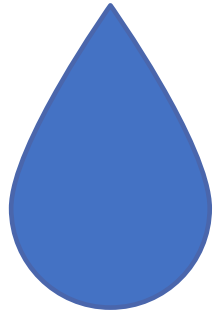

Drinking Water Sampling Procedures for PFAS



TRAINING FOR

U.S. EPA REGION III
DECEMBER 2020

Drinking Water Sampling Procedures for PFAS Outline

1. Introduction

2. Certified Laboratories

3. Basic PFAS Chemistry

4. Selecting an Analytical Method

5. Equipment and Supplies

6. Health and Safety

7. Sample Collection, Preservation, Handling, Shipping
and Holding Times

8. Interferences, Sources of Cross-Contamination and
Precautionary Measures

9. Data Records/Management

10. QA/QC

1. Introduction



This training supplements the October 2014 Region III training entitled “Drinking Water Sampling Procedures”



Some differences in sampling procedures, QA/QC



Primary difference relates to precautionary measures to avoid cross-contamination



2. Certified Laboratories

Certified Laboratories

- PFAS are not currently regulated in drinking water at the federal level.
- In Region III, Delaware regulates PFOA + PFOS (sum) at 70 ng/L.
- Delaware maintains a list of State-approved laboratories for PFAS by the Department of Natural Resources and Environmental Control (DNREC) under the Hazardous Substance Cleanup Act (HSCA).

Certified Laboratories (cont.)

Delaware-approved laboratories for PFAS include:

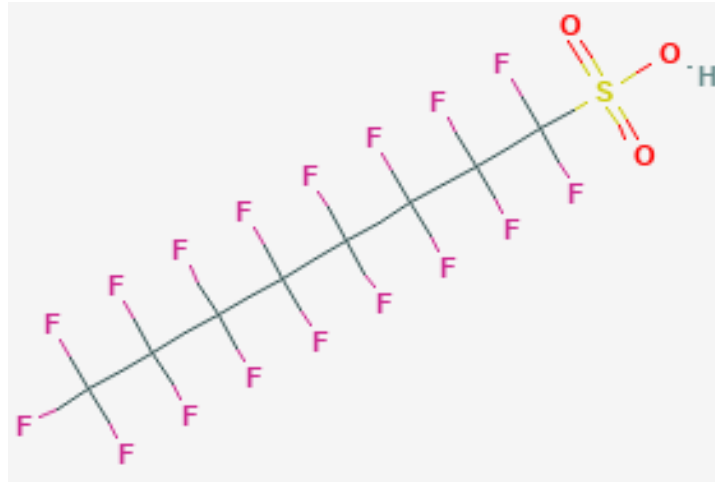
- ALS Environmental in **Rochester, NY**
- Hampton-Clarke/Veritech in **Fairfield, NJ**
- Eurofins Lancaster Laboratories in **Lancaster, PA**
- Eurofins TestAmerica-Burlington in **Burlington, VT**
- Eurofins TestAmerica-Edison in **Edison, NJ**
- Spectrum Analytical, Inc. in **North Kingstown, RI**



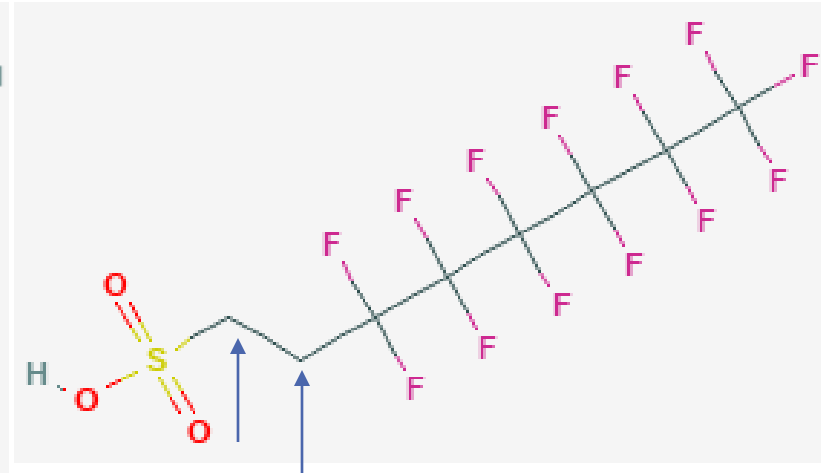
3. Basic PFAS Chemistry

Basic PFAS Chemistry

- Per- and Polyfluoroalkyl substances – alkyl protons are completely (per-) or almost completely (poly-) substituted by fluorine



