Housekeeping

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

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PFAS: Beyond the Basics Training

- Sampling
- Analytical Methods
- Qualitative Analyses
- Data Evaluation
- PFAS Occurrence in Air

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

Today's PFAS Trainers

Kristi Herzer
Vermont Department of Environmental Conservation

Elizabeth Denly
TRC

Chris Zevitas
US DOT

Jamie Fox
Enthalpy Analytical

Alex MacDonald
Retired

ITRC PFAS Resources

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

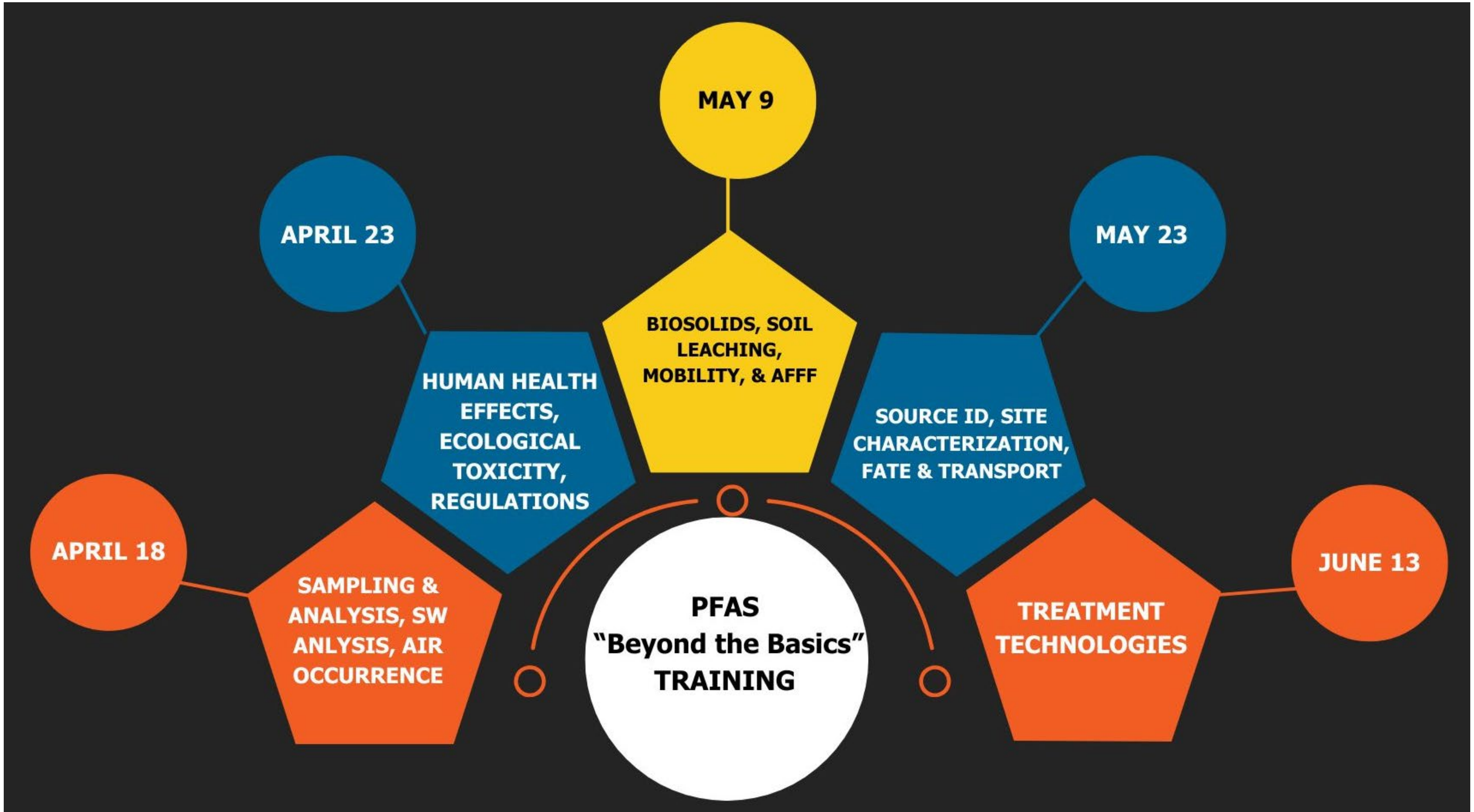
PFAS Introductory Training

- 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: 2024 "Beyond the Basics" Training Modules



PFAS "Beyond the Basics" TRAINING

APRIL 18
SAMPLING & ANALYSIS, SW ANLYSIS, AIR OCCURRENCE

APRIL 23
HUMAN HEALTH EFFECTS, ECOLOGICAL TOXICITY, REGULATIONS

MAY 9
BIOSOLIDS, SOIL LEACHING, MOBILITY, & AFFF

MAY 23
SOURCE ID, SITE CHARACTERIZATION, FATE & TRANSPORT

JUNE 13
TREATMENT TECHNOLOGIES

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

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

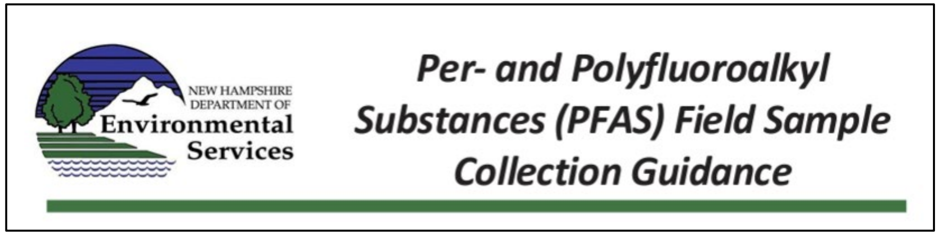
- **Table 11-2,** Finalized published methods basics
- **Table 11-3**, Finalized published methods specifics
- **Table 11-4**, Published methods analyte lists
- **Table 11-5,** Draft published methods
- **Table 11-6,** PFAS analytical data usability table

Section 16.4: Surface Water, Sampling & Analysis

Section 16.5: Surface Water Foam

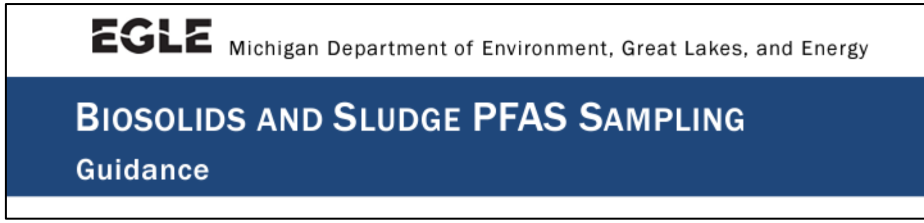
Published Sampling Guidance

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



NEW HAMPSHIRE DEPARTMENT OF Environmental Services

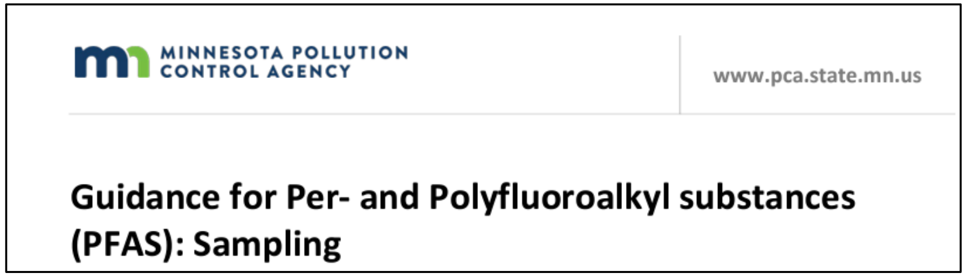
Per- and Polyfluoroalkyl Substances (PFAS) Field Sample Collection Guidance



EGLE Michigan Department of Environment, Great Lakes, and Energy

BIOSOLIDS AND SLUDGE PFAS SAMPLING

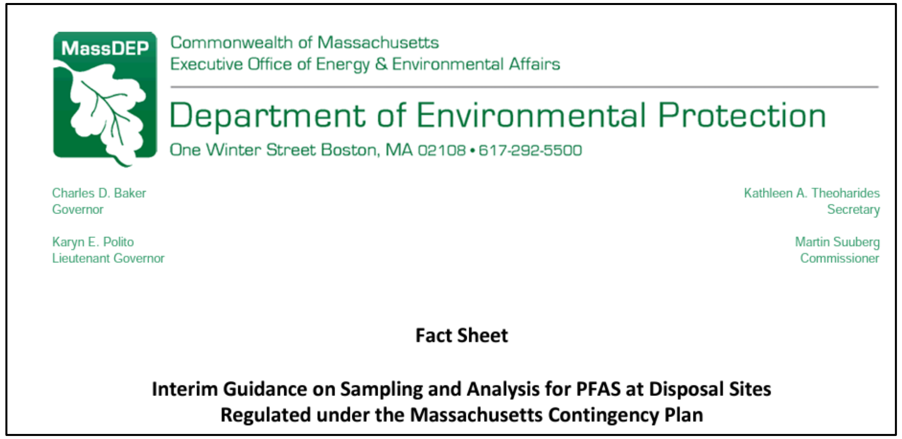
Guidance



MINNESOTA POLLUTION CONTROL AGENCY

www.pca.state.mn.us

Guidance for Per- and Polyfluoroalkyl substances (PFAS): Sampling



MassDEP

Commonwealth of Massachusetts
Executive Office of Energy & Environmental Affairs

Department of Environmental Protection

One Winter Street Boston, MA 02108 • 617-292-5500

Charles D. Baker Governor	Kathleen A. Theoharides Secretary
Karyn E. Polito Lieutenant Governor	Martin Suuberg Commissioner

Fact Sheet

Interim Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the Massachusetts Contingency Plan

Links provided within technical regulatory guidance document

PFAS-1, Section 11.1.1 Sampling.

Site-specific QAPP or Work Plan

Planning Considerations

- What quantitation levels are needed for the specific application?
- What certifications are held by the laboratory that relate to the method in question?
- What are the QC parameters in place for monitoring extraction performance, instrument performance, sample response bias and target analyte mass loading bias?
- What is the calibration model that is used? What constitutes an acceptable calibration?
- What are the QC criteria for acceptable recovery of isotopic analogs (or surrogates if isotope dilution is not used)?
- Is there an isotopic analog for each of the native compounds to be analyzed for?
- How does the laboratory handle particulates in aqueous samples?
- Does the method use isotope dilution?
- What is the compound list?
- Which of the methodologies listed in Section 11.2 will the lab be using?
- Does the lab participate in a proficiency testing program and at what frequency? Can recent results be shared?

PFAS-1, Sections 11.1.1 and 11.3.1, Figure 11-2

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

PFAS-1, Sections 11.1.1 and 11.3.1

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)

PFAS-1, Section 11.3.1

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

- Fluorinated ethylene-propylene (FEP)
- Ethylene tetrafluoroethylene (ETFE)
- Low-density polyethylene (LDPE)
- Polyvinylidene fluoride (PVDF)
- Polytetrafluoroethylene (PTFE)
- Waterproof coatings containing PFAS
- Pipe thread compounds and tape

PFAS-1, Section 11.1.2 Equipment and Supplies.

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

PFAS-1, Section 11.1.2 Equipment and Supplies.

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

PFAS-1, Section 11.1.3 Bottle Selection.

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.

