019), Byrne et al. (2017), de la Torre et al. (2019), Giovanoulis et al. (2019), Young et al. (2020), Zheng et al. (2020)

Source: Figure developed using ggplot2 (Wickham 2016)

Precipitation

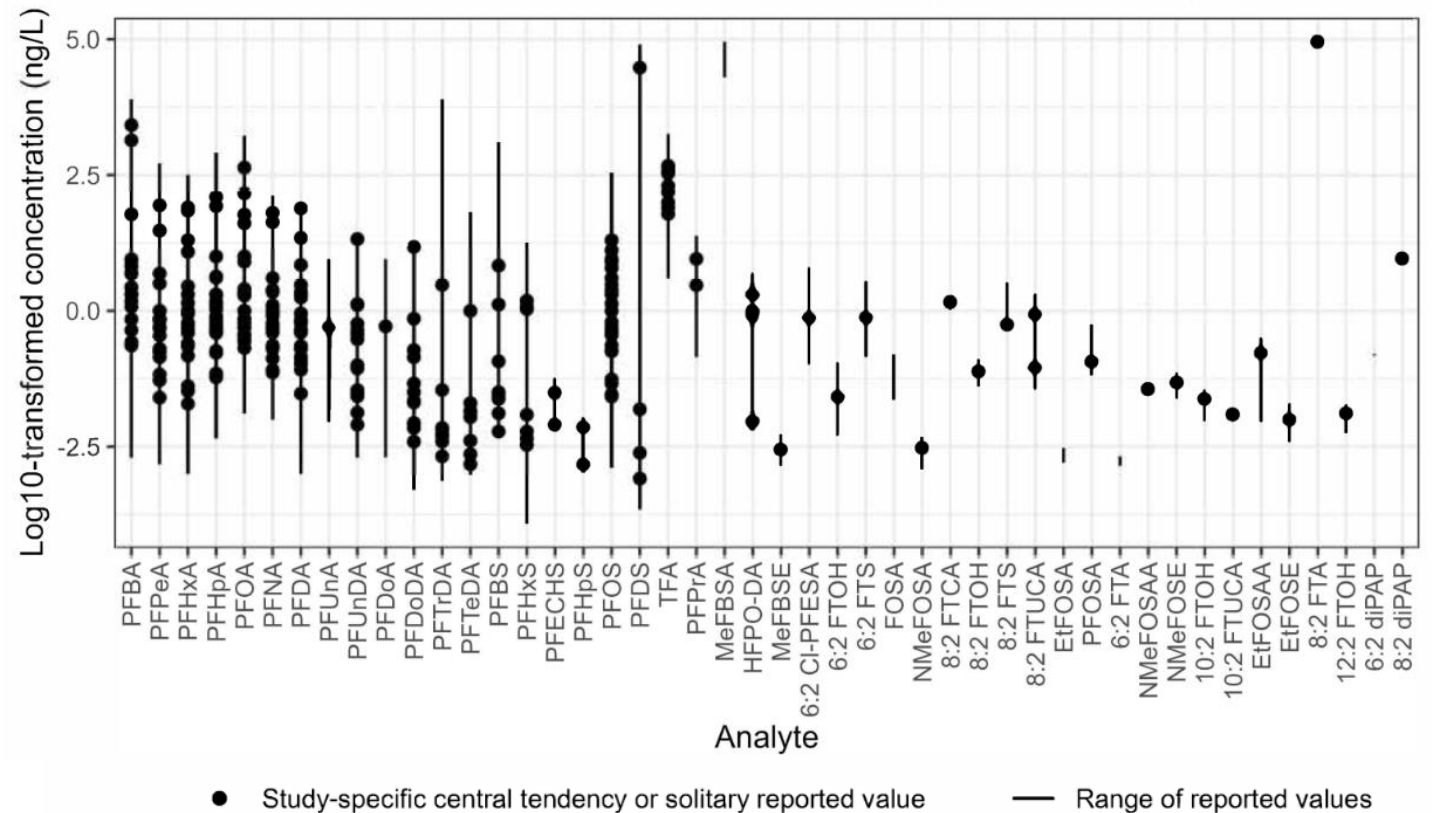
PFAS observed in rainwater, surface and subsurface snow, sea ice, and meltwater

Based on review of the literature (thru 2022):

- Concentrations vary over **many orders of magnitude**
- PFOA and PFOS** typically <1 ng/L in **remote areas** and >1,600 ng/L and 50 ng/L, respectively, in more **populated regions**
- FTOHs and FTSA** > 100 ng/L and **FTUCAs** as high as ~2 ng/L
- GenX** found in precipitation as high as 5 ng/L