Perfluorinated PFAS



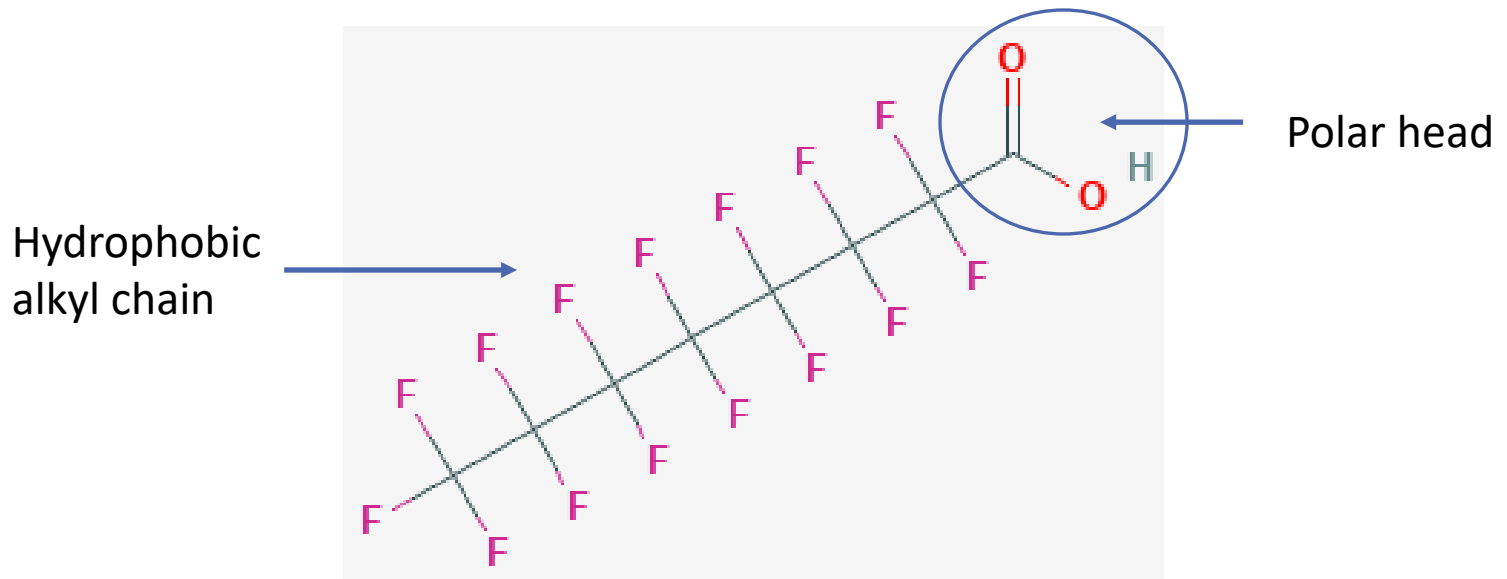
Non-fluorinated aliphatic carbons

Polyfluorinated PFAS

All structures from PubChem (NLM): <https://pubchem.ncbi.nlm.nih.gov/>

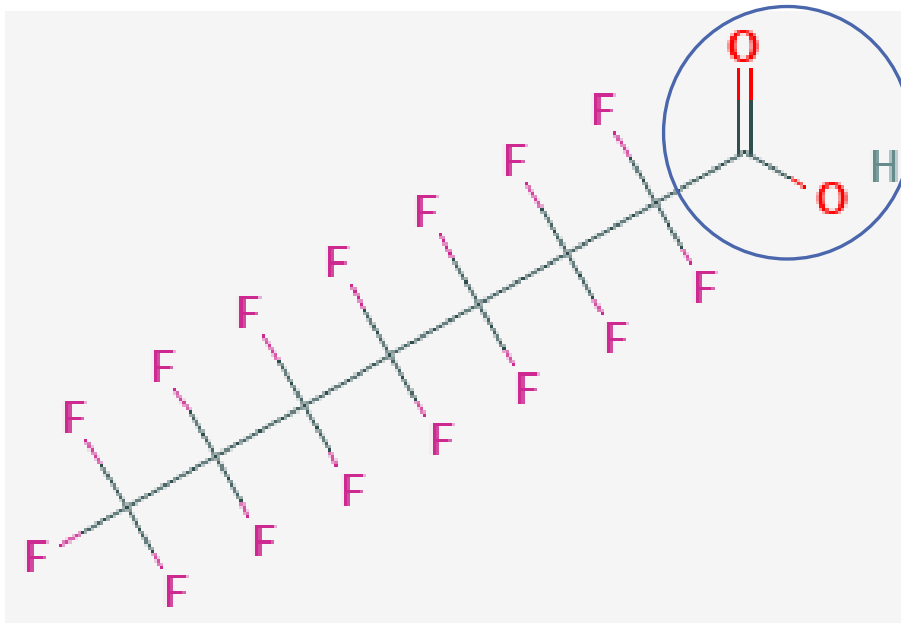
Basic PFAS Chemistry (cont.)

- Consist of a relatively hydrophobic alkyl chain with a polar “head” (much like a surfactant)
- Alkyl chains have dense electron cloud due to high electronegativity of fluorine (large effect on properties)