PFAS-1, Section 11.1.1

Holding Time/Preservation Differences

Method	Preservative	Holding Time
EPA Method 537.1 **Drinking water**	Trizma®; ship at ≤ 10◦C; store at lab ≤ 6◦C	**Extraction:** within 14 days of collection **Analysis:** within 28 days of extraction
EPA Method 533 **Drinking water**	Ammonium acetate; ship at ≤ 10◦C; store at lab ≤ 6◦C	**Extraction**: within 28 days of collection **Analysis:** within 28 days of extraction
SW-846 8327 **SW, GW, WW**	≤ 6◦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 covered on next slide

PFAS-1, Section 11.1. Sampling Table 11-2

EPA Method 1633 Preservation & Holding Times

Matrix	Preservation/Extraction	Analysis
Aqueous **Landfill leachate: 100 mL** **Other: 500 mL**	• If stored ≤ -20◦C, 90 days from collection • If stored 0-6◦C, 28 days from collection if **perfluorooctane sulfonamide ethanols** and **perfluorooctane sulfonamidoacetic acids** of concern, 7 days from collection	• 90 days from extraction* *issues observed for some **ether sulfonates** after 28 days
Soil/Sediment **5 grams**	• If stored ≤ -20◦C or 0-6◦C, 90 days from collection	
Biosolids **0.5 grams**	• If stored ≤ -20◦C or 0-6◦C, 90 days from collection ≤ -20◦C recommended if storing more than few days due to production of gases from microbiological activity at 0-6◦C	
Tissue **2 grams**	• If stored ≤ -20◦C or 0-6◦C, 90 days from collection ≤ -20◦C required for fish if sample will not be received by lab within 24 hours	

If NFHDA of concern in soil/sediment/biosolids/tissue, extract ASAP

PFAS-1, Section 11.1. Sampling Table 11-5

USEPA Method 1633, https://www.epa.gov/cwa-methods

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

PFAS-1, Section 11.1.7 Sampling Procedures

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.

PFAS-1, Section 11.1.7 Sampling Procedures

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

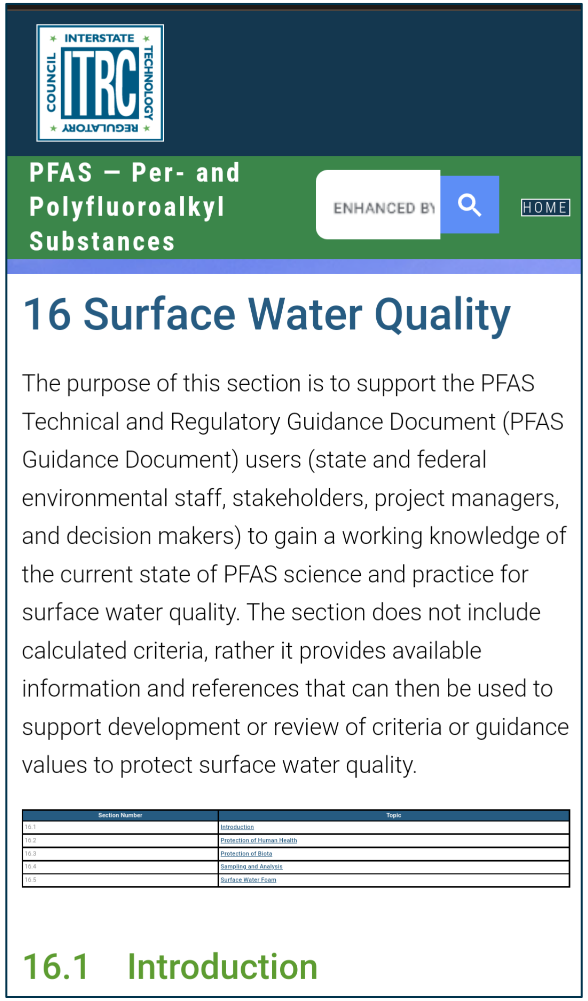
Laboratory centrifugation is a good alternative

PFAS-1, Section 11.2.1.2. Sample Preparation.

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



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 Biota
16.4	Sampling and Analysis
16.5	Surface Water Foam

16.1 Introduction

Published June 2023

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

Photo by AdriannaNicole, CC BY-SA 4.0, via Wikimedia Commons.

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Sampling Considerations

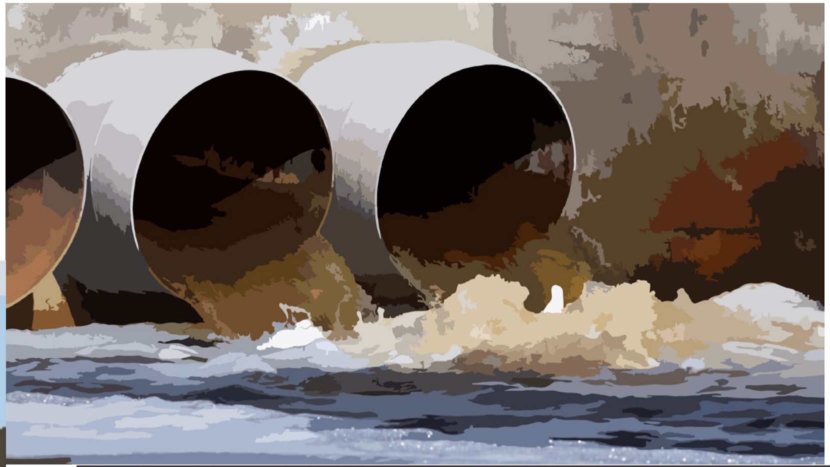
Assigned **beneficial use**

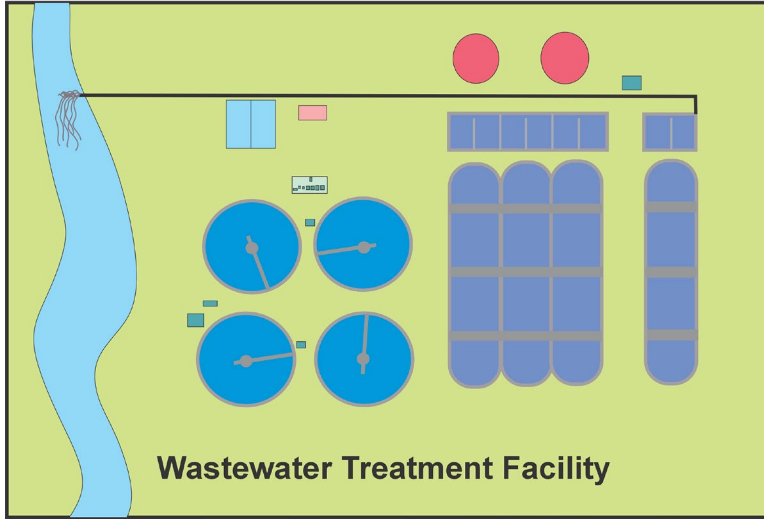
- Determine what samples to collect

Potential PFAS **sources**

- Stormwater runoff
- Wastewater discharges
- Biosolids application

Stormwater Runoff





Figures by A. MacDonald.
Used with permission.

ITRC 2023, PFAS-1, Section 16.4 Sampling and Analysis

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**

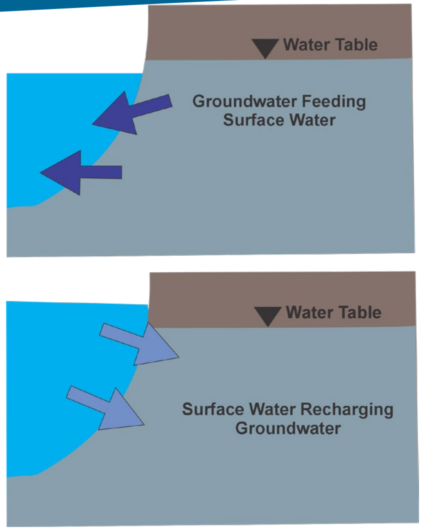


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Photo by Linda Logan

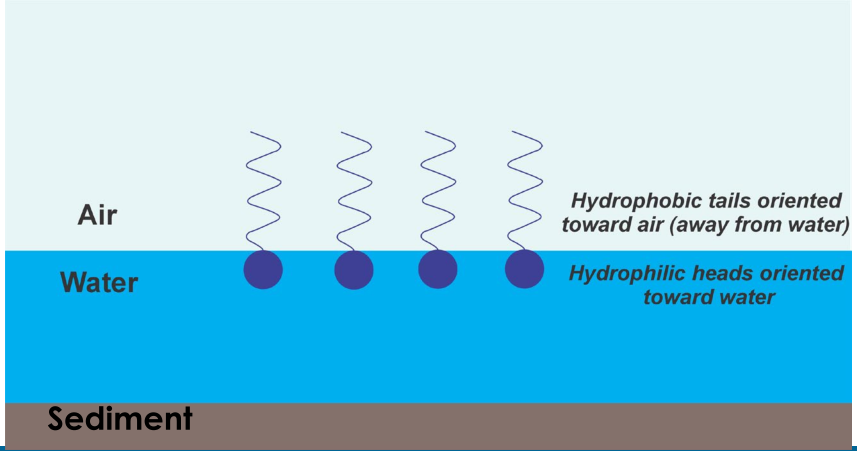


Figure by A. MacDonald, adapted from, Figure 4.1, ITRC 2023, PFAS-1

ITRC 2023, PFAS-1, Section 16.4 Sampling and Analysis; Section 5.3.4.1. fate and transport

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

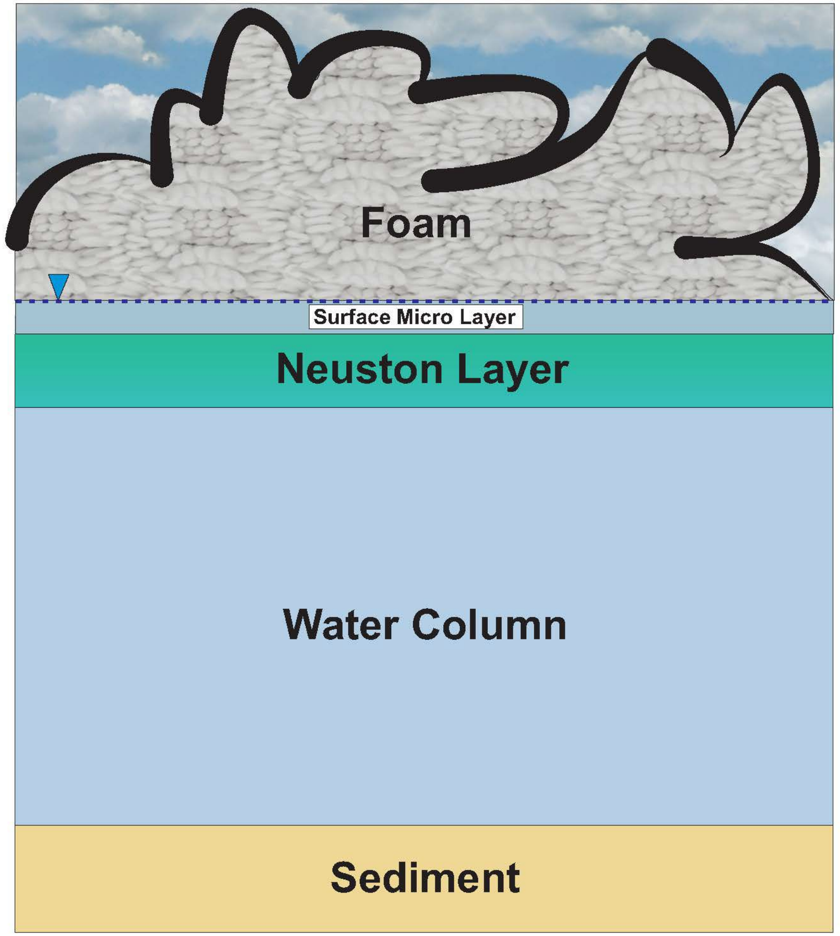


Figure 16-2, PFAS -1

not to scale

ITRC 2023, PFAS-1, Section 16.5

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

ITRC 2023, PFAS-1, Section 16.5, Surface Water Foam

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.

