



Sampling for PFAS in Different Media

PFAS Sampling For Environmental Professionals

CTCPA Education Center, Rocky Hill, CT

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Jim Occhialini
Alpha Analytical

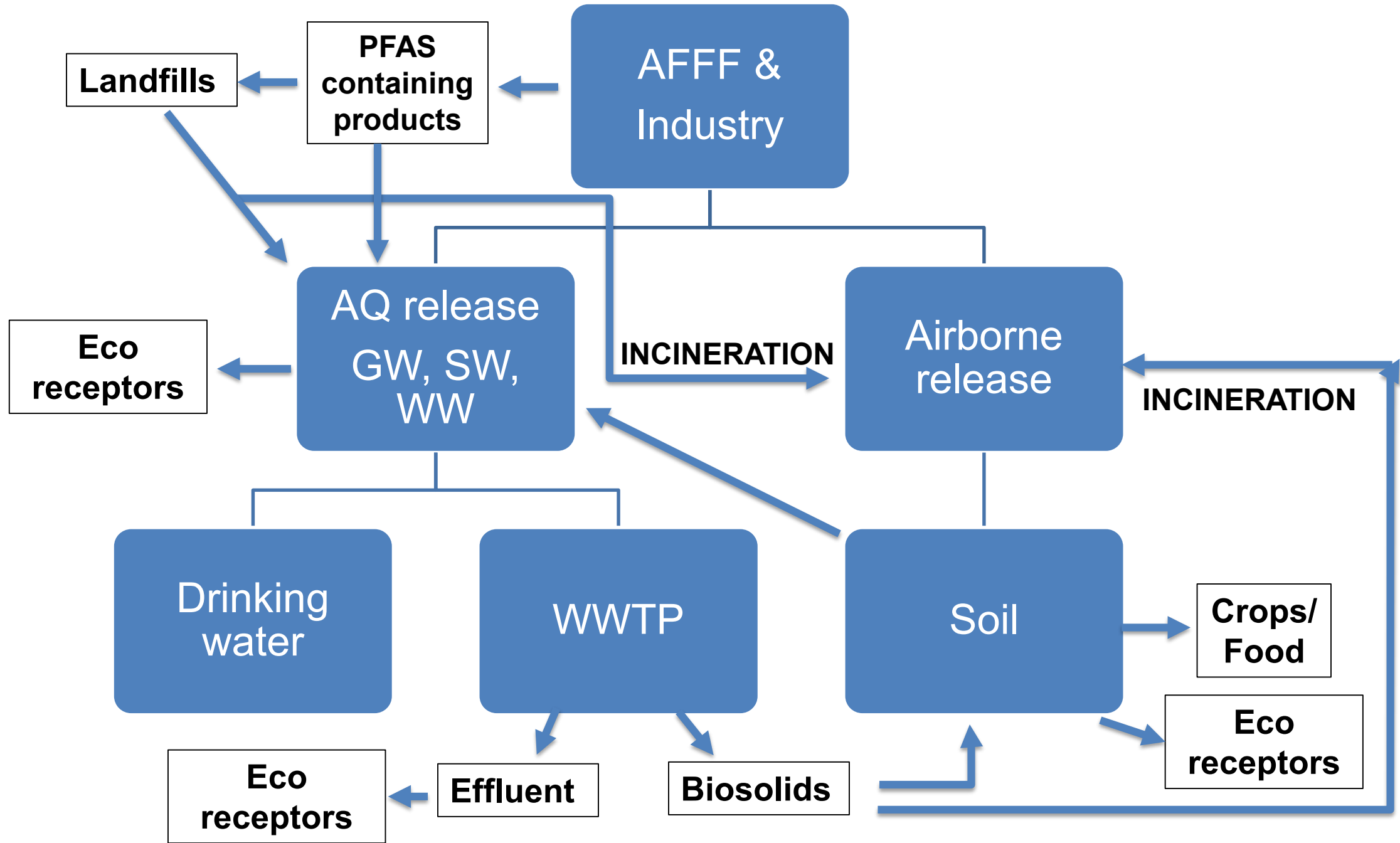


Topics for Discussion

"What we find in the environment often depends on what we look for and how hard we look" USGS website

- **Drinking water**
- **Other media**
- **State specific guidance - Where / what to sample?**
- **Cross contamination avoidance guidance**
- **Cross contamination study results**





Drinking Water Sampling Method 537 / 537.1

- Sampling for SDWA compliance?
 - Use Method 537 / 537.1
 - Designed for chlorinated public water supplies
 - UCMR 3 method
 - Amenable to a specific 14 / 18 compound PFAS target list
- Specific method requirements
 - Trizma® de-chlorinating agent/buffer
 - Field reagent blanks (FRB)
- FRB must be handled along with each sample set
 - Sample set is composed of samples collected from the same sample site and at the same time

Method 537 Section 8.3: FRB must be handled along with each sample set

- Method 537 Section 8.3
- For each FRB, an empty sample bottle (no preservatives) will also be shipped
 - Sampler must open the shipped FRB and pour the preserved reagent water into the empty shipped sample bottle, seal and label this bottle as the FRB
 - Treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures
 - The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAAs were not introduced into the sample during sample collection/handling.



Field Quality Control

- Other than FRB for compliance drinking water sampling...
 - Inclusion of PFAS field QC in sampling program
 - Same concept as non-PFAS sampling programs
- Follow regulatory guidelines where applicable
 - i.e. MassDEP sampling DW under the MCP
 - Sampling in duplicate, use of trip blanks
- Field QC options
 - Precision
 - Field duplicates, split samples
 - Accuracy
 - PE / PT samples
 - MS/MSD

PFAS Sampling Instructions for SDWA (Drinking Water) Compliance for EPA Method 537

Please read instructions entirely prior to sampling event.

It should be noted that there is considerable information available from the US EPA as well as a multitude of state regulatory agencies regarding the potential for PFAS cross-contamination during sampling. It is recommended that samplers consult the applicable regulatory guidance prior to sampling. The following instructions are drawn from "METHOD 537, Version 1.1, September 2009, EPA Document #: EPA/600/R-08/092".

The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

Each sample requires a set of containers to comply with the method as indicated below.

Container Count	Container Type	Preservative
2 Sampling Containers - Empty	275 mL container	Pre preserved with Trizma
Reagent Water for Field Blank use	275 mL container	Pre preserved with Trizma
1 Field Blank (FRB) Container - Empty	275 mL container	Unpreserved

**** Sampling container must be filled to the neck.** For instructional purposes a black line has been drawn to illustrate the required fill level for each of the 2 Sample containers**

The Field blank, for SDWA compliant samples only, must be included and handled with each sample set at the sampling location. A sample set consists of samples collected from the same site at the same time.