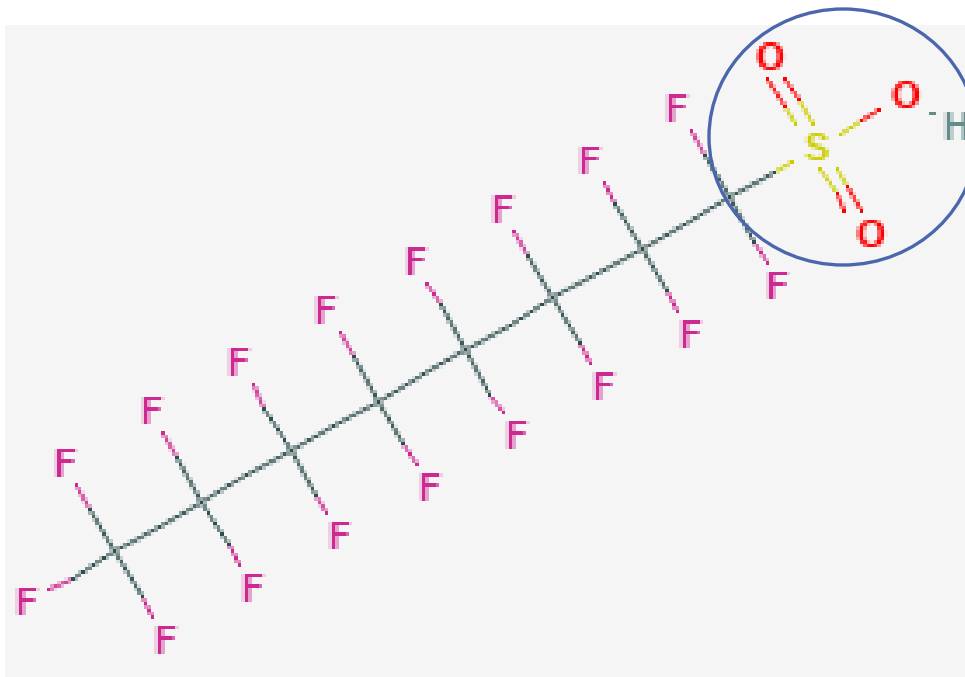
Basic PFAS Chemistry (cont.)

- Polar head may be:
 - Carboxylic acid/carboxylate



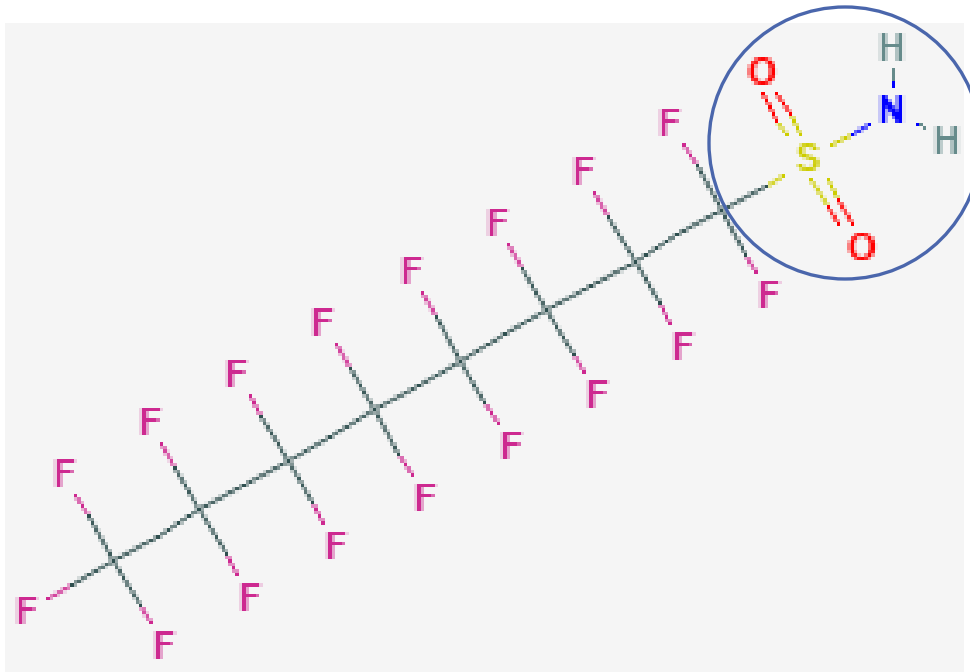
Basic PFAS Chemistry (cont.)

- Polar head may be:
 - Sulfonic acid/sulfonate



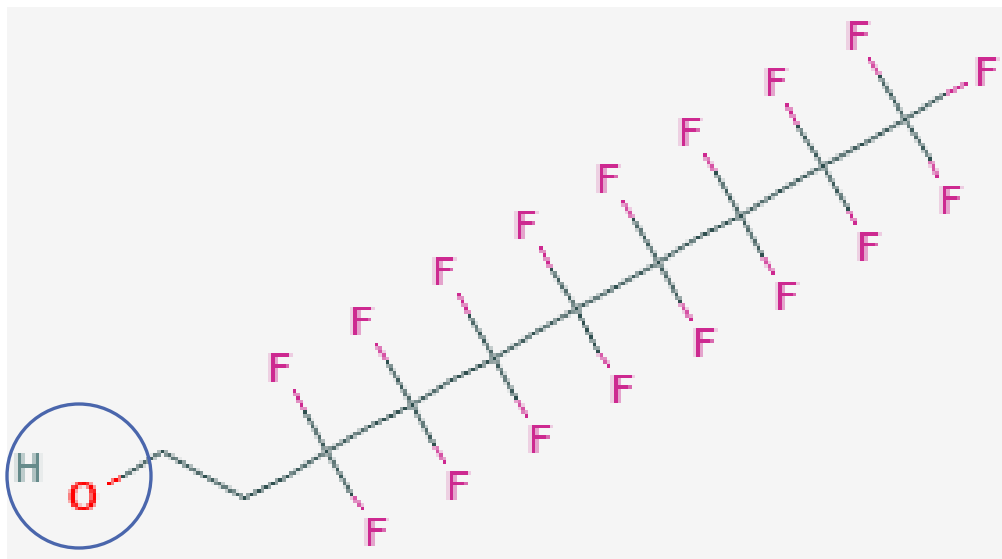
Basic PFAS Chemistry (cont.)