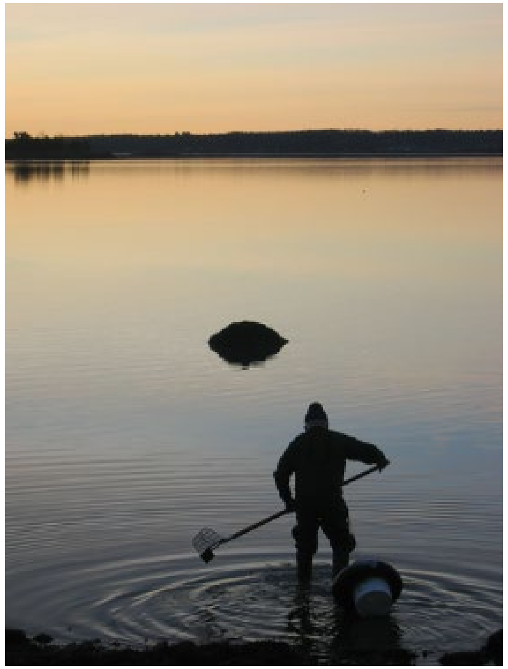
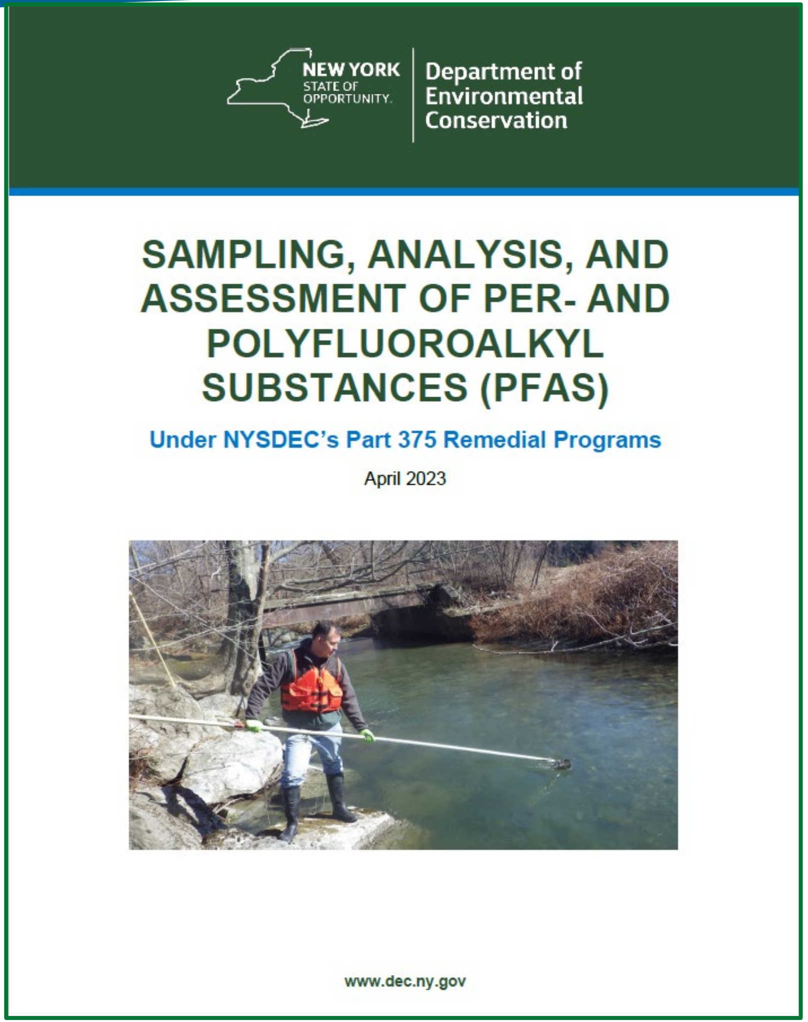


Photo courtesy of J. Petali, NH Department of Environmental Services. Used with permission.

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



NEW YORK STATE OF OPPORTUNITY. | Department of Environmental Conservation

SAMPLING, ANALYSIS, AND ASSESSMENT OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

Under NYSDEC's Part 375 Remedial Programs

April 2023

www.dec.ny.gov

ITRC 2023, PFAS-1, Section 16.4. Sampling and Analysis, NY, APR. 2023. Sampling, Analysis, and Assessment of Per-and Polyfluoroalkyl Substances (PFAS).

Case Study

PFAS-Containing Foam

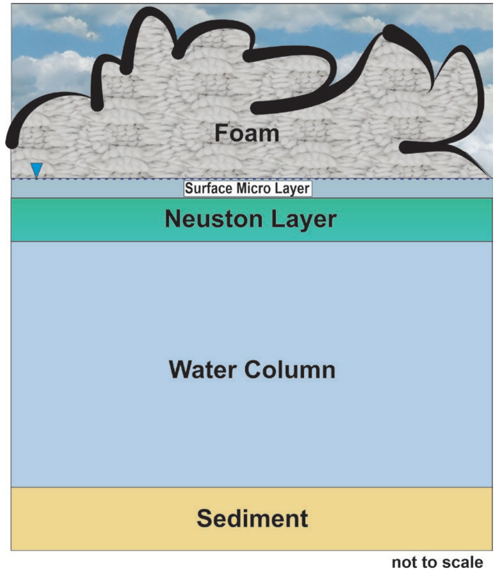
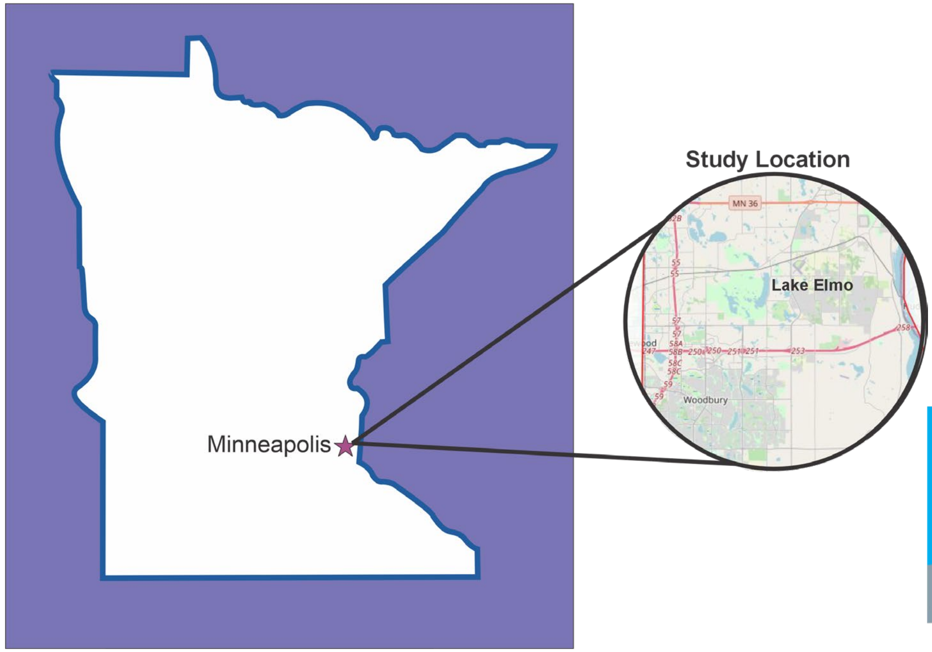


Figure 16-2, PFAS-1



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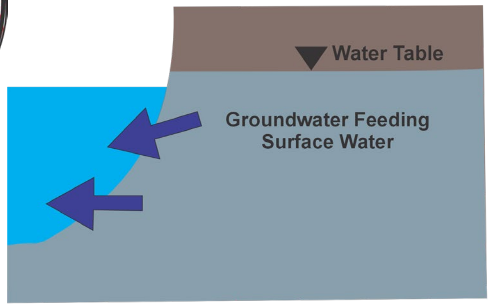
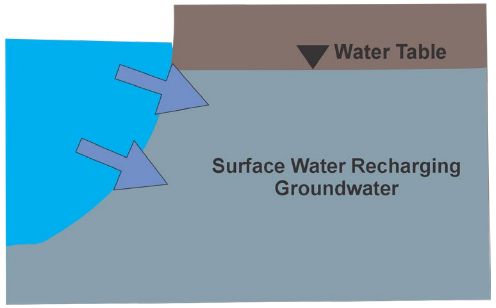




Groundwater/Surface Water Interaction

ITRC 2023, PFAS-1, Section 15.5, Surface Water Foam

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?

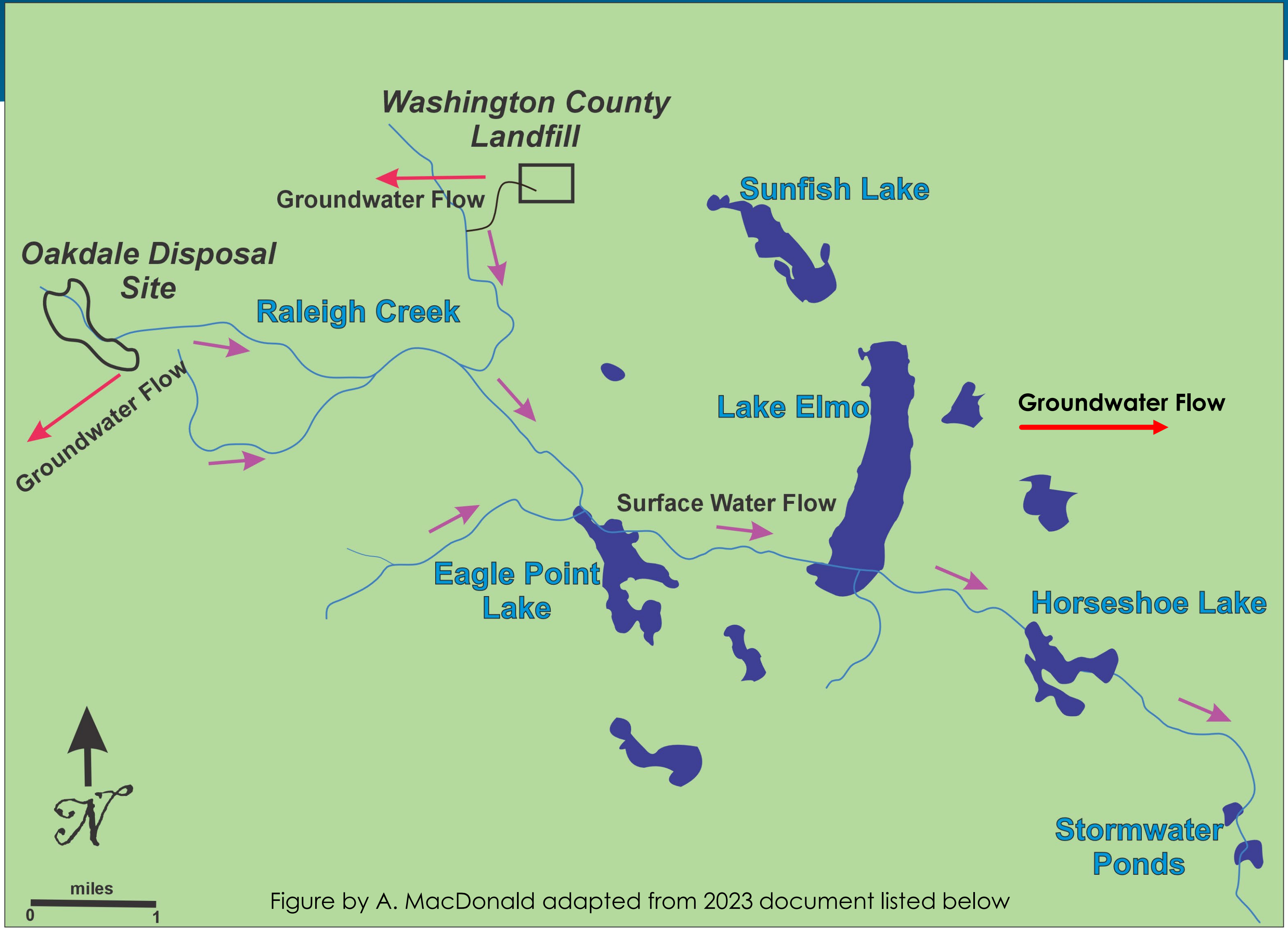


Figure by A. MacDonald adapted from 2023 document listed below

Groundwater Flow Direction

Surface Water Flow Direction

PFAS-1, Section 15.5.2, Surface Water/Groundwater Interaction Case Study;
Source Project 1007 Minnesota Pollution Control, Agency 2023

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.