Field Blank Instructions:

1. Locate the Reagent Water container from the bottle order. The Reagent Water container is prefilled with PFAS-free water and preserved with Trizma.
2. Locate the empty container labeled "Field Blank".
3. Open both containers and proceed to transfer contents of the "Reagent Water" container into the "Field Blank" container.

Both the empty Reagent Water container and the filled Field Blank container must be returned to the laboratory along with the samples taken.

Sampling Instructions:

1. Each sampling event requires 2 containers to be filled to the neck of the provided containers for each sampling location.
2. Before sampling, remove faucet aerator, run water for 5 min, slow water to flow of pencil to avoid splashing and fill sample containers to neck of container (as previously illustrated) and invert 5 times.
3. Do not overfill or rinse the container.
4. Close containers securely.
5. Ensure Chain-of-Custody and all labels on containers contain required information.

Place sample, Field Blank and empty Reagent Blank containers in ice filled cooler and return to the laboratory. Samples should be kept at 4°C ±2. Samples must not exceed 10°C during first 48 hours after collection. Hold time is 14 days.

Please contact your project manager with additional questions or concerns.



PFAS Sampling Instructions for non-Drinking Water (non-SDWA) for EPA Method 537 and/or LC/MS/MS Incorporating the Isotope Dilution Technique

Please read instructions entirely prior to sampling event.

It should be noted that there is considerable information available from the US EPA as well as a multitude of state regulatory agencies regarding the potential for PFAS cross-contamination during sampling. It is recommended that samplers consult the applicable regulatory guidance prior to sampling. For additional information, please refer to "METHOD 537, Version 1.1, September 2009, EPA Document #: EPA/600/R-08/092".

The sample handler should wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

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**** Sampling container must be filled to the neck.** For instructional purposes a black line has been drawn to illustrate the required fill level for each of the 2 Sample containers**

Sample containers for field blanks are included with your container order. If you wish to submit field blanks (billable samples) in addition to your field samples, please prepare them as instructed below:

Field Blank Instructions:

1. Locate the Reagent Water container from the bottle order. The Reagent Water container is prefilled with PFAS-free water and preserved with Trizma.
2. Locate the empty container labeled "Field Blank".
3. Open both containers and proceed to transfer contents of the "Reagent Water" container into the "Field Blank" container.

Both the empty Reagent Water container and the filled Field Blank container must be returned to the laboratory along with the samples taken.

Sampling Instructions:

1. Each sampling event requires 2 containers to be filled to the neck of the provided containers for each sampling location.
 2. Fill sample containers to neck of container (as previously illustrated) and invert 5 times.
 3. Do not overfill or rinse the container.
 4. Close containers securely.
 5. Ensure Chain-of-Custody and all labels on containers contain required information.
- Place sample, Field Blank and empty Reagent Blank containers in ice filled cooler and return to the laboratory. Samples should be kept at 4°C ±2. Samples must not exceed 10°C during first 48 hours after collection. Hold time is 14 days.

Please contact your project manager with additional questions or concerns.





Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)



Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

PFAS contamination poses site characterization, sampling, and analytical challenges. PFAS have unique chemical and physical properties and they often occur in complex mixtures that can change over time. At environmental investigation sites, very low concentrations of several different PFAS must be sampled and analyzed. Many materials used in the course of environmental investigation can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff affect sample results.

EUSEPA has compiled an online resource for PFAS that includes topics such as policy and guidance, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about sampling and analytical methods (NGWA 2017).

2 Site Characterization Considerations

The purpose of site characterization is to understand the sources of contamination, site-specific contaminant fate and transport, and potential exposures and risks posed by a site. The site characterization techniques and study principles for PFAS-contaminated sites are generally the same as for any other site contaminated by hazardous substances. General site investigation principles and techniques will not be covered in this fact sheet, as these are well described in many existing guidance documents (for example, ASTM International 2011, 2013a, 2013b, 2014a, 2014b; Intergovernmental Data Quality Task Force (IDQTF) 2005; USEPA 1987, 1988a, 2000a, 2006c, 2013a, 2016).

The unique chemical characteristics, uses, and transport mechanisms of PFAS should be accounted for when characterizing a contaminated site. PFAS sources (including ambient sources) pose many challenges, including their frequent occurrence as mixtures, the role of precursors, and the persistence and mobility of PFAS relative to other environmental contaminants.

2.1 Sources and Site Identification

The *Environmental Fate and Transport* fact sheet contains conceptual site models, including descriptions and figures, for four different common source scenarios. Phase 1 site characterization investigations (ASTM 2013c) may miss the potential for PFAS contamination at a site because these chemicals historically were not considered hazardous. Comparing timelines of site history (for example, processes, layout, chemical use, and release history) with the timeline of PFAS use and with existing drinking water data (for example, the UCMR3 data [USEPA 2017f]) can be helpful in determining source identification. A solid understanding of historical uses and the past presence of PFAS is critical to identifying PFAS that may have been released at a site. See the *History and Use* fact sheet for more information.

Another challenge is that commercial products and industrial releases may consist of complex PFAS mixtures that change over time through fate and transport mechanisms and may include unidentified PFAS. Changes in manufacturing practices as well as formula modifications also complicate the source identification. When characterizing source areas, there is often a focus on only perfluoroalkyl acids (PFAAs), particularly perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), which are the current chemicals of concern. These and other chemicals of concern were often released as part of original PFAS mixtures, but also may be transformation products of PFAA precursors. The focus on PFAAs means that significant portions of the total PFAS contamination might be missed, leading to underestimates of plume life expectancy for groundwater and mass flux as well as PFAS contaminant mass.

The variation in mixtures of PFAS, associated with different processes and products, may provide signatures that help identify source areas and distinguish between multiple sources. However, careful analysis is needed to distinguish between signatures associated with differing sources and those due to environmental partitioning or multiple releases over time.

Knowledge of PFAS fate, transport, and mode of release is essential to placing sampling locations. Some PFAS released at aqueous film-forming foam (AFFF) training or application sites or by industrial air emissions may result in large, diffuse areas of soil contamination (rather than point sources) that act as sources of groundwater contamination. Air emissions

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies regarding PFAS. This fact sheet describes methods for evaluating PFAS in the environment, including:

- site characterization considerations
- sampling precautions
- laboratory analytical methods

3 Sampling

Sampling conducted to determine PFAS concentrations in water, soil, sediment, air, biota and other sources is similar to that for other chemical compounds, but with several additional specific considerations and protocols. If regulatory procedures, methods, or guidelines are inconsistent with the needs of a PFAS sampling program, then the governing agency should be contacted directly to determine an alternate approach or if an exception can be made. Other considerations for PFAS sampling include low laboratory detection limits, state and federal screening levels, and in some cases, cleanup criteria and potential for background concentrations of PFAS in the environment.