- Polar head may be:
 - Sulfonamide



Basic PFAS Chemistry (cont.)

- Polar head may be:
 - Alcohol



Basic PFAS Chemistry (cont.)

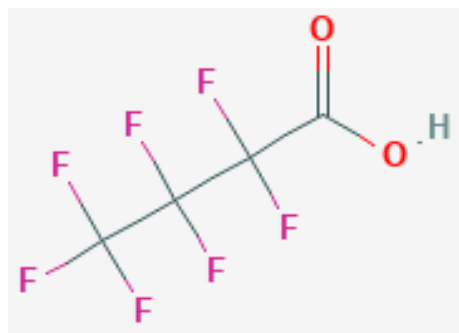
- Polar head may be:
 - Combinations of these functional groups
- Most PFAS can exist as mixtures of linear and branched alkyl chains.

Basic PFAS Chemistry (cont.)

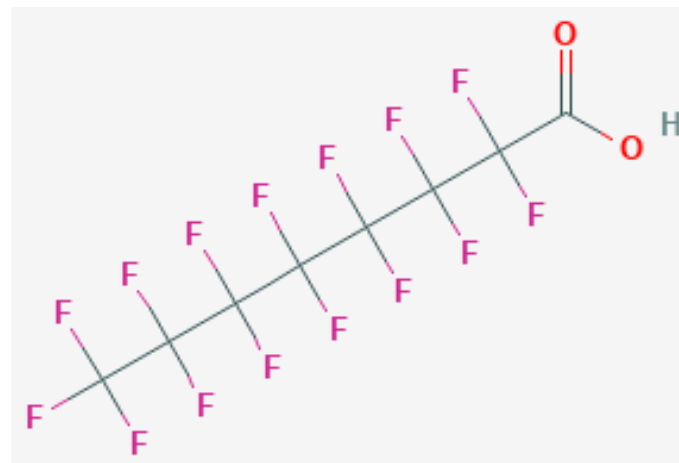
- EPA drinking water methods quantitate linear and branched but complexity was better understood when **537.1** and **533** were developed.
- PFAS can exist as salts or ions; EPA drinking water methods quantitate as them as ions.

Basic PFAS Chemistry (cont.)

- Short-chain and long-chain



Short-chain PFAS ($<C_6$ sulfonic acids and $<C_7$ carboxylic acids)



Long-chain PFAS ($\geq C_6$ sulfonic acids and $\geq C_7$ carboxylic acids)

Basic PFAS Chemistry (cont.)

- Some longer-chain PFAS (e.g, PFOA and PFOS) phased out in favor of shorter-chain PFAS.
- Very high environmental persistence.
- May be formed from other PFAS and/or released by industry-specific approved PFAS in Significant New Use Rules (SNUR).



4. Selecting an Analytical Method

Selecting an Analytical Method

- ❑ **EPA Method 537 (2009):** Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Version 1.1
- ❑ **EPA Method 537.1 (2018; updated 2020):** Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Version 2.0
- ❑ **EPA Method 533 (2019):** Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry

Selecting an Analytical Method (cont.)

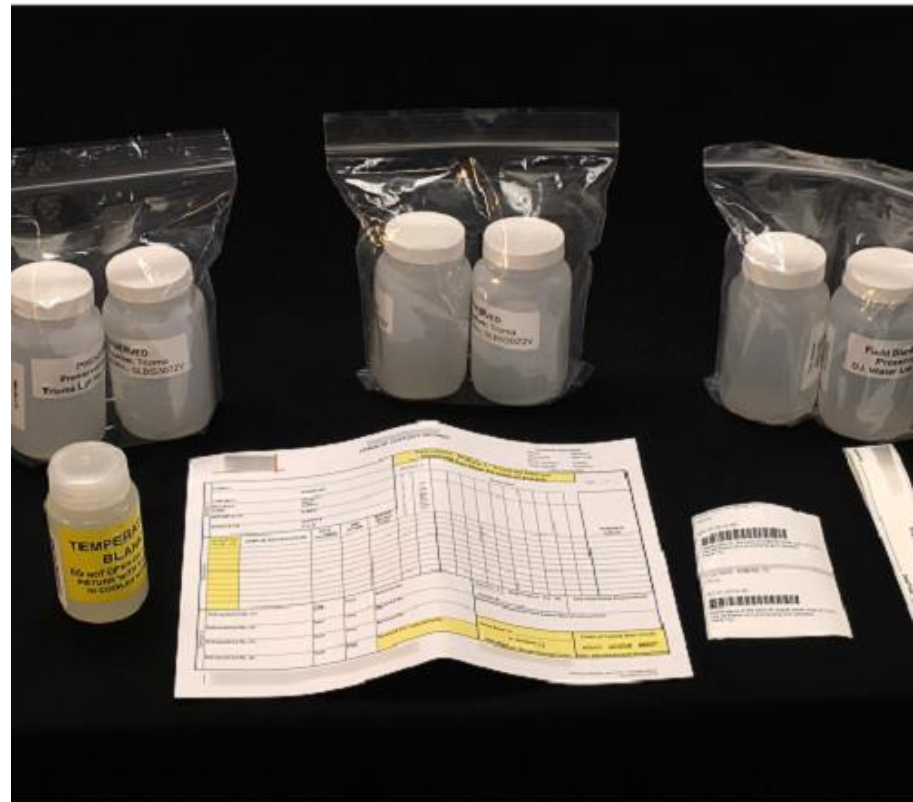
EPA Method 537 (2009)	EPA Method 537.1 (2018; 2020)	EPA Method 533 (2019)
Contains 14 target PFAS	Contains the 14 target analytes in Method 537 plus four additional PFAS	Contains 14 of the 18 target analytes in Method 537.1 plus 11 additional PFAS
	Developed as an update to EPA Method 537 with greater sensitivity	Focus on short-chain PFAS (C ₄ -C ₁₂)
<p>In general:</p> <ul style="list-style-type: none"> <input type="checkbox"/> Use EPA Method 537.1 instead of EPA Method 537 if possible (levels of potential health concern may not be met by EPA Method 537). <input type="checkbox"/> For the 14 analytes common to both 537.1 and 533, individual analyte sensitivity varies; check with laboratory. 		