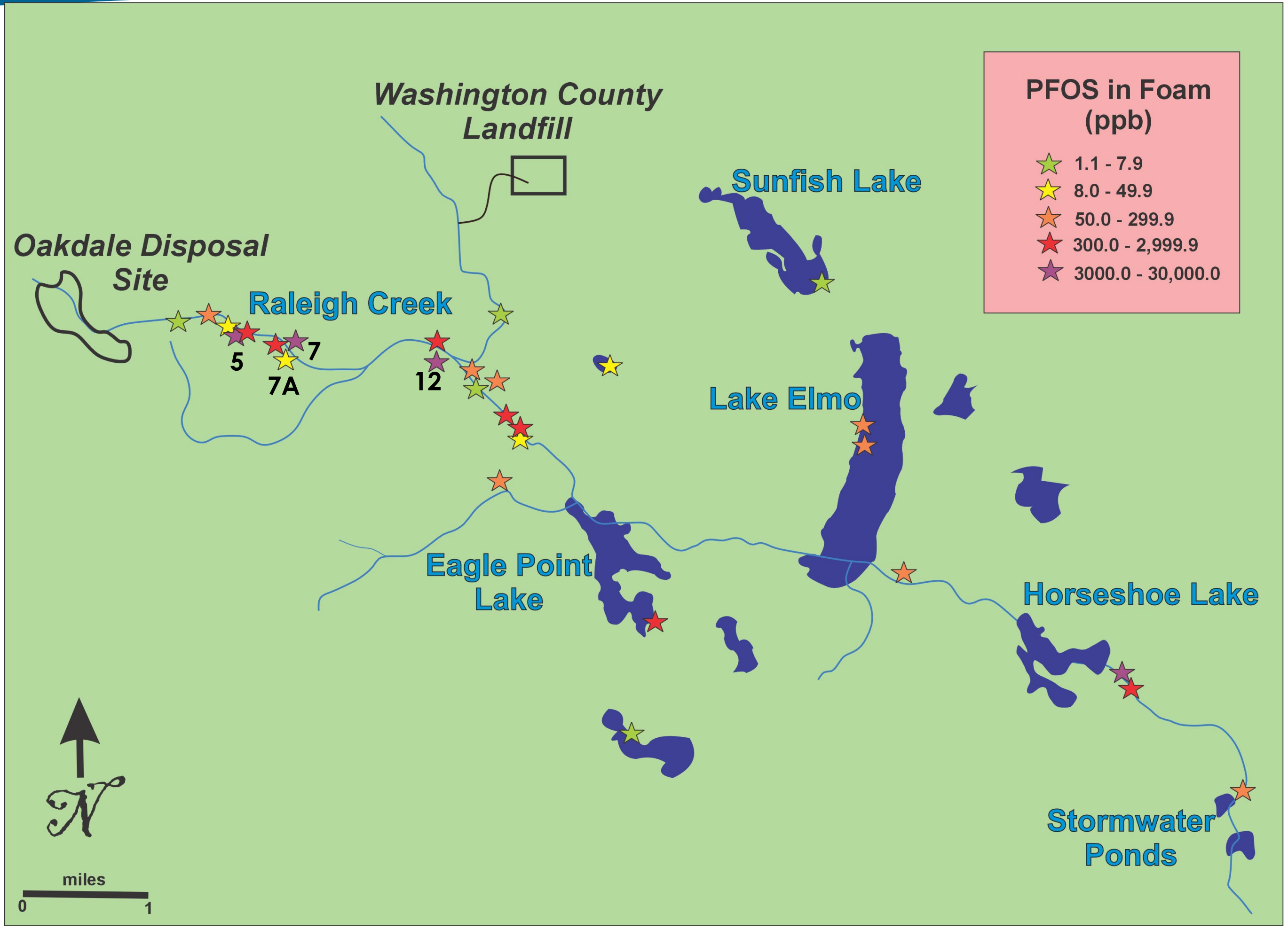
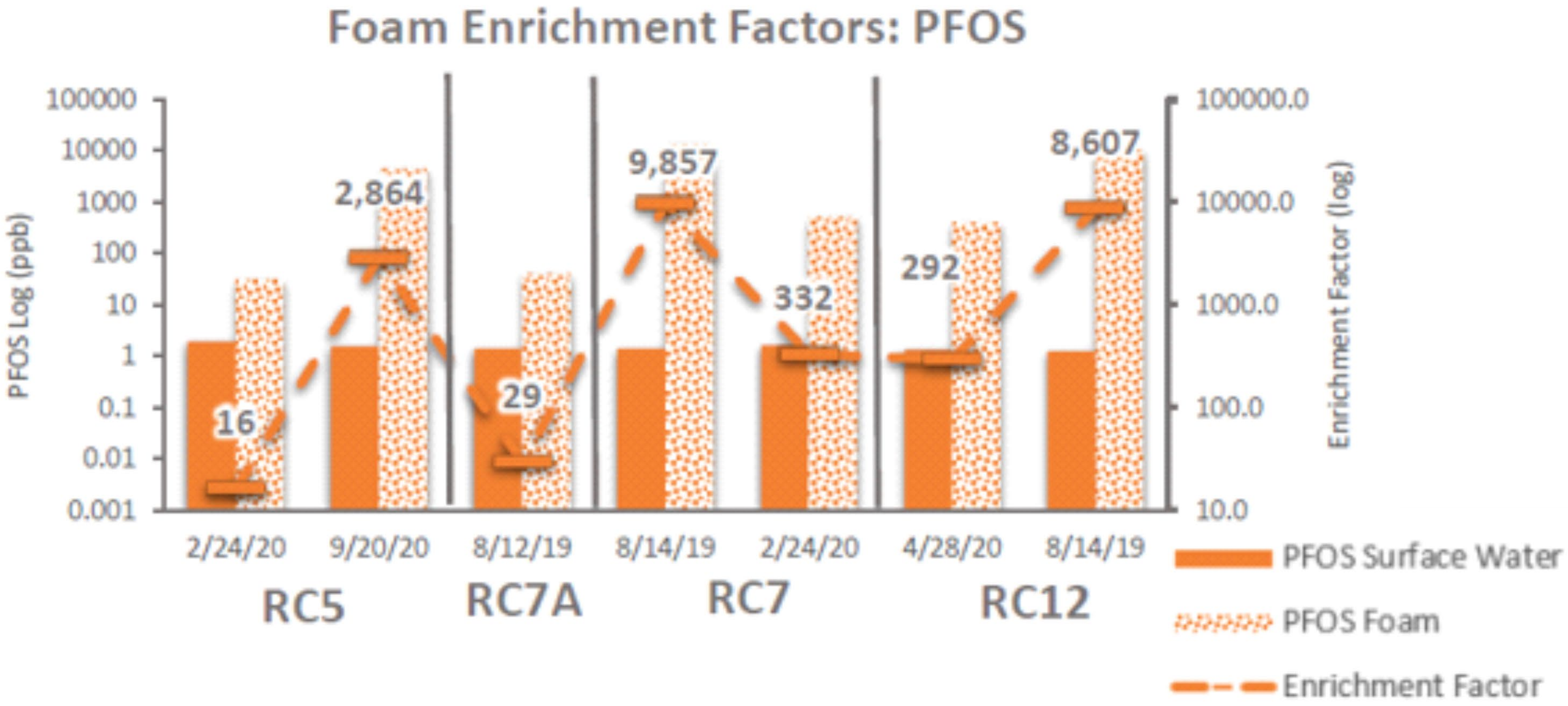


Figure by A. MacDonald adapted from 2023 document listed below

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



ITRC 2023, PFAS-1, Section 15.5.1, PFAS-Containing Foam Case Study, Figure 15-27. *Source: MPCA 2023.*

Case Study

🟢 **Well with no advisory (non-detect to low)**

🔵 **Well above advisory level**

▨ **PFAS Source Area**

■ **Groundwater monitor well**

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

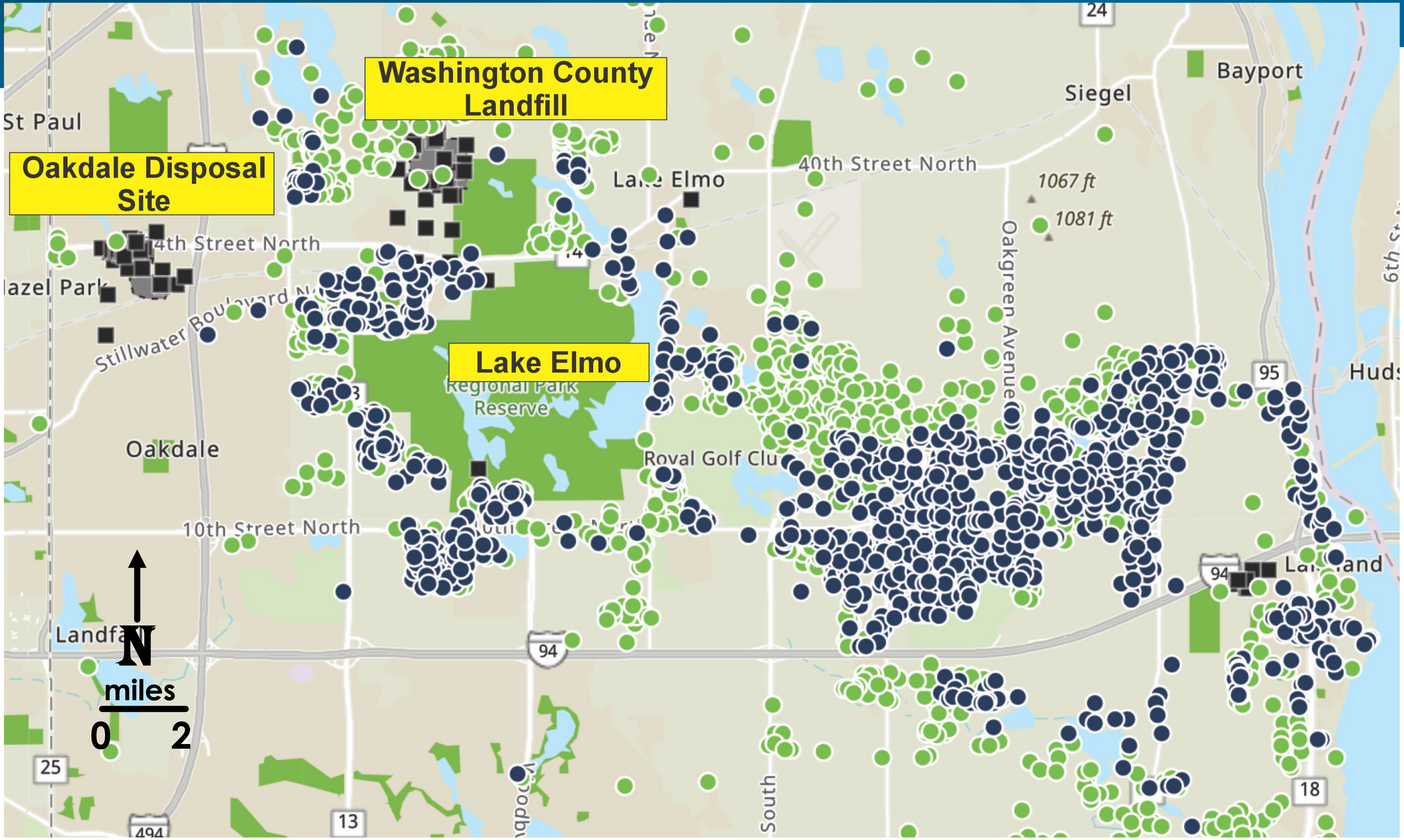


Figure by A. MacDonald with [map from Minnesota Dept. of Health](#).