Per- and Polyfluoroalkyl Substances (PFAS) Team

March 2018



ITRC

50 F St. NW, Suite 350
Washington, DC 20001
itrcweb.org



Sampling Protocols and Lab Analyses

Peter Sandin

NHDES Hazardous Waste Remediation Bureau

PFAS Stakeholder Meeting

April 11, 2017



Topics

- ▶ **Developing a Sampling Plan**
 - Site Prioritization
 - Existing Conceptual Site Model
 - Historical knowledge not previously considered for CSM
 - Provide sound justification for approach
- ▶ **Sampling Protocols**
 - Field Equipment Selection
 - Personal Considerations
 - QA/QC
- ▶ **Laboratory Analyses and Considerations**



Fact Sheet

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

June 19, 2018

How to Sample for PFAS

Because of the potential presence of PFAS in common consumer products and in equipment typically used to collect soil, groundwater, surface water, sediment, and drinking water samples as well as the need for very low reporting limits, special handling and care must be taken when collecting samples for PFAS analysis to avoid sample contamination. In general, items that are specifically identified as waterproof, water resistant or stain-resistant should be avoided or examined for the potential presence of PFAS. There is extensive guidance available online¹² and it is not MassDEP's intent to the use and avoidance of certain products, particularly as formulations may change over time.

Specific recommendations are less important than the LSP's awareness and consideration of how product formulation or analytical methodologies may affect the results at a site.

Sample collection method/sequence

Using new nitrile gloves, collect the sample for PFCs prior to collecting samples for any other analysis to avoid contact with other types of sample containers, bottles or package materials.

As with all samples, do not place the sample bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.

When the sample is collected and capped, place the sample bottle(s) in an individual sealed plastic bag, separate from all other sample parameter bottles, and place in shipping container packed only with ice

Groundwater, surface water, or drinking water samples should not be field filtered as the glass fiber on the filter can potentially absorb PFAS, resulting in underestimates of PFAS concentration. No sub-sampling/sample transfer should occur in the field. Water samples should be placed in sealed plastic bags to avoid contamination during transport.

Collection of Groundwater Samples for Perfluorooctanoic Acid (PFOA) and Perfluorinated Compounds (PFCs) from Monitoring Wells Sample Protocol

Samples collected using this protocol are intended to be analyzed for perfluorooctanoic acid (PFOA) and other perfluorinated compounds by Modified (Low Level) Test Method 537.

The procedure used must be consistent with the NYSDEC March 1991 Sampling Guidelines and Protocols http://www.dec.ny.gov/docs/remediation_hudson_pdf/sgpsect5.pdf with the following materials limitations.

At this time acceptable materials for sampling include: stainless steel, high density polyethylene (HDPE), PVC, silicone, acetate and polypropylene. Equipment blanks should be generated at least daily. Additional materials may be acceptable if pre-approved by NYSDEC. Requests to use alternate equipment should include clean equipment blanks. **NOTE: Grunfos pumps and bladder pumps are known to contain PFC materials (e.g. Teflon™ washers for Grunfos pumps and LDPE bladders for bladder pumps). All sampling equipment components and sample containers should not come in contact with aluminum foil, low density polyethylene (LDPE), glass or polytetrafluoroethylene (PTFE, Teflon™) materials including sample bottle cap liners with a PTFE layer.** Standard two step decontamination using detergent and clean water rinse will be performed for equipment that does come in contact with PFC materials. Clothing that contains PTFE material (including GORE-TEX®) or that have been waterproofed with PFC materials must be avoided. Many food and drink packaging materials and "plumbers thread seal tape" contain PFCs.

All clothing worn by sampling personnel must have been laundered multiple times. The sampler must wear nitrile gloves while filling and sealing the sample bottles.

Pre-cleaned sample bottles with closures, coolers, ice, sample labels and a chain of custody form will be provided by the laboratory.

1. Fill two pre-cleaned 500 mL HDPE or polypropylene bottle with the sample.
2. Cap the bottles with an acceptable cap and liner closure system.
3. Label the sample bottles.
4. Fill out the chain of custody.
5. Place in a cooler maintained at $4 \pm 2^\circ$ Celsius.

Collect one equipment blank for every sample batch, not to exceed 20 samples.

Collect one field duplicate for every sample batch, not to exceed 20 samples.

Collect one matrix spike / matrix spike duplicate (MS/MSD) for every sample batch, not to exceed 20 samples.

Request appropriate data deliverable (Category A or B) and an electronic data deliverable.

Sampling Guidance by Sample Media Review

- Use same standard of care as any other environmental sampling program
 - Plus added precautions for potential PFAS cross-contamination
 - Use PFAS-free water
- Groundwater
 - Sampling equipment
 - Pumps, bailers, tubing, etc.
 - Dedicated equipment?, no PTFE tape
- Surface water
 - Rinse capped containers with surface water
 - Remote sampling using an extension rod?
 - PFAS enrichment at the air/water interface?

Sampling Guidance by Sample Media Review

- **Pore water**
 - Peristaltic pumps, tubing
 - Piezometers
- **Soils / Sediments**
 - Stainless steel grab samples or cores
 - Plastic inserts?
 - Waders or PFDs?
- **Fish / Biota**
 - Same considerations/ questions as other as other biota sampling
 - Sampling & handling
 - Discuss with laboratory for best approach

[Public Hearing on Draft Air Permit for Air Pollution Control Equipment at Saint-Gobain Performance Plastics and Information Meeting to Provide Update on Southern New Hampshire PFAS Investigation](#)

Posted on [October 8, 2019](#) by [Jim Martin](#)

News from the New Hampshire Department of Environmental Services FOR IMMEDIATE RELEASE DATE: October 8, 2019 CONTACT: Jim Martin, (603) 271-3710 des.nh.gov twitter.com/NHDES Public Hearing on Draft Air Permit for Air Pollution Control Equipment at Saint-Gobain Performance Plastics and Information Meeting to Provide Update on Southern New Hampshire PFAS Investigation Concord, NH



Guidance for Waste Sites

Since 2016, NHDES has requested sampling at waste sites per the provisions of the NH Code of Administrative Rules, Chapters Env-Or 600 and Env-Or 700. A letter clarifying which sites need to complete an initial screening for PFAS was issued in [October 2017](#). The purpose of this sampling is to determine whether any drinking water sources may be at risk associated with releases from the site. Sites that are found to have PFAS releases are subsequently managed through the NHDES Hazardous Waste Remediation Bureau (HWRB).

The types of sites that are required to sample for PFAS include, but are not limited to:

- Sites subject to Groundwater Release Detection Permits
- Landfills (lined, unlined, active, and/or closed) that are subject to groundwater monitoring requirements
- Active hazardous waste sites and sites undergoing environmental site assessment reviewed by the HWRB where either:
 - Site history indicates that releases at a site are associated with activities that use or used PFAS containing products, and/or
 - Sites where Class B firefighting foam [e.g., aqueous film forming foam (AFFF)] may have been used or released.