5. Equipment and Supplies

Equipment and Supplies

- Sample bottles with preservatives provided by laboratory



Analytical Method	Sample Container	Preservative or De-chlorinating Agent
EPA 537 and EPA 537.1	250-mL polypropylene bottles with polypropylene screw caps	<p>Trizma[®] at 5.0 g/L (1.25 g per 250-mL bottle)</p> <p>Ship on ice; do not exceed 10 °C for first 48 hours. Samples must be documented to be ≤10 °C upon receipt by laboratory.</p>
EPA 533	Bottle size determined by lab (typically 250-mL); polypropylene bottles with polypropylene screw caps or polyethylene bottles (per QC requirements) with polypropylene screw caps	Ammonium acetate at 1.0 g/L; ship on ice; samples valid if any ice remains in cooler when it is received at the lab or bottles are received within 2 days of collection and < 10 °C.

Equipment and Supplies (cont.)

- Ensure sufficient bottles to collect Laboratory Fortified Sample Matrix and Duplicate(s) (LFSM + LFSMD) and Field Duplicate(s).
- Bottles for Field Reagent Blanks (FRB) will also be provided by laboratory.
- Determination of the number of LFSMs/LFSMDs, FRBs and Field Blanks is discussed later in QA/QC section.

Equipment and Supplies (cont.)

- ☐ Alconox or Liquinox soap
- ☐ Disposable nitrile gloves
- ☐ Labels for sample bottles and indelible ink pen (no Sharpies)
- ☐ Paper towels and Ziploc bags (large and small)
- ☐ Analyte-free deionized water

Equipment and Supplies (cont.)

- ☐ Chain of Custody (CoC)
- ☐ Sample tags with unique numbers for tagging bottles
- ☐ Sturdy cooler and double-bagged ice (PFAS may be present in source water for ice) - Do not use blue ice
- ☐ Custody seals for cooler
- ☐ Dilute (1:6) bleach solution (reduces possibility of cross contamination from previous samples in cooler)
- ☐ Shipping labels

A thick, dark blue wavy line that starts on the left, dips down towards the center, and then rises slightly towards the right, separating the top purple header area from the white content area.

6. Health and Safety

Health and Safety

- Toxicity of PFAS not fully characterized.
- PFOA is classified as “likely to be carcinogenic to humans”.
- EPA Methods 537, 537.1 and 533 do not specify additional toxicological concerns.
- Identify all safety issues and required level of personal protective equipment (PPE).
- At a minimum, use Level D PPE - work clothing that provides protection from nuisance contamination and contamination of samples.
- Safety glasses, closed-toe shoes and nitrile gloves (gloves are disposable and must be changed at each sampling location).

Health and Safety (cont.)

- Since sample bottles provided by laboratory contain chemical preservatives; do not overfill bottles, but leave some headspace for laboratory additives.