Air Sampling

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

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

Sample and analyze PFAS targets from stationary sources

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

PFAS-1, Section 11.1.7.9.1 Emissions to Air.

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

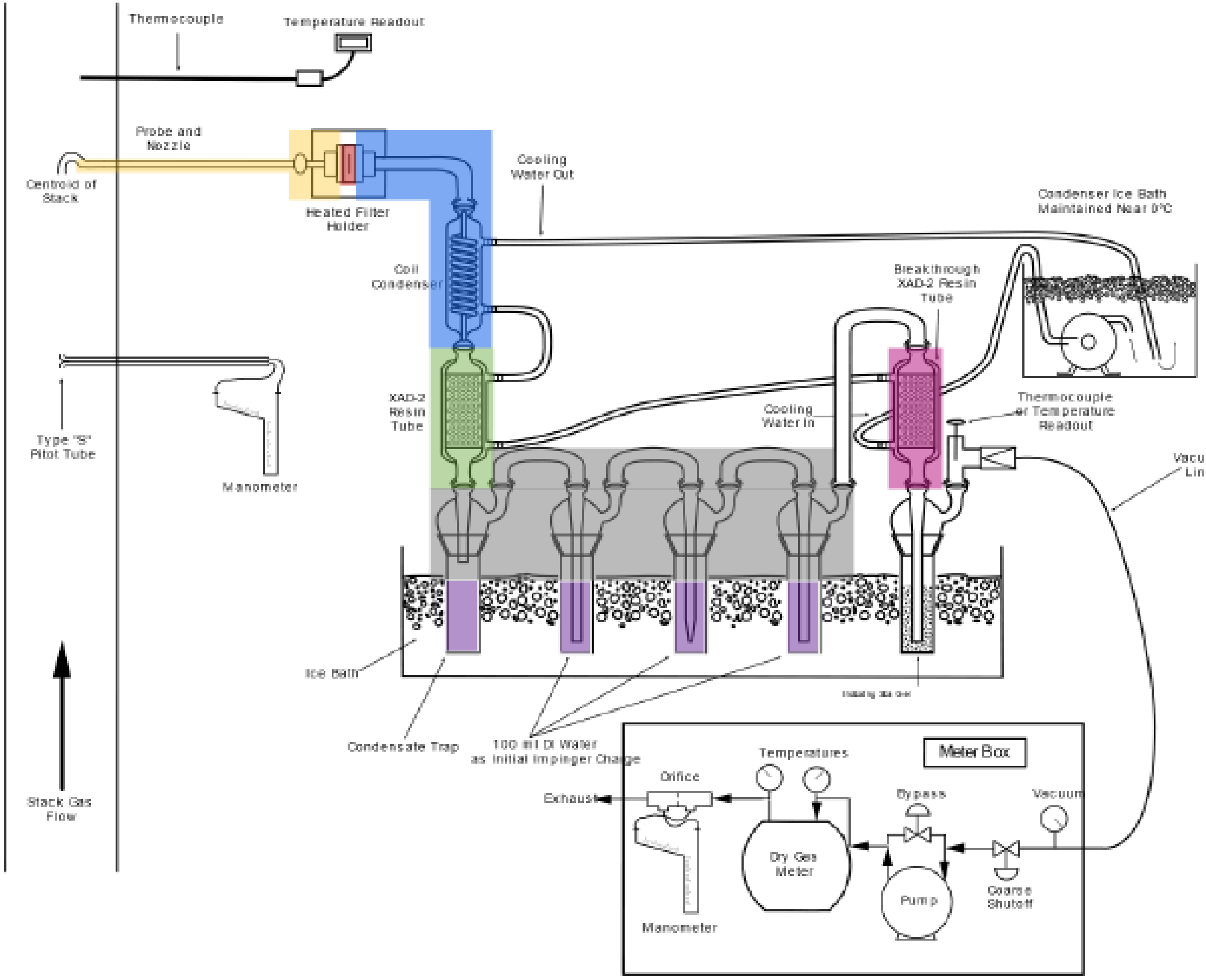


Figure OTM-45-1. Sampling Train

OTM 45 Visual Container Guide

🟥 #1 Filter

🟨 #2 Front Half Rinse

🟩 #3 XAD-2

🟦 #4 Back half Rinse

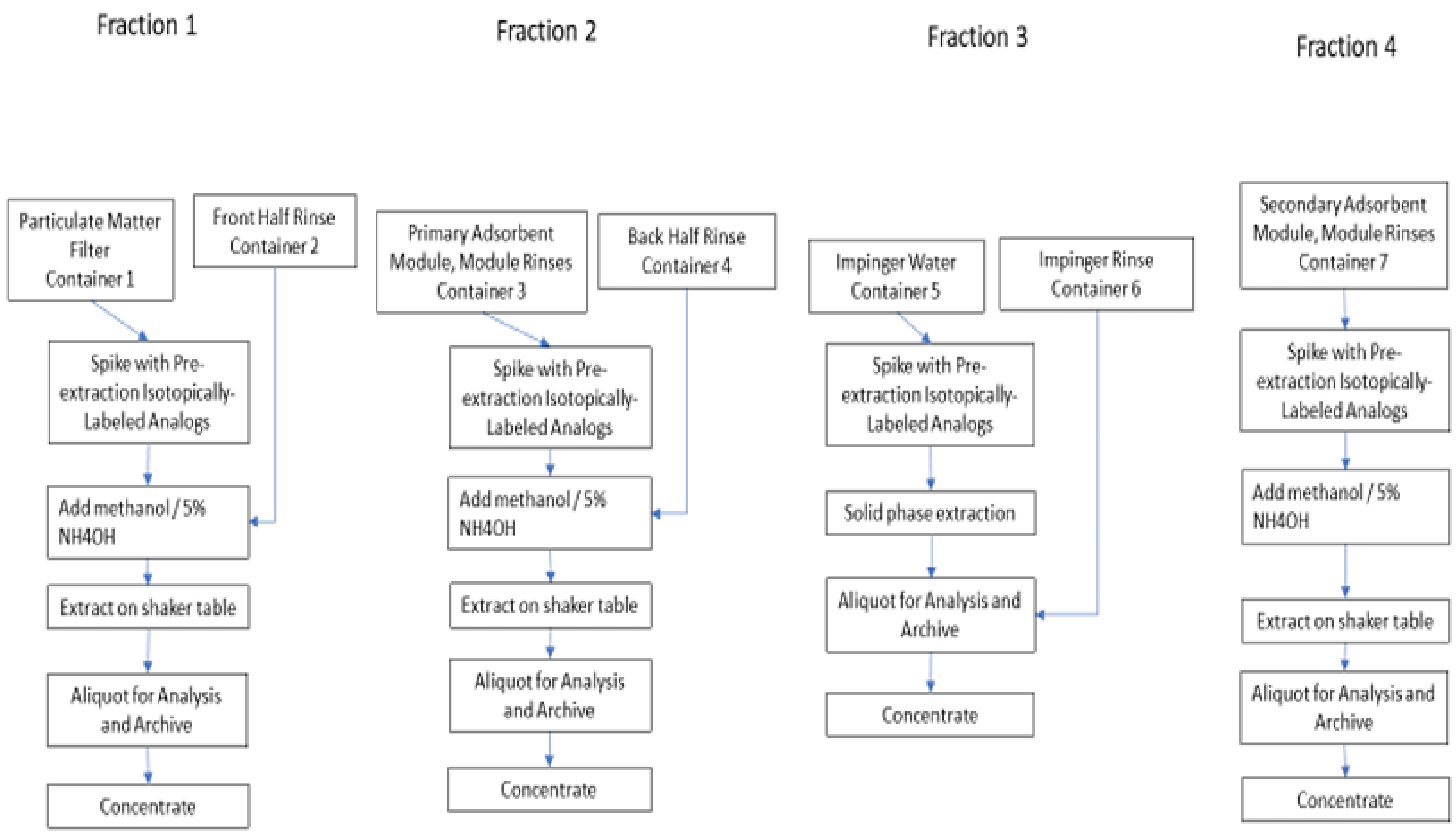
🟪 #5 Condensate and Impinger Water

⬜ #6 Impinger Rinse

🟪 #7 Breakthrough XAD-2

Figures Source: Draft OTM-45 method. https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

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



Fraction 1

Particulate Matter Filter Container 1
Front Half Rinse Container 2
Spike with Pre-extraction Isotopically-Labeled Analogs
Add methanol / 5% NH4OH
Extract on shaker table
Aliquot for Analysis and Archive
Concentrate

Fraction 2

Primary Adsorbent Module, Module Rinses Container 3
Back Half Rinse Container 4
Spike with Pre-extraction Isotopically-Labeled Analogs
Add methanol / 5% NH4OH
Extract on shaker table
Aliquot for Analysis and Archive
Concentrate

Fraction 3

Impinger Water Container 5
Impinger Rinse Container 6
Spike with Pre-extraction Isotopically-Labeled Analogs
Solid phase extraction
Aliquot for Analysis and Archive
Concentrate

Fraction 4

Secondary Adsorbent Module, Module Rinses Container 7
Spike with Pre-extraction Isotopically-Labeled Analogs
Add methanol / 5% NH4OH
Extract on shaker table
Aliquot for Analysis and Archive
Concentrate

- 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/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

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

PFAS-1, Section 11.1.6 Field QC Samples.

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).

PFAS-1, Section 11.1.6. Table 11-1 Typical field QC Samples.

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

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. 2020. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Revision 2.0. Washington, D. C.

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. 2019. Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. EPA/815-B-19-20. Cincinnati, OH.

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 hiera

PFAS-1, Section 11.2. External Table 11-4 Analyte Lists, see also Section 2.3.2. Table 2-4.

USEPA Method 1633

USEPA Method 1633 (January 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

PFAS-1, Section 11.2.1 Quantitative Techniques.

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

PFAS-1, Table 11-3 Finalized Published PFAS Analytical Methods.
Section 11.1.7.14 Potential High Concentration Samples

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

PFAS-1, Section 11.2.1 Quantitative Techniques.

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

- January 2021
  - Single-laboratory validated
- 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

PFAS-1, Section 11.2.1 Quantitative Techniques.