NHDES requests that PFAS analytical data be uploaded to the NHDES Environmental Monitoring Database (EMD). Analytical data for regulated PFAS that are uploaded to EMD are posted to the [NHDES PFAS Investigation Sampling Map](#). Site-specific summary reports are available from the NHDES OneStop database for individual sites.

ADDITIONAL RESOURCES

[Water Line Extension Projects Investigation Documents](#)
[Be Well Informed Guide](#)
[Pease Tradeport Investigation Archive](#)

RECENT POSTS

[Public Hearing on Draft Air Permit for Air Pollution Control Equipment at Saint-Gobain Performance Plastics and Information Meeting to Provide Update on Southern New Hampshire PFAS Investigation](#)
[Update on Southern New Hampshire PFAS Investigation](#)
[Summary of the Technical Background Report for the Proposed Maximum Contaminant Levels and Ambient Groundwater Quality Standards for PFOA, PFOS, PFNA](#)

February 2019



Sampling for 1,4-Dioxane and Per- and Polyfluoroalkyl Substances (PFAS) Under DEC's Part 375 Remedial Programs

Objective

The Department of Environmental Conservation (DEC) is requiring sampling of all environmental media and subsequent analysis for the emerging contaminants 1,4-Dioxane and PFAS as part of all remedial programs implemented under 6 NYCRR Part 375, as further described in the guidance below.

Sample Planning

The number of samples required for emerging contaminant analyses is to be the same number of samples where "full TAL/TCL sampling" would typically be required in an investigation or remedial action compliance program.

Upon a new site being brought into any program (e.g., SSF, BCP), PFAS and 1,4-dioxane will be incorporated into the investigation of potentially affected media, including soil, groundwater, surface water, and sediment as an addition to the standard "full TAL/TCL sampling." Biota sampling may be necessary based upon the potential for biota to be affected as determined pursuant to a Fish and Wildlife Impact analysis. Soil vapor sampling for PFAS and 1,4-dioxane is not required.



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Sample Planning

The number of samples required for emerging contaminant analyses is to be the same number of samples where "full TAL/TCL sampling" would typically be required in an investigation or remedial action compliance program.

Sampling of all media for ECs is required at all sites coming into or already in an investigative phase of any DER program. In other words, if the sampling outlined in the guidance hasn't already been done or isn't part of an existing work plan to be sampled for in the future, it will be necessary to go back out and perform the sampling prior to approving a SC report or issuing a decision document.

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Upon an emerging contaminant being identified as a contaminant of concern (COC) for a site, those compounds must be assessed as part of the remedy selection process in accordance with Part 375 and DER-10 and included as part of the monitoring program upon entering the site management phase.

Soil imported to a site for use in a soil cap, soil cover, or as backfill must be sampled for 1,4-dioxane and PFAS contamination in general conformance with DER-10, section 5.4(e). Assessment of the soil data will be made on a site-specific basis to determine appropriateness for use.

The work plan should explicitly describe analysis and reporting requirements, including laboratory analytical procedures for modified methods discussed below.

June 2019



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Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)

3.1 Equipment and Supplies

Many materials used in the course of environmental investigation can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff affect sample results. Therefore, a conservative approach is recommended to exclude materials known to contain PFAS. Obtain and review all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling. Materials to avoid include:

- Teflon, polytetrafluoroethylene (PTFE)
- waterproof coatings containing PFAS
- food containers
- anything with fluoro in the name
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- low density polyethylene (LDPE), polyvinylidene fluoride (PVDF)

Many waterproof coatings contain PFAS, such as Gore-tex treated PPE or most waterproof papers, but some products are waterproofed with acceptable materials such as polyurethane, rubber, or PVC. Individual product specifications should be examined closely. In the case of Tyvek PPE, plain Tyvek does not contain PFAS while coated Tyvek does. In addition, materials incidentally transported to sites may contain PFAS. For example, fast food wrappers may contain PFAS. Due to the ubiquitous nature of PFAS, sampling crews must review all materials used to avoid contamination. Collection of quality assurance and quality control (QA/QC) samples is a useful tool to assess field contamination.

Two guidance documents identify materials and equipment that can be used in PFAS-focused investigations, as well as materials that should be avoided because they are known or suspected to be potential sources of PFAS:

- *Bottle Selection and other Sampling Considerations When Sampling for Per-and Poly-Fluoroalkyl Substances (PFAS)* (USDOD EDQW 2017b)
- *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), Contaminated Sites Guidelines*, (Government of Western Australia, Department of Environment Regulation 2016)

Field Sampling Guidelines for PFAS

Using EPA Method 537 or 537.1

Please read entire instruction sheet prior to sampling.

Sampling for PFAS using EPA method 537 or 537.1 can be challenging due to the prevalence of PFAS compounds in consumer products. Many materials normally used in field and laboratory operations contain PFAS such as tubing, sample containers, and sampling tools. Since these products can contain PFAS, they cannot be used in sampling for PFAS. In addition, many consumer goods, such as water-resistant jackets or fast food wrappers, brought to a sampling site may contain PFAS that can also contaminate samples.





PerFluorinated Compound (PFC) Sample Collection Guidance

The purpose of this document is to provide guidance on groundwater sampling protocols when collecting a sample(s) for PFCs. Detection of these compounds at very low levels can be influenced by materials that are present at the sampling site, materials used by the sampling agent, or sample container handling practices.

The following table provides a summary of items that are likely to contain PFCs (i.e. prohibited items) and therefore should not be used by the sampling agent at the sampling site.

Category	Prohibited Items	Allowable Items
Pumps and Tubing	Teflon® and other fluoropolymer containing materials	High-density polyethylene (HDPE), low density polyethylene (LDPE) , or silicone tubing, peristaltic pump or stainless steel submersible pump
Decontamination	Decon 90	Alconox® or Liquinox®, potable water followed by deionized rinse.
Sample Storage and Preservation	LDPE or glass bottles, PTFE-or Teflon®-lined caps, chemical ice packs	Laboratory-provided sample container - <i>preferred</i> ; or, HDPE or polypropylene bottles, regular ice
Field Documentation	Waterproof/treated paper or field books, plastic clipboards, non-Sharpie® markers, Post-It® and other adhesive paper products	Plain Paper, metal clipboard, Sharpies®, pens
Clothing	Clothing or boots made of or with Gore-Tex™ or other synthetic water resistant and/or stain resistant materials, Tyvek® material	Synthetic or cotton material, previously laundered clothing (preferably previously washed greater than six times) without the use of fabric softeners
Personal Care Products (for day of sample collection)	Cosmetics, moisturizers, hand cream and other related products	Sunscreens: Alba Organics Natural Yes to Cucumbers Aubrey Organics Jason Natural Sun Block Kiss My Face Baby-safe sunscreens ('free' or 'natural') Insect Repellents: Jason Natural Quit Bugging Me Repel Lemon Eucalyptus Herbal Armor California Baby Natural Bug Spray BabyGanics Sunscreen and Insect Repellents: Avon Skin So Soft Bug Guard-SPF 30
Food and Beverage	Pre-packaged food, fast food wrappers or containers	Bottled water or hydration drinks

For samples collected from monitoring wells

- When feasible, use single-use, disposable polyethylene or silicone materials (tubing, bailers, etc.) for monitoring well purging and sampling equipment.
- When reuse of materials or sampling equipment across multiple sampling locations is necessary, follow project decontamination protocols with allowed materials identified in the table above, and incorporate collection of equipment rinseate blanks into sampling program, as appropriate.
- When using positive displacement/submersible pump sampling equipment, familiarize yourself with the sampling pump/accessory equipment specifications to confirm that device components are not made of nor contain Teflon® or PTFE.