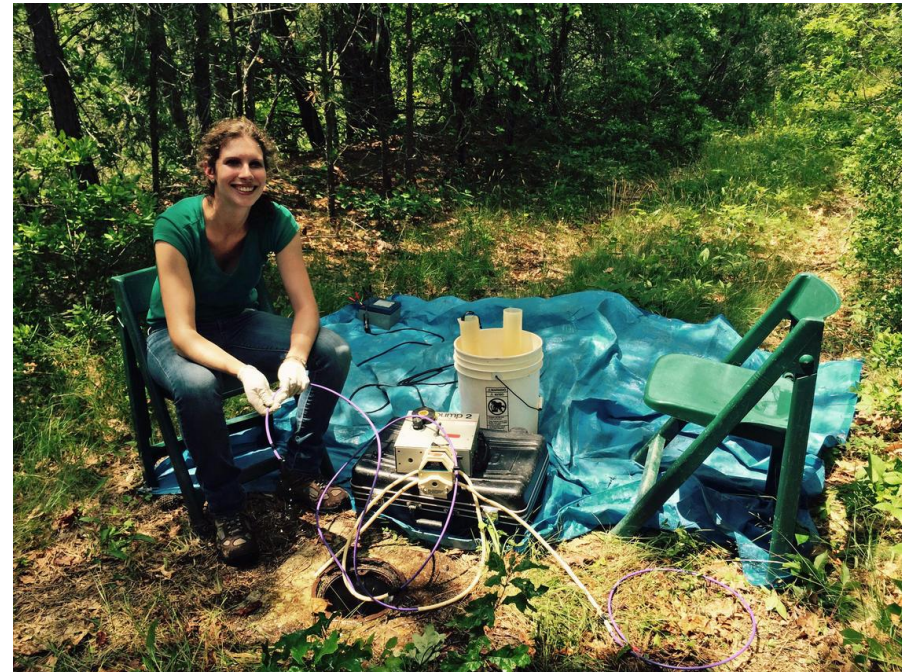
7. Sample Collection, Preservation, Handling, Shipping and Holding Times

Planning

- ☐ Confirm samplers have successfully completed all required training and certification:
 - Region III Drinking Water Sampler Training (or equivalent)
 - Appropriate field health and safety training pursuant to OSHA regulations at 29 CFR 1910.120
 - Any additional required field safety training (e.g., EPA's Field Safety & HAZWOPR)
- ☐ Review sampling location(s) in EPA Sampling Plans and/or QAPPs.
- ☐ Review safety issues and required personal protective equipment.

Planning (cont.)

- ❑ Visit site to confirm access to sampling locations
(Private/industrial sites require legal authority to access).
- ❑ Assess potential sources of PFAS:
 - Plumber's tape
 - Consumer products
 - Site operations
 - Teflon
 - Non-stick surfaces



Planning (cont.)

- At least two weeks prior to sampling:
 - ☐ Call laboratory to schedule delivery of pre-preserved sample bottles.
 - ☐ Ensure sampling team has sufficient labels and CoC(s).
 - ☐ Ensure sufficient bottles for LFSM/LFSMD, FRB and field duplicates.
 - ☐ Confirm method(s), preservatives and holding times with laboratory.
 - ☐ Arrange for courier pick up or confirm sample acceptance date at laboratory (if shipping).
 - ☐ Clean sample cooler(s) with dilute bleach solution (1:6) and wipe dry. (Bleach reduces the possibility of cross contamination from previous samples in cooler.)

Labeling Sample Bottles

- Fill out majority of label prior to sampling event.
- Use indelible ink, but no Sharpies.
- Include the following information on label:
 - ☐ Project Name/Number
 - ☐ Sampling location Number/ID
 - ☐ Sampling date and time

Labeling Sample Bottles (cont.)

- Once the sample has been collected, add the collection time to the label.



Sample Collection

1. Wash hands prior to sampling with laboratory-certified PFAS-free deionized water and Alconox or Liquinox soap and don Level D PPE.
2. Inspect faucet to ensure that it is relatively clean.



Sample Collection (cont.)

3. Do not sample from faucets that are fitted with hoses or treatment devices, those with swivel action, or those in disrepair (leak).
4. Select a faucet that allows the sample bottle to fit comfortably under the faucet without touching the faucet.
5. It is not necessary to remove aerators, if present.

No need to remove aerator
for PFAS sampling



Sample Collection (cont.)

6. Turn on the cold water and allow the water to run for 3-5 minutes.
7. Slow the stream to about the thickness of a pencil and collect the sample, taking care not to rinse any of the preservative from the bottle.
8. Do not fill bottle to the brim to leave some headspace for laboratory additives.
9. Cap the sample and swirl/invert several times to bring the preservative into solution.
10. Record the collection time on the label and store sample in cooler on ice. (*Reminder: double bag ice*)

Sample Collection (cont.)

- If the drinking water samples are substantially above 10 °C at the time of collection, a period of refrigeration or extra time on ice pre-shipping may be required to ensure that adequate ice remains in the cooler for the samples to meet temperature requirements.



Sample Collection (cont.)

Field Reagent Blanks (FRB)	Laboratory Fortified Sample Matrix and Duplicate(s) (LFSM + LFSMD)	Field Duplicates
At least one set per sample set (group of samples collected from same site at same time)	At least one set per extraction batch (there are 20 samples per extraction batch)	May be collected to serve as LFSM/LFSMD, as supplemental QA/QC data and/or in case of loss or breakage of primary sample(s)

In general:

- ☐ Collect LFSM/LFSMD, FRB and Field Duplicates per Sampling Plan/QAPP or analytical methods being used (also discussed further in QA/QC).
- ☐ EPA Methods **537**, **537.1** and **533** require the analysis of either a LFSMD or a Field Duplicate.
- ☐ Trip blanks are optional for all three methods – provided by laboratory.

Preparing Samples for Shipping, Courier Pickup or Delivery to Laboratory

- Confirm shipment schedule or verify courier service with laboratory.
- Seal CoC in a ziploc bag (if shipping); otherwise wait until courier signs the CoC.
- Ensure all bottle caps are firmly sealed.