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

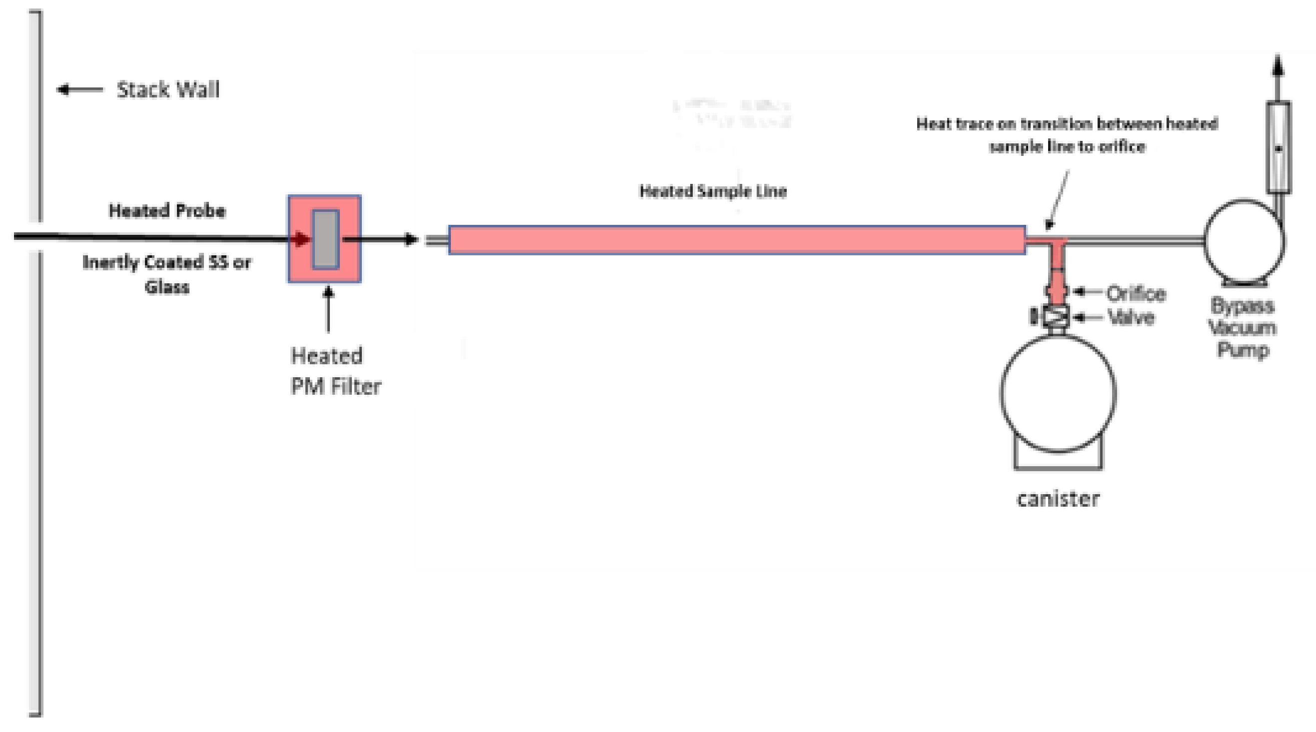


Figure OTM-50-1. Direct VFC Sampling System

Compound Name	CAS #	Chemical Formula
Carbon tetrafluoride	75-73-0	CF_4
Hexafluoroethane (FC-116)	76-16-4	C_2F_6
Tetrafluoroethene	116-14-3	C_2F_4
Trifluoromethane (HFC-23)	75-46-7	CHF_3
Octafluoropropane	76-19-7	C_3F_8
Difluoromethane (HFC-32)	75-10-5	CH_2F_2
Fluoromethane (HFC-41)	593-53-3	CH_3F
Pentafluoroethane (HFC-125)	354-33-6	C_2HF_5
Hexafluoropropene	116-15-4	C_3F_6
Hexafluoropropene oxide (HFPO)	428-59-1	C_3F_6O
Decafluorobutane	355-25-9	C_4F_{10}
Dodecafluoropentane	678-26-2	C_5F_{12}
Tetradecafluorohexane	355-42-0	C_6F_{14}
1H-Perfluoropentane	375-61-1	C_5HF_{11}
Hexadecafluoroheptane	335-57-9	C_7F_{16}
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1)	3330-15-2	$C_5HF_{11}O$
1H-Perfluorohexane	355-37-3	C_6HF_{13}
1H-Perfluoroheptane	375-83-7	C_7HF_{15}
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	3330-14-1	$C_8HF_{17}O_2$
1H-Perfluorooctane	335-65-9	C_8HF_{17}
Octadecafluorooctane	307-34-6	C_8F_{18}
1H-Nonafluorobutane	375-17-7	C_4HF_9
1H-Heptafluoropropane	2252-84-8	C_3HF_7
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	$C_2H_2F_4$
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	$C_2H_3F_3$
Chlorodifluoromethane (HCFC-22)	75-45-6	$CHClF_2$
Chlorotrifluoromethane (CFC-13)	75-72-9	CF_3Cl
Octafluorocyclobutane (FC-C318)	115-25-3	C_4F_8
Octafluorocyclopentene (FC-C1418)	559-40-0	C_5F_8
Trichloromonofluoromethane (CFC-11)	75-69-4	CCl_3F

www.epa.gov/system/files/documents/2024-01/otm-50-release-1_0.pdf

DoD AFFF01

December 2021

- Multi-laboratory validated

LC-MS/MS (PFOA and PFOS only)

AFFF Concentrates

- Compliance for military specifications MIL-PRF-24385

PFAS-1, Section 11.2.1 Quantitative Techniques.

Other Published Methods

Finalized Methods

- ISO Method 25101 (ISO 2009): water
- ASTM D7979-20 (ASTM 2020): water
- ASTM D7968-17a (ASTM 2017): soil
- FDA C-010.01 Version 2019: food
- CDC:6304.09: blood serum

Draft Methods

- ISO/CD 21675:2019 (E): water

PFAS-1, Section 11.2.1 Quantitative Techniques.

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

PFAS-1, Section 11.2.1.3 Sample Analysis

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
  - $^{13}C_4$PFBA is EIS associated with PFBA
  - $^{13}C_4$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

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

PFAS-1, Section 11.2.1.3 Sample Analysis

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

PFAS-1, Section 11.2.1.3 Sample Analysis

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	
DoD AFFF01	SPE	**Isotope Dilution**	Yes	2 PFOA/PFOS	
EPA 1633-Aqueous	SPE	**Isotope Dilution**/EIS	Yes	40	Landfill leachate: 10-250 ng/L Other: 2-50 ng/L
EPA 1633-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

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)

All use LC/MS/MS

PFAS-1, Section 11.2.1.3 Sample Analysis and Table 11-3.

Aqueous Samples with Particulates

<u>Issue</u>: Sorption of PFAS to particulates or solids. Longer-chain PFAS and PFSAs 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

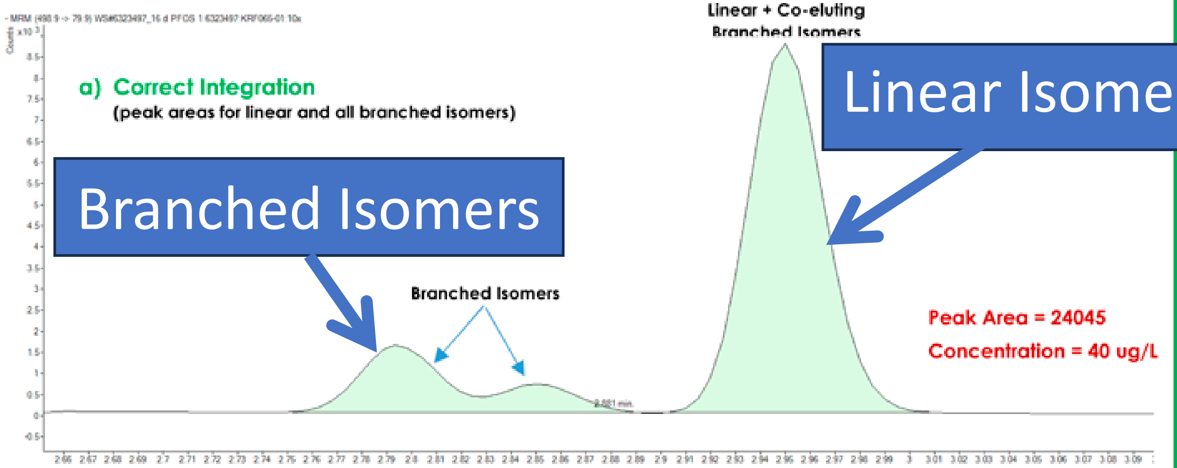
Surface Water:

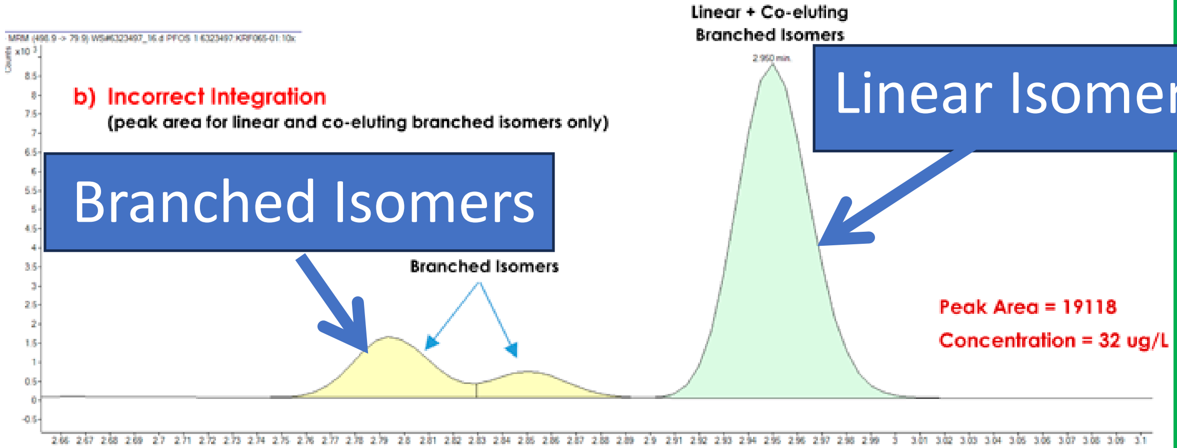
Consider "total" measurement if for compliance, permitting, remedial design, risk assessment

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



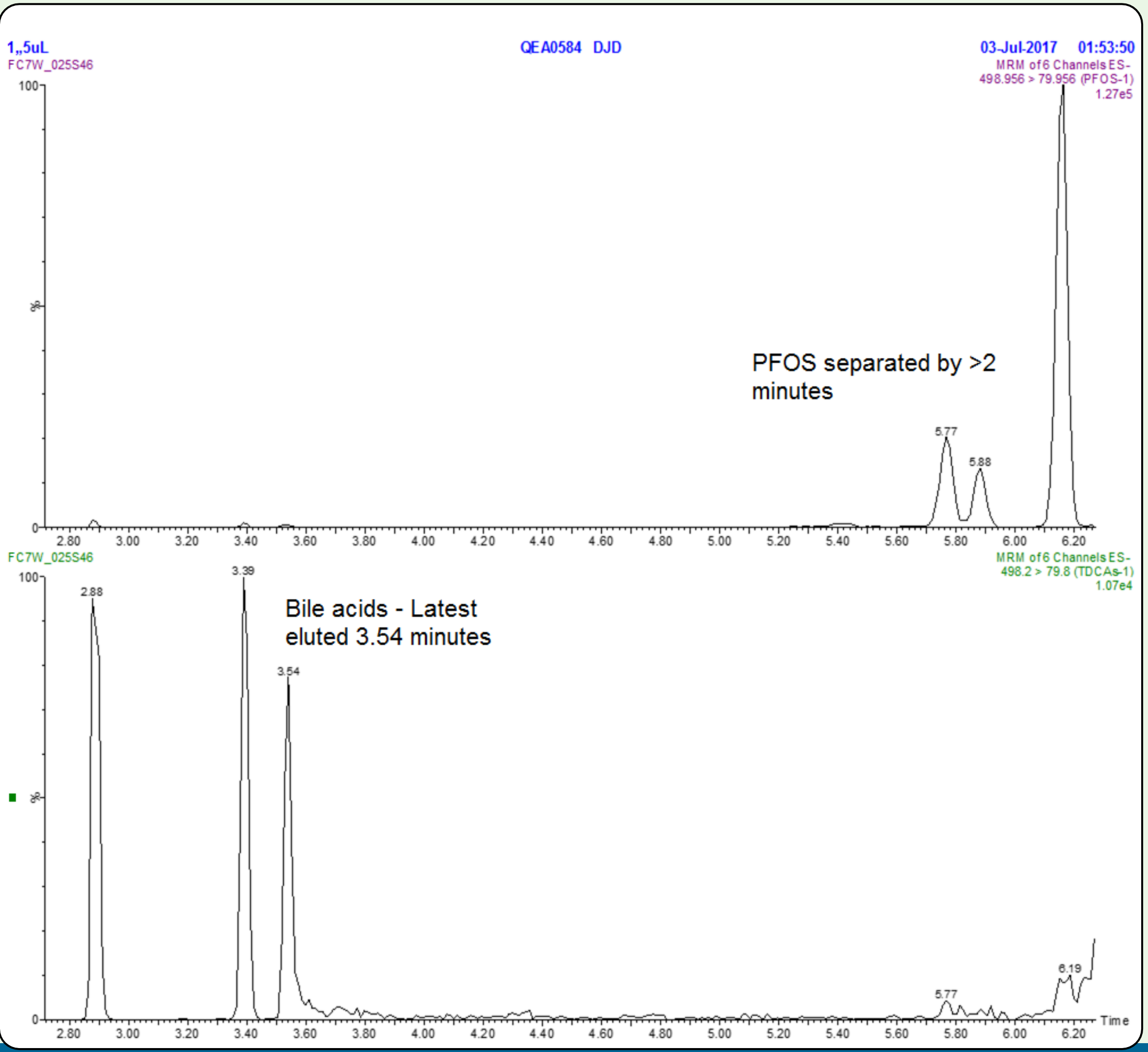


Currently labs reporting L&B consistently for: PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA

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

PFAS-1, Section 11.3.5 Linear and Branched Isomers
Figure 11-3, Source: Bureau Veritas Laboratories, Mississauga, Ontario, Canada. Used with permission.