For samples collected during production well pumping tests

- If feasible, do not use Teflon® tape or pipe thread paste on pipe fittings or sampling tap threads on the pump discharge pipe.
- As with all other sample parameters, the sample for PFCs should be collected at the last hour (or hours) of the pumping portion of the testing program.
- Discharge water should be purged through the sampling tap on the discharge pipe for a minimum of 20 minutes prior to collection of samples.

For samples collected from active production wells

- If feasible, avoid contact with any Teflon® tape or pipe thread paste on pipe fittings or sampling tap threads on the water supply discharge pipe.
- The sample for PFCs should be collected while the production well pump is operating, and, preferably, has been operating for at least one hour.
- Discharge water should be purged through the sampling tap on the discharge pipe for a minimum of 20 minutes prior to collection of samples.

Sample collection method/sequence

- Using new nitrile gloves collect the sample for PFCs *first*, prior to collecting samples for any other parameters into any other containers; this avoids contact with any other type of sample container, bottles or package materials.
- As with all other samples, do not place the sample bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.
- When sample is collected and capped, place the sample bottle(s) in an individual sealed plastic bag (e.g. Ziploc®) separate from all other sample parameter bottles, and place in shipping container packed only with ice.

GENERAL PFAS SAMPLING GUIDANCE

This document contains an introduction to PFAS, biosecurity recommendations, and general recommendations to decrease the possibility of cross-contamination.

Michigan
Department of
Environmental
Quality

Revised 10/16/2018

4. General PFAS Sampling

The following sections discuss technical issues such as the need to use PFAS-free water; information about PFAS-free clothing and PPE; and laboratory issues that should be considered when sampling for PFAS.

4.1 Sampling Objectives

Before conducting any PFAS sampling, it is recommended that a project-specific Quality Assurance Project Plan (QAPP) should be developed. The QAPP must meet MDEQ policy and should include the analyte list, method of analysis, environmental matrices, and reporting limits, which are based on the project objectives. All of these considerations will be discussed in more detail in this guidance document.

4.2 PFAS Cross-Contamination Potential Sources

Potential sources of PFAS cross-contamination in the typical sampling environment include water used during drilling or decontamination, materials used within the sampling environment, sampling equipment, field clothing and personal protective equipment (PPE), sun and biological protection products, personal hygiene and personal care products (PCPs), food packaging, and the environment itself.

The materials associated with sampling that have the potential for PFAS cross-contamination have been divided into three major groups:

- Prohibited (●) identifies items and materials that should not be used when sampling. It is well documented that they contain PFAS or that PFAS are used in their manufacture.
- Allowable (■) identifies items and materials that have been proven not to be sources of PFAS cross contamination and are considered allowable for sampling.
- Needs Screening (▲) identifies items and materials that have the potential for PFAS cross-contamination due to a lack of scientific data or statements from manufacturers to prove otherwise. These items and materials are further sub-divided into two categories.
 - o **Category 1:** Items and materials that will come in direct contact with the sample. These should not be used when sampling unless they are known to be PFAS-free, by collecting an equipment blank sample prior to use.
 - o **Category 2:** Items and materials that will not come in direct contact with the sample. These should be avoided, if possible, unless they are known to be PFAS-free by collecting an equipment blank sample prior to use.

All of the materials or items discussed in each of the MDEQ PFAS Sampling Guidance Documents will be divided into ● Prohibited, ■ Allowable, or ▲ Needs Screening. Several examples of prohibited and allowable materials and materials that need screening are listed in the MDEQ PFAS Sampling Quick Reference Field Guide at the end of this document. Also, materials and items that are specific to a particular environmental media or sampling method will be thoroughly explained in that media's sampling guidance document (such as peristaltic pumps for groundwater sampling).

NOTE: If recommended PPE will be used during sampling, Category 2 materials are not expected to be a source of cross-contamination as long as they do not come into contact with the samples.

MDEQ PFAS SAMPLING QUICK REFERENCE FIELD GUIDE¹

All Items Used During Sampling Event

Prohibited
<ul style="list-style-type: none"> Items or materials that contain fluoropolymers such as <ul style="list-style-type: none"> Polytetrafluoroethylene (PTFE), that includes the trademarks Teflon® and Hostaflon® Polyvinylidene fluoride (PVDF), that includes the trademark Kynar® Polychlorotrifluoroethylene (PCTFE), that includes the trademark Neoflon® Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel® Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP Items or materials that contain any other fluoropolymer

Pumps, Tubing, and Sampling Equipment

Prohibited	Allowable	Needs Screening ²
<ul style="list-style-type: none"> Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape) 	<ul style="list-style-type: none"> High-density polyethylene (HDPE) Low-density polyethylene (LDPE) tubing Polypropylene Silicone Stainless-steel Any items used to secure sampling bottles made from: <ul style="list-style-type: none"> Natural rubber Nylon (cable ties) Uncoated metal springs Polyethylene 	<ul style="list-style-type: none"> Any items or materials that will come into direct contact with the sample that have not been verified to be PFAS-free <ul style="list-style-type: none"> Do not assume that any sampling items or materials are PFAS-free based on composition alone

Sample Storage and Preservation

Prohibited	Allowable	Needs Screening ²
<ul style="list-style-type: none"> Polytetrafluoroethylene (PTFE): Teflon® lined bottles or caps 	<ul style="list-style-type: none"> Glass jars⁴ Laboratory-provided PFAS-Free bottles: <ul style="list-style-type: none"> HDPE or polypropylene Regular wet ice Thin HDPE sheeting LDPE resealable storage bags (i.e. Ziploc®) that will not contact the sample media⁵ 	<ul style="list-style-type: none"> Aluminium foil⁴ Chemical or blue ice⁵ Plastic storage bags other than those listed as Allowable Low-density polyethylene (LDPE) bottles