Figure 6-1D and Table 17-1C

Figure 6-1D: Observed concentrations of PFAS in precipitation



Sources: Barton et al. (2017), Casal et al. (2017), Casas et al. (2021), Chen et al. (2019), Garnett et al. (2021), Gewurtz et al. (2019), Kim and Kannan (2007), Lu et al. (2018), MacInnis et al. (2019), Pike et al. (2020), Taniyasu et al. (2008), Wang et al. (2019), Xie et al. (2020), Yeung et al. (2017), Zhen et al. (2015)

Source: Figure developed using ggplot2 (Wickham 2016)

Learning Objectives – Recap

Key elements that make **PFAS sampling** different from other sampling events

Best practices for preparing for and **conducting a PFAS sampling event**
Focus on Surface Water/Foam Sampling

Current state of **PFAS analytical methods**

Basics of **compound-specific PFAS analysis**

Alternative analytical techniques and how they can be useful

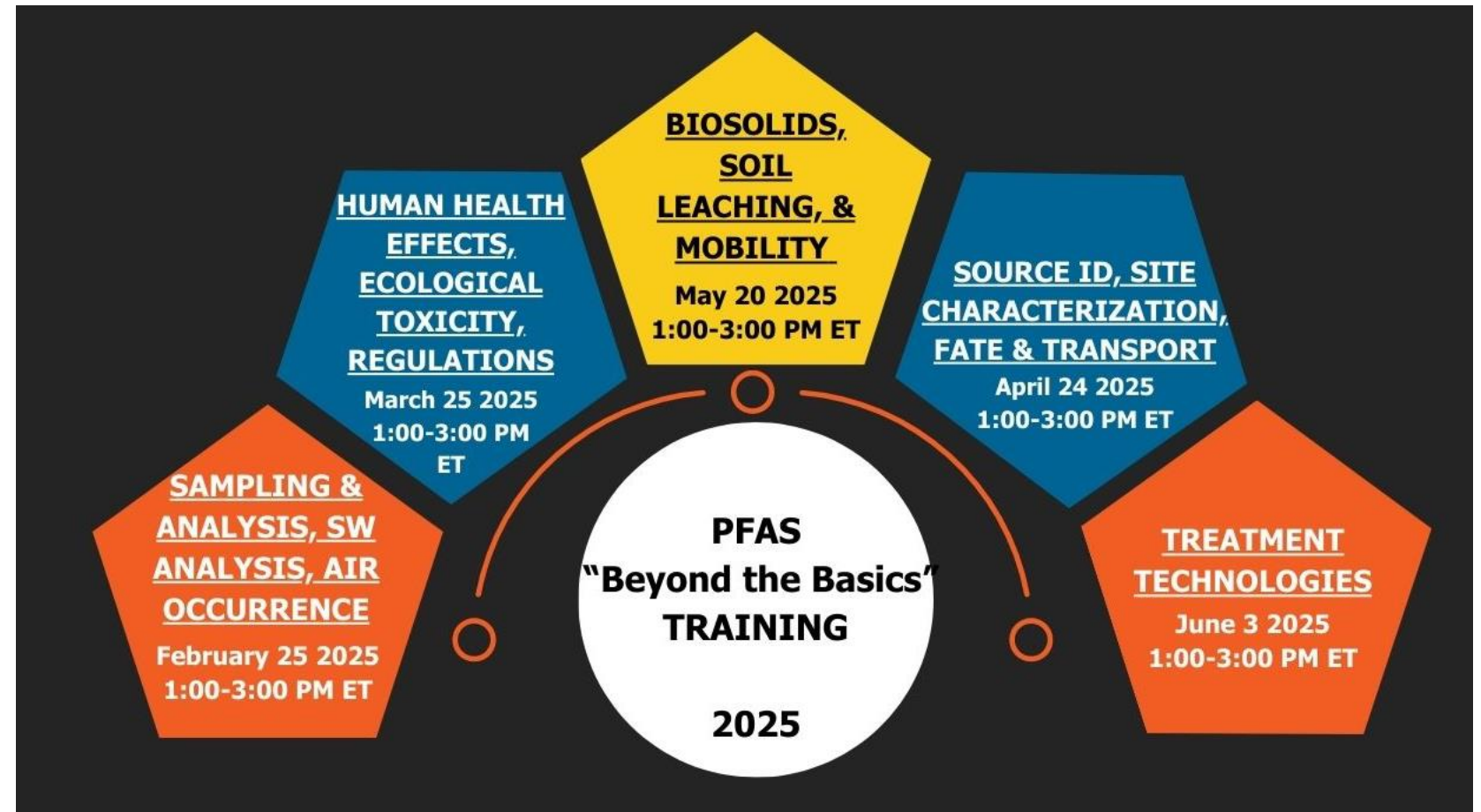
Occurrence of **PFAS in air**

Questions



Feedback Form & Certificate:

<https://www.clu-in.org/conf/itrc/PFAS-BTB-1/>



<https://pfas-1.itrcweb.org/>