TDCA Interference: Tissue and Wastewater Matrices



PFOS separated by >2 minutes

Bile acids - Latest eluted 3.54 minutes

- 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 1633 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

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

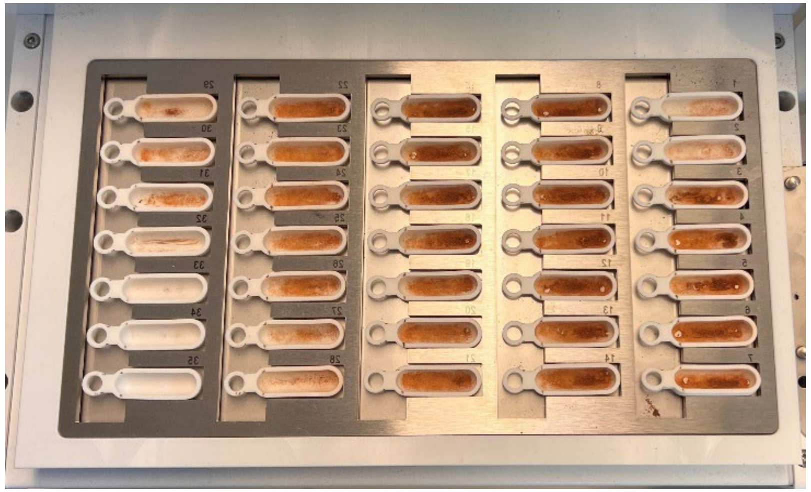
PFAS-1, Section 11.2.2.2 TOP Assay

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"



PFAS-1, Section 11.2.2.4 Adsorbable Organic Fluorine with Combustion Ion Chromatography

Photo courtesy of M. Maier, Montrose Environmental

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

PFAS-1, Section 11.2.2.5 High Resolution Mass Spectrometry (qTOF)
PFAS-1, Section 11.4.3 Nontargeted Analysis (NTA)

Sampling & Analysis

Analytical Methods

Qualitative Analyses

Data Evaluation

PFAS Occurrence in Air

Section 11.3

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

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.

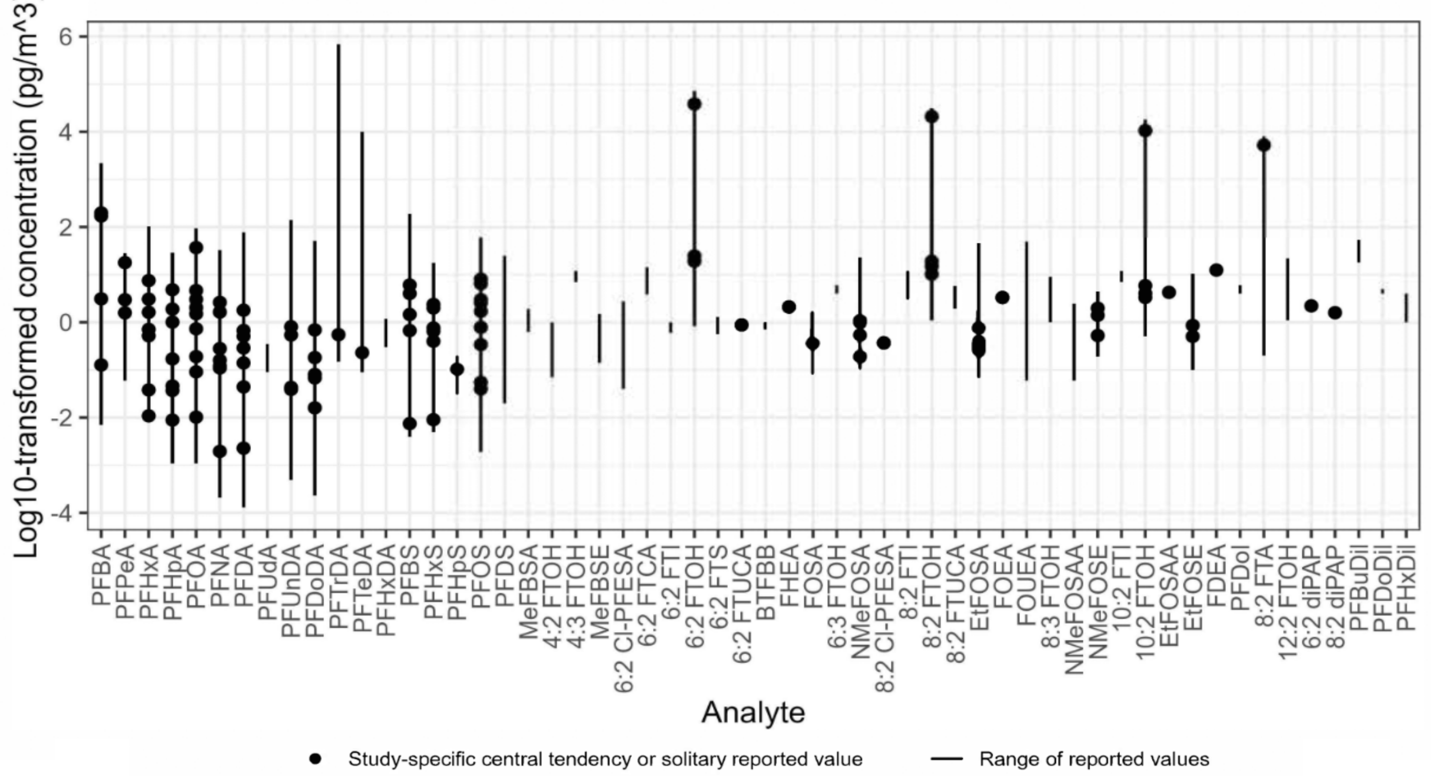
Outdoor Air

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

- Typical range for **PFOA and PFOS** ~1-30 pg/m^3
- **Near major industrial sources** (China and S. Korea)
  - **Max. PFOA** ~ 50-200 pg/m^3
  - **PFOS** > 2,000 pg/m^3
- **FTOHs** in the hundreds of pg/m^3

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

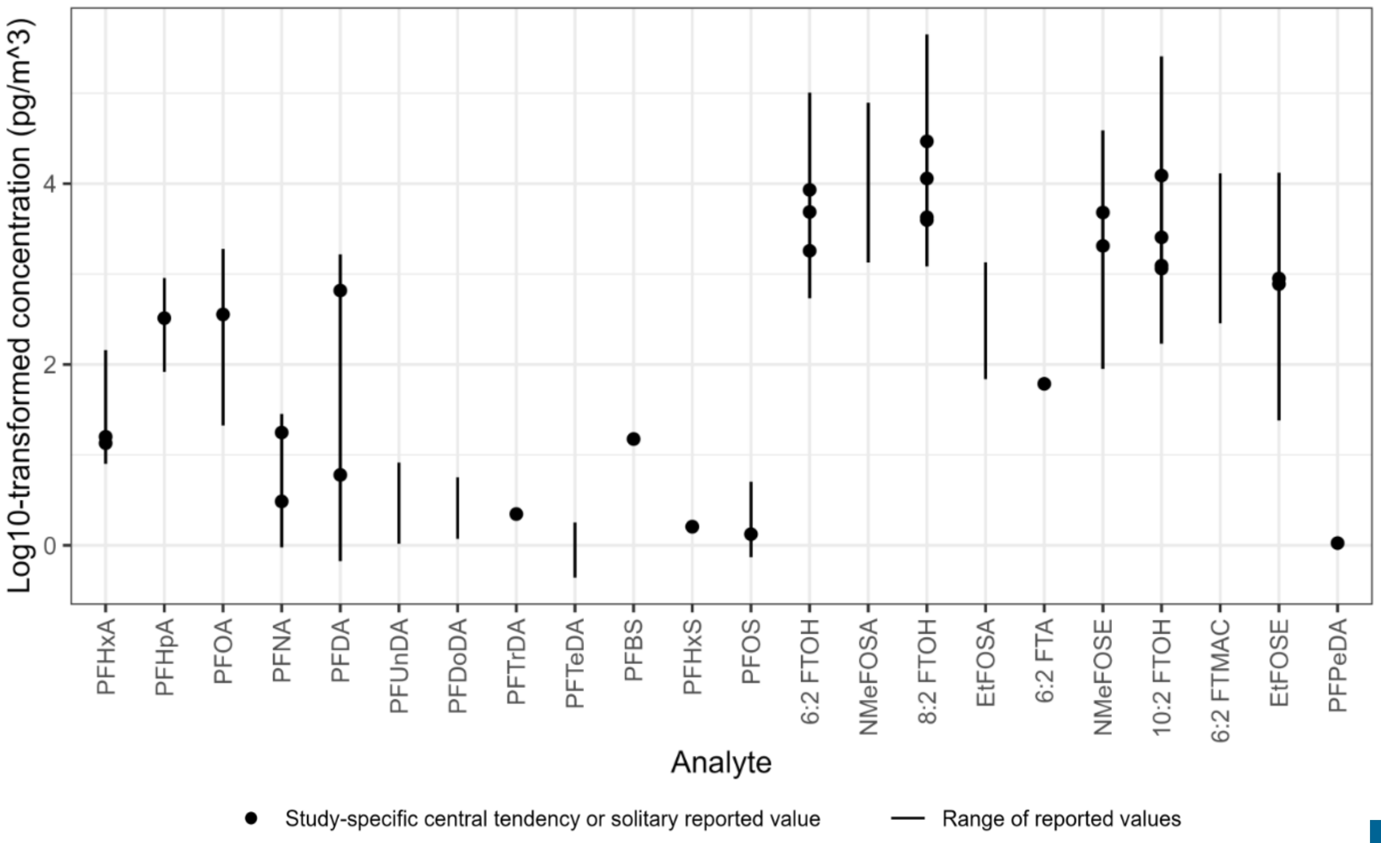
Concentrations can be higher than outdoors due to the presence of indoor sources

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

- **PFOA** (in $PM_{2.5}$) ranged from ~ 200-1,900 pg/m^3 in **kindergartens** (Hong Kong)
- In Finnish **homes**, **max. PFOA and PFOS** ~ 100 pg/m^3 and 7 pg/m^3, respectively
- **FTOHs** observed in the **hundreds of thousands of pg/m³** 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