Field Documentation

Prohibited	Allowable	Needs Screening ²
<ul style="list-style-type: none"> Clipboards coated with PFAS Notebooks made with PFAS treated paper PFAS treated loose paper PFAS treated adhesive paper products 	<ul style="list-style-type: none"> Loose paper (non-waterproof, non-recycled) Rite in the Rain® notebooks Aluminium, polypropylene, or Masonite field clipboards Ballpoint pens, pencils, and Fine or Ultra-Fine Point Sharpie® markers 	<ul style="list-style-type: none"> Plastic clipboards, binders, or spiral hard cover notebooks All markers not listed as Allowable Post-It® Notes or other adhesive paper products Waterproof field books

Decontamination

Prohibited	Allowable	Needs Screening ²
<ul style="list-style-type: none"> Decon 90® PFAS treated paper towel 	<ul style="list-style-type: none"> Alconox®, Liquinox®, or Citranox® Triple rinse with PFAS-free deionized water Cotton cloth or untreated paper towel 	<ul style="list-style-type: none"> Municipal water Recycled paper towels or chemically treated paper towels

Clothing, Boots, Rain Gear, and PPE

Prohibited	Allowable	Needs Screening ²
<ul style="list-style-type: none"> New or unwashed clothing Anything made of or with: <ul style="list-style-type: none"> Gore-Tex™ or other water-resistant synthetics Anything applied with or recently washed with: <ul style="list-style-type: none"> Fabric softeners Fabric protectors, including UV protection Insect resistant chemicals Water, dirt, and/or stain resistant chemicals 	<ul style="list-style-type: none"> Powderless nitrile gloves Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners Made of or with: <ul style="list-style-type: none"> Polyurethane Polyvinyl chloride (PVC) Wax coated fabrics Rubber / Neoprene Uncoated Tyvek® 	<ul style="list-style-type: none"> Latex gloves Water and/or dirt resistant leather gloves Any special gloves required by a HASP Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

Food and Beverages

Prohibited	Allowable
<ul style="list-style-type: none"> No food should be consumed in the staging or sampling areas, including pre-packaged food or snacks. <ul style="list-style-type: none"> If consuming food on-site becomes necessary, move to the staging area and remove PPE. After eating, wash hands thoroughly and put on new PPE. 	<ul style="list-style-type: none"> Brought and consumed only outside the vicinity of the sampling area: <ul style="list-style-type: none"> Bottled water Hydration drinks (i.e. Gatorade®, Powerade®)

Personal Care Products (PCPs) - for day of sample collection⁶

Prohibited	Allowable	Needs Screening ²
<ul style="list-style-type: none"> Any PCPs⁶, sunscreen, and insect repellent applied in the sampling area. 	<p>PCPs⁶, sunscreens, and insect repellents applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands: PCPs⁶:</p> <ul style="list-style-type: none"> Cosmetics, deodorants/antiperspirants, moisturizers, hand creams, and other PCPs⁶ <p>Sunscreens:</p> <ul style="list-style-type: none"> Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30 Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30 Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30 Banana Boat® Sport Performance Sunscreen Stick SPF 50 Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50 Coppertone® Sport High Performance AccuSpray Sunscreen SPF 30 Coppertone® Sunscreen Stick Kids SPF 55 L'Oréal® Silky Sheer Face Lotion 50 Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50 Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30 Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50 Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70 Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70 Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30 Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+ Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30 <p>Insect Repellents:</p> <ul style="list-style-type: none"> OFF® Deep Woods Sawyer® Permethrin 	<ul style="list-style-type: none"> Products other than those listed as Allowable

¹ This table is not considered to be a complete listing of prohibited or allowable materials. All materials should be evaluated prior to use during sampling. The manufacturers of various products should be contacted in order to determine if PFAS was used in the production of any particular product.

² Equipment blank samples should be taken to verify these products are PFAS-free prior to use during sampling.

³ For surface water foam samples: LDPE storage bags may be used in the sampling of foam on surface waters. In this instance, it is allowable for the LDPE bag to come into direct contact with the sample media.

⁴ For fish and other wildlife samples: Depending on the project objectives, glass jars and aluminum foil might be used for PFAS sampling. PFAS has been found to bind to glass and if the sample is stored in a glass jar, a trace of the jar is required during the sample analysis. PFAS are sometimes used as a protective layer for some aluminum foil. An equipment blank sample should be collected prior to any aluminum foil use.

⁵ Regular ice is recommended as there are concerns that chemical and blue ice may not cool and maintain the sample at or below 42.8°F (5°C) (as determined by EPA 40 CFR 136 - NPDES) during collection and through transit to the laboratory.

⁶ Based on evidence, avoidance of PCPs is considered to be precautionary because none have been documented as having cross-contaminated samples due to their use. However, if used, application of PCPs must be done at the staging area and away from sampling bottles and equipment, and hands must be thoroughly washed after the use of any PCPs prior to sampling.



**Per- and Polyfluoroalkyl Substances (PFAS) Laboratory Testing Primer
 for State Drinking Water Programs and Public Water Systems**

Category	Prohibited Items/Actions that could introduce PFAS Sample Contamination	Allowable Items
Pumps and Tubing	Teflon® and other fluoropolymer containing materials	High-density polyethylene (HDPE), low density polyethylene (LDPE) or silicone tubing
Sample Container Storage	Containers should not come in to contact with carpeting or upholstery inside buildings or vehicles	Containers should be stored in a zip-lock bag and transported in coolers.
Stacked Glassware	Foil should not be used as a layer between stacked glassware	Plain paper
Field Documentation	Waterproof/treated paper or field books, plastic clipboards, non- Sharpie® markers, Post-It® and other adhesive paper products	Plain Paper, metal clipboard, Sharpies®, pens
Clothing	Clothing or boots made of or with Gore-Tex™ or other synthetic water resistant and/or stain resistant materials, Tyvek® material	Synthetic or cotton material, previously laundered clothing (preferably previously washed greater than six times) without the use of fabric softeners
Personal Care Products (for day of sample collection)	Cosmetics, moisturizers, hand cream and other related products	<p>Sunscreens:</p> <ul style="list-style-type: none"> Alba Organics Natural Yes to Cucumbers Aubrey Organics Jason Natural Sun Block Kiss My Face Baby-safe sunscreens ('free' or 'natural') <p>Insect Repellents:</p> <ul style="list-style-type: none"> Jason Natural Quit Bugging Me Repel Lemon Eucalyptus Herbal Armor California Baby Natural Bug Spray BabyGanics <p>Sunscreen and Insect Repellents:</p> <ul style="list-style-type: none"> Avon Skin So Soft Bug Guard-SPF 30
Food and Beverage	Pre-packaged food, fast food wrappers or containers	

Sampling Recommendations

"composite of multiple sources, refer to EPA, regulatory agencies"

"OK"