Preparing Samples for Shipping, Courier Pickup or Delivery to Laboratory (cont.)

- Ensure there is adequate ice in cooler (no blue ice).
- If utilizing a laboratory-provided courier service, wait until courier signs the CoC to acknowledge custody of the samples and then secure cooler with tape/custody seal.
- If using a commercial shipping service (e.g., FedEx, UPS), seal samples and CoC in cooler with secure tape or custody seal and adhere shipping label to cooler. Maintain a copy of the bill-of-lading.
- Indicate shipping tracking number in notes field of CoC.
- Temperature blanks are not necessary since all samples must meet temperature requirements upon receipt by the laboratory.

CoC Documentation

- CoC must contain the following data elements:
 - ☐ Sampling team leader's signature.
 - ☐ Sample IDs and all other information from the sample bottle label.
 - ☐ Any issues observed during sampling that are relevant to the integrity of the samples and/or the results.
 - ☐ Include only one sample per line item.

Holding Times

EPA Method 537 (2009)	EPA Method 537.1 (2018; 2020)	EPA Method 533 (2019)
Extract ASAP , but must be within 14 days of collection		Extract ASAP , but must be within 28 days of collection
Store extracts at room temperature and analyze extracts within 28 days of extraction.		



8. Interferences, Sources of Cross-Contamination and Precautionary Measures

Environmental/Commercial Sources of PFAS



Teflon seals, caps
and bottles



Blue ice



Sharpies



Waterproof paper



Pipe thread
compounds and tape

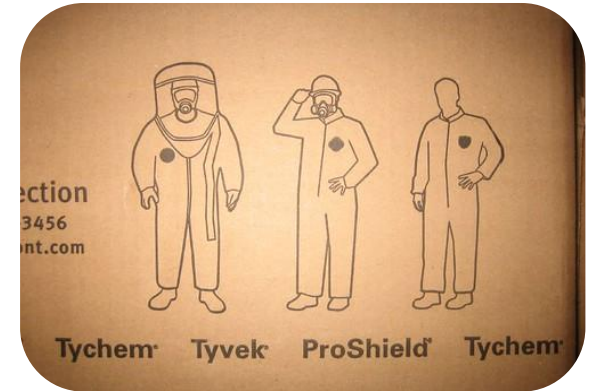
Environmental/Commercial Sources of PFAS



Stain-repellent clothing



Food wrappers and
aluminum foil



Coated Tyvek or
Tychem



Water-repellent clothing



Personal care products

Environmental/Commercial Sources of PFAS (cont.)

- See Michigan Department of Environmental Quality (MIDEQ). 2018. General PFAS Sampling Guidance; lists of products that contain PFAS and those that do not:

[https://www.michigan.gov/documents/pfasresponse/General PFAS Sampling Guidance 634597 7.pdf](https://www.michigan.gov/documents/pfasresponse/General_PFAS_Sampling_Guidance_634597_7.pdf)

Precautions

Do NOT...

- ☐ Eat on-site.
- ☐ Re-use any sampling equipment that has not been adequately decontaminated (see sampling plan for decontamination procedures).
- ☐ Use fabric softeners that contain PFAS.
- ☐ Use any field clothing washed with fabric softener.
- ☐ Use any field clothing treated for water repellence, stain-resistance, insect resistance, or ultraviolet protection.
- ☐ Use shampoo, conditioner, body gel, nail polish, deodorant, or cosmetics for at least 24 hours prior to sampling.

Precautions

Best Practices...

- ☐ Designate “clean hands” and “dirty hands” roles for this project.
- ☐ Wear 100% cotton clothing.
- ☐ Wash new field clothing at least 6-10 times prior to use for sampling.
- ☐ Use only disposable nitrile gloves.
- ☐ Wash hands after eating and before returning to the sampling site(s).
- ☐ Wash hands with laboratory-certified PFAS-free deionized water and Alconox or Liquinox soap.
- ☐ Wash hands and change gloves between each sampling location.



9. Data Records/Management

Data Records/Management

- Maintain field notebook and record all observations that might affect analytical results.
- Record field observations that are relevant to the laboratory (e.g., known hazards such as ignitable vapors, radioactivity, etc.) on CoC.
- Always retain a copy of signed CoC.
- Maintain and update SOPs on Resiliency and Preparedness for DCDI SharePoint site.
- Follow the Region 3 Records Management SOP.



10. QA/QC

Laboratory Fortified Sample Matrix and Duplicate(s) (LFSM + LFSMD)

- Field sample that is fortified by the laboratory at known concentrations of target analytes.
- **LFSM** used to identify whether characteristics of the water matrix being analyzed may be interfering with the accurate measurement of target analytes; expressed as percent recovery.
- **LFSMD** used to evaluate the precision associated with any potential matrix effects observed in the LFSM; expressed as Relative Percent Difference (RPD).
- Collect as two additional bottles at same time as parent sample.

All three EPA drinking water methods for PFAS require the analysis of either a LFSMD or a Field Duplicate.