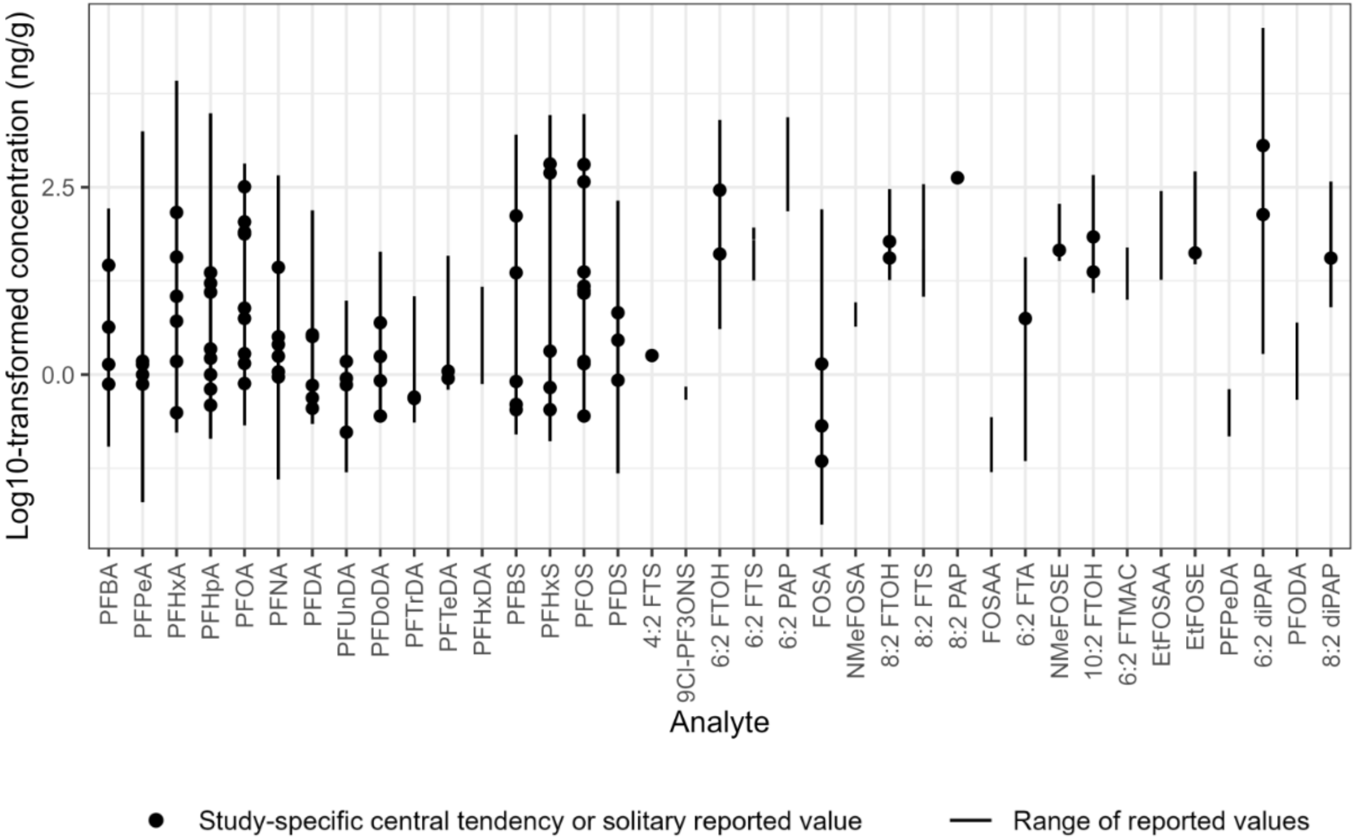
PFAS found in dust from floors, A/C filters, and carpets in schools, childcare facilities, homes, and workplaces

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



Sources: Ao et al. (2019), Beesoon et al. (2012), Besis 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

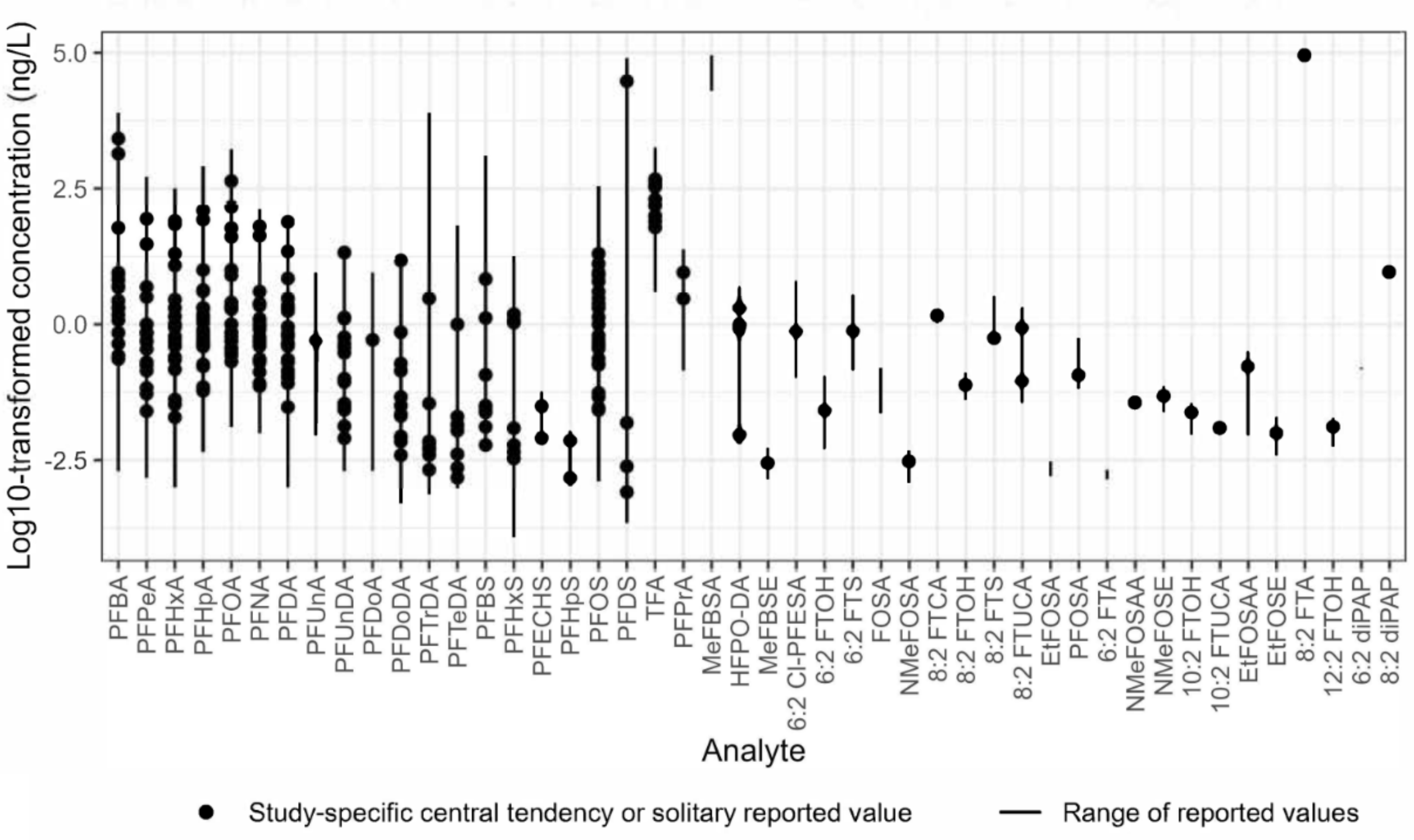
PFAS observed in rainwater, surface and subsurface snow, sea ice, and meltwater

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**

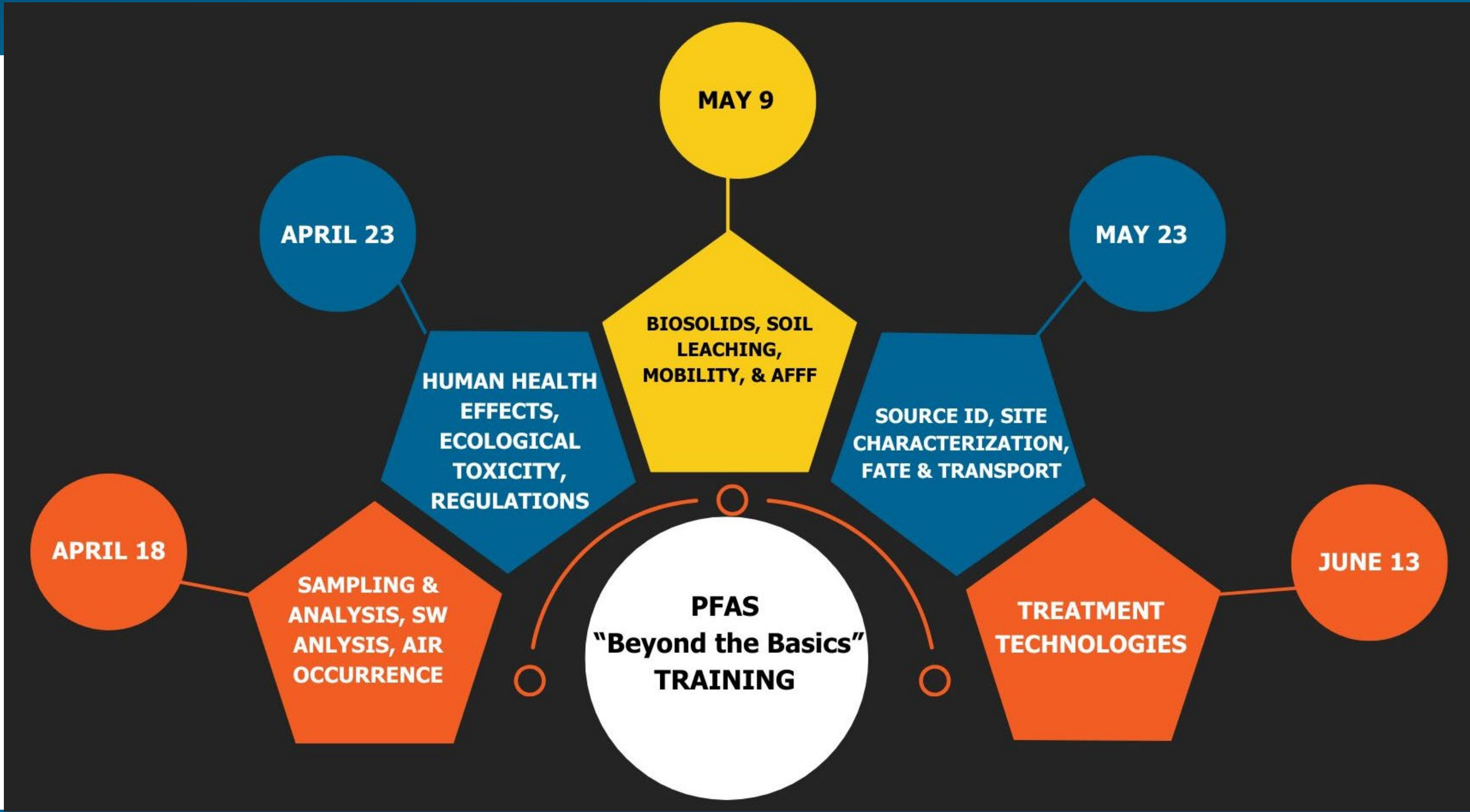
Basics of **compound-specific PFAS analysis**

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/



APRIL 18

SAMPLING & ANALYSIS, SW ANLYSIS, AIR OCCURRENCE

APRIL 23

HUMAN HEALTH EFFECTS, ECOLOGICAL TOXICITY, REGULATIONS

MAY 9

BIOSOLIDS, SOIL LEACHING, MOBILITY, & AFFF

MAY 23

SOURCE ID, SITE CHARACTERIZATION, FATE & TRANSPORT

JUNE 13

TREATMENT TECHNOLOGIES

PFAS "Beyond the Basics" TRAINING

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