- **Field Equipment**

- HDPE bottles, silicon tubing, loose paper, aluminum clipboards, nitrile gloves
-

- **Clothing / PPE**

- “Well laundered”, preferably cotton

- **Personal care products**

- None, see “allowable” sun screens & insect repellants

"NOT OK"

- **Field Equipment**

- LDPE bottles, PTFE caps, PTFE tubing, waterproof field books, plastic clipboards/binders, "stickie notes", cold packs

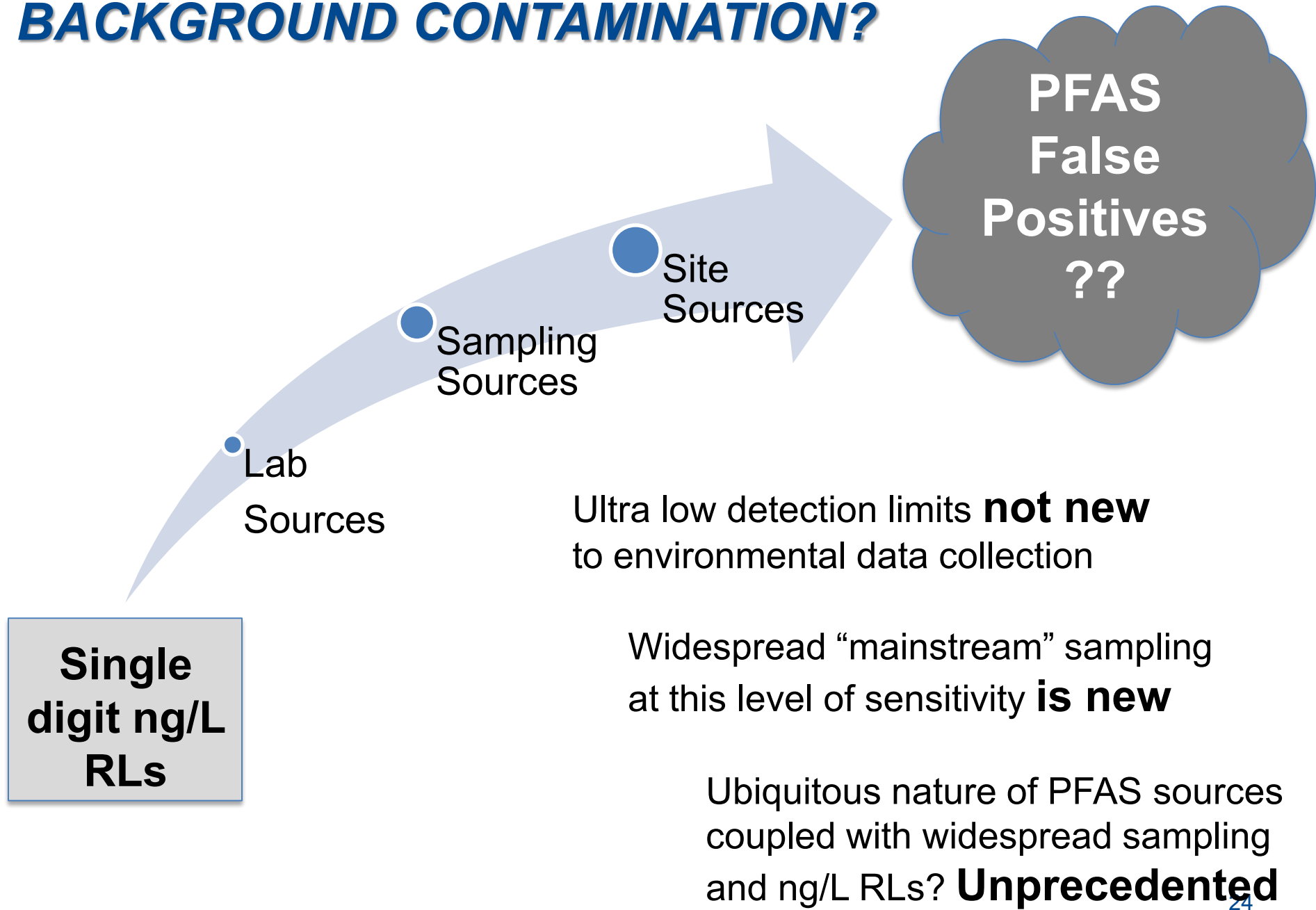
- **Clothing / PPE**

- No fabric softener, treated water repellent fabrics, protective suits

- **Personal care products**

- No cosmetics, moisturizers, etc. as part of personal cleaning/showering routine on morning of sampling
- Verify allowable sun screens / insect
- Food packaging

BACKGROUND CONTAMINATION?



PFAS in Sampling Supplies: Fact or Fiction?



HDPE Tubing



Bag



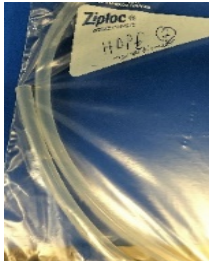
Aluminum Foil



Note Pad



Polyethylene Bladder



HDPE Tubing: 1/8" ID
3/8" OD

DOI: 10.1002/rem.21614

RESEARCH ARTICLE

WILEY

Per- and polyfluoroalkyl substances in environmental sampling products: Fact or fiction?

Elizabeth Denly¹ | Jim Occhialini² | Phil Bassignani² | Michael Eberle³ | Nidal Rabah⁴



Suit



PTFE Tubing



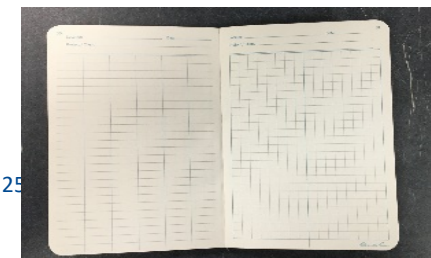
Passive Diffusion Bag



Nitrile Gloves



Bailer Line



Field Book
(cover & pages)

Concept



- **Objective:**
 - Can PFAS be transferred from common field and other commercial products during sampling?
- **Disclaimer**
 - A first look at aqueous leachability
 - Worst case scenario
 - Snapshot
 - Not an in depth study
 - Products chosen at random
 - Generic product names are used as descriptions but not to endorse or invalidate any individual product for use
 - Nothing implied concerning a given product's results
 - Sources, manufacturers, product ID, lot #, etc.