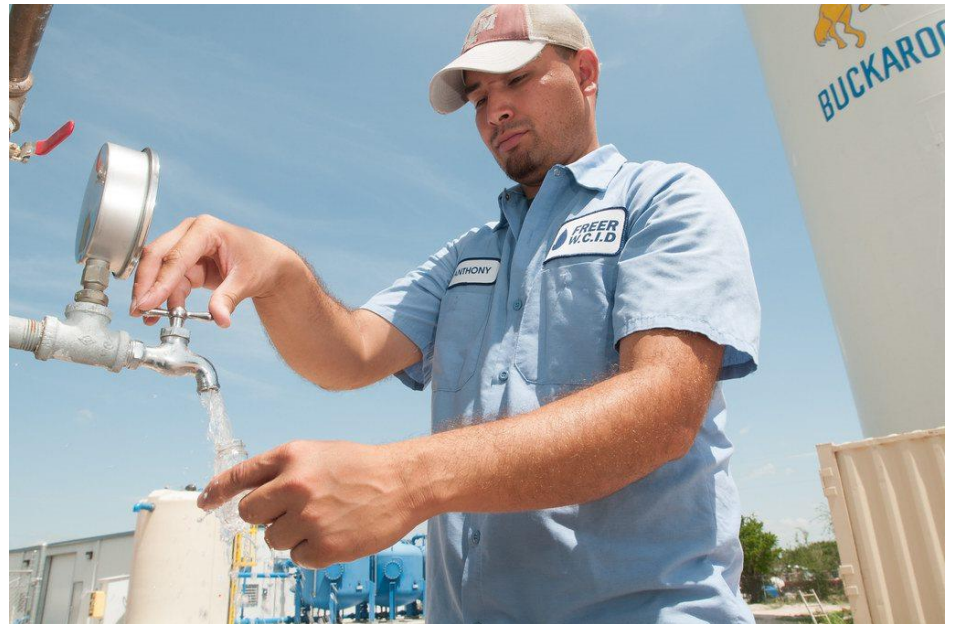
LFSMD vs. Field Duplicate

- Depends on the concentration(s) of target analytes that are observed in field samples.
- If target analytes are **typically observed** in field samples at concentrations that can reliably be reported, then the analysis of a **Field Duplicate** is acceptable.
- If target analytes are **not typically observed** in field samples, are present only at very low concentrations, or if unknown then the analysis of a **LFSMD** is a better choice.

At least one LFSMD or Field Duplicate is required for each extraction batch.

Field Reagent Blanks (FRB)

- A sample of laboratory reagent water that is provided by the laboratory; used to assess potential contamination of samples due to ambient site conditions.
- One FRB required for **each sample set** (a group of samples that is collected from the same site and at the same time).



FRB

- For EPA Methods **537** and **537.1**, FRB is a sample bottle containing laboratory reagent water and method preservatives from the same batch of preservatives that are used for the field samples.
 - This is prepared by the laboratory and sent to the sampler(s).
- A second empty bottle (no preservatives) is also provided by the laboratory.
 - This empty bottle is opened at the sampling site and the preserved reagent water is poured into the empty bottle which is then submitted as the FRB.

FRB

- For EPA Method **533**, FRB is a sample bottle containing laboratory reagent water (no preservatives).
 - This is prepared by the laboratory and sent to the sampler(s).
- A second bottle (containing only preservatives from the same batch of preservatives that are used for the field samples) is also provided by the laboratory.
 - This second bottle is opened at the sampling site and the unpreserved reagent water is poured into the second bottle which is then submitted as the FRB.

FRB: Factors
to consider:
*How many
FRBs are
required?*

- Definition of sample set contains two subjective elements: 1) what constitutes the same site? and 2) what constitutes the same time?
- Programmatic/site specific decision that should be addressed by the project manager prior to sample collection.
- Unless there is knowledge of a temporal event that might lead to changes in ambient levels of PFAS at the sampling site, for these purposes, "the same time" can be taken to mean within 15 minutes of one another (per Clean Water Act definition of a grab sample).
- If sampling is to be conducted at a residence, very high probability that all faucets therein are served by the same source of drinking water.

FRB: Factors
to consider:
*How many
FRBs are
required?*

- More than one FRB may be warranted if:
 - The system has multiple entry points to the distribution system.
 - The sampling site (residential or commercial) contains sources of PFAS.



Trip Blank (optional for all three EPA Drinking water methods for PFAS)

- A sample bottle containing laboratory reagent water and method preservatives from the same batch of preservatives that are used for the field samples.
- Prepared by the laboratory and remain sealed from the time they are shipped by the laboratory until they are shipped back to the laboratory and analyzed.
- Stored with the sample bottles and then the collected samples and are used to evaluate whether ambient conditions at the laboratory, during shipping to the sampler(s), at a sampling location or while being returned to the laboratory may be contributing target analytes to the water samples.



Thank you, any questions?

Reference EPA's PFAS Sampling
SOP for summarized information

QA Information

- Prepared by the Cadmus Group LLC
- Revised
 - December 3, 2020 (Cadmus)
 - December 29, 2020 (EPA, R3, Heather Arvanaghi)

Cadmus Project Manager: Katherine Martel

Cadmus QA Officer: Shari Ring

EPA Designated Project Manager: Patti Kay Wisniewski (COR)

EPA Delegated Approving Official: Heather Arvanaghi (Alt-COR)