Experimental Design, Leaching Step



■ Leaching Step

- Shaker table, 24 hr. contact time then decant
 - 2 replicate extractions per product, batch leach & method blanks
- PFAS-free water
- 250 mL volume
 - neutral pH, moderate conductivity: 300 us/cm
- 10 x 10 in product surface area (ideally)
 - Leaching containers
 - HDPE 250 ml bottles

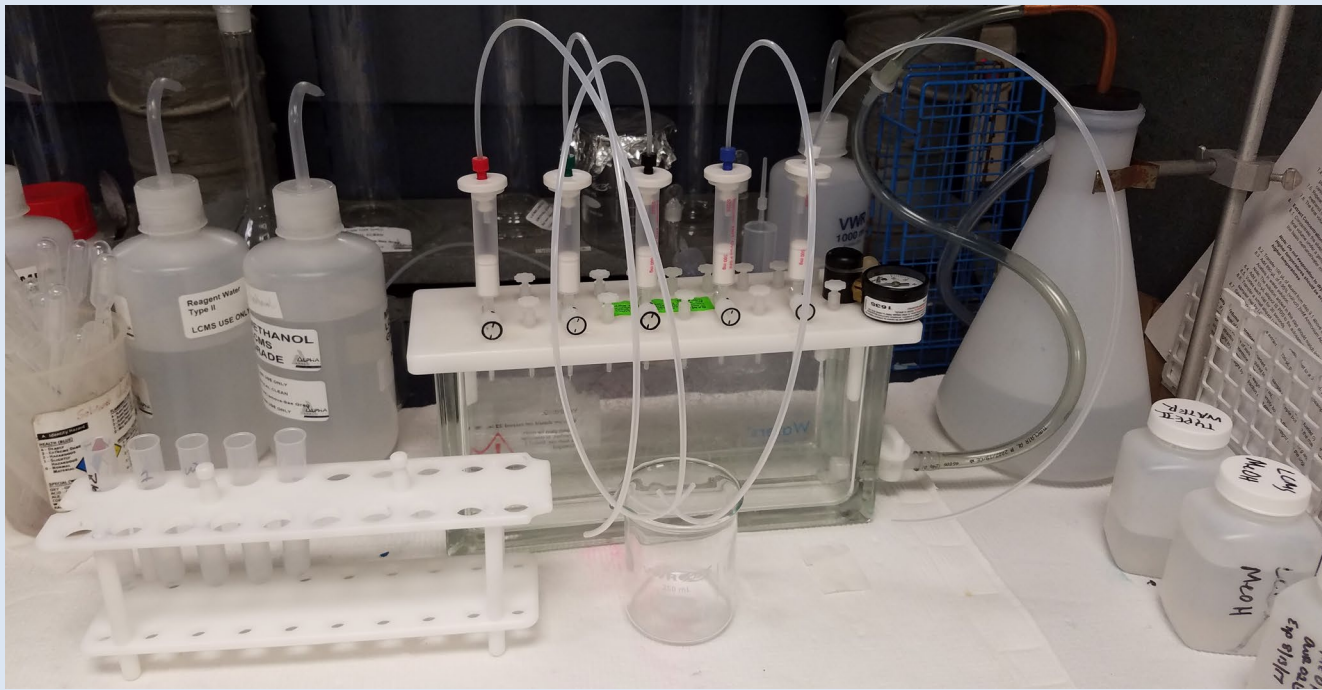
■ Leaching blanks



Bentonite

- Leaching procedure
 - 100 grams placed in metal pan, water added
 - Pelletized, coated bentonite was removed from the water once coating dissolved
 - Otherwise, the bentonite was removed from water once it started to expand
 - Standard preparation procedure from there





Quality Control:

Method Blanks

LCS

Calibration Checks

Extracted IS

Matrix Spikes

Experimental Design Analysis

Solid phase extraction

LC/MS/MS, isotope dilution

24-compound target list

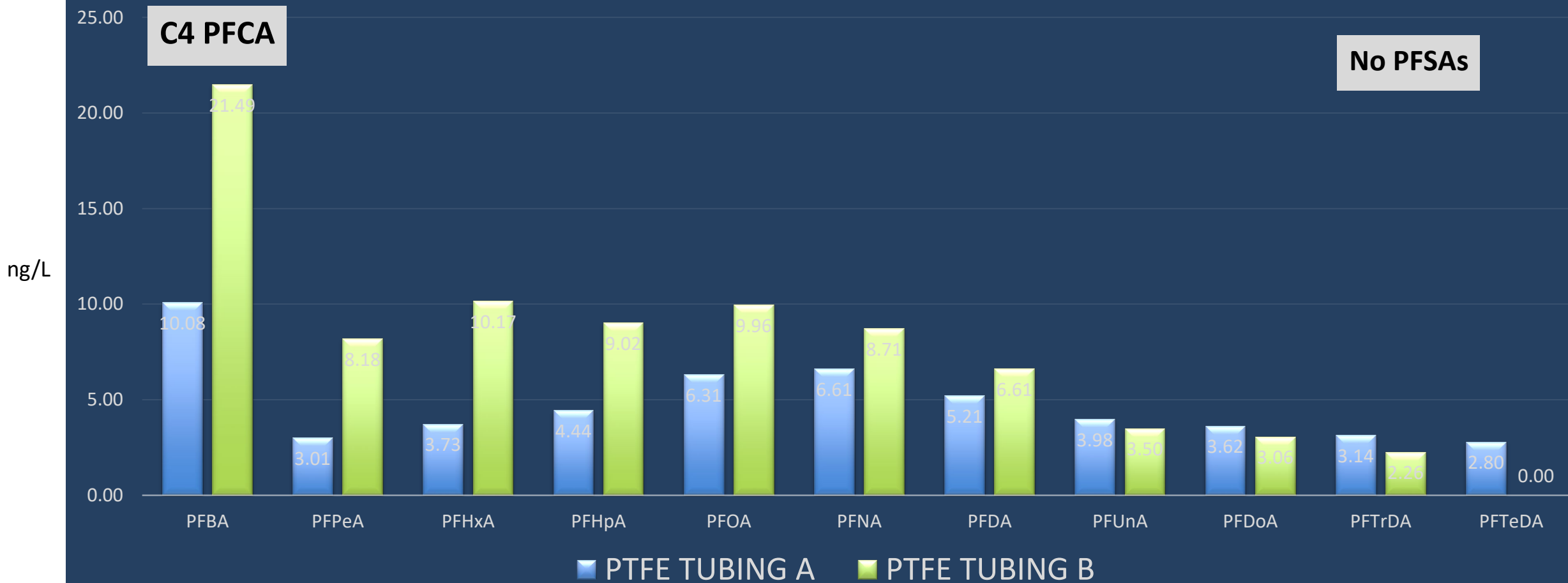
Analyte	Acronym	CAS #
4:2 Fluorotelomer sulfonic acid	4:2FTS	n/a
6:2 Fluorotelomer sulfonic acid	6:2FTS	27619-97-2
8:2 Fluorotelomer sulfonic acid	8:2FTS	39108-34-4
N-methyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-ethyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorooctane sulfonamide	FOSA	754-91-6
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8

RL = 2 ng/L

PTFE Tubing



PTFE Tubing (ng/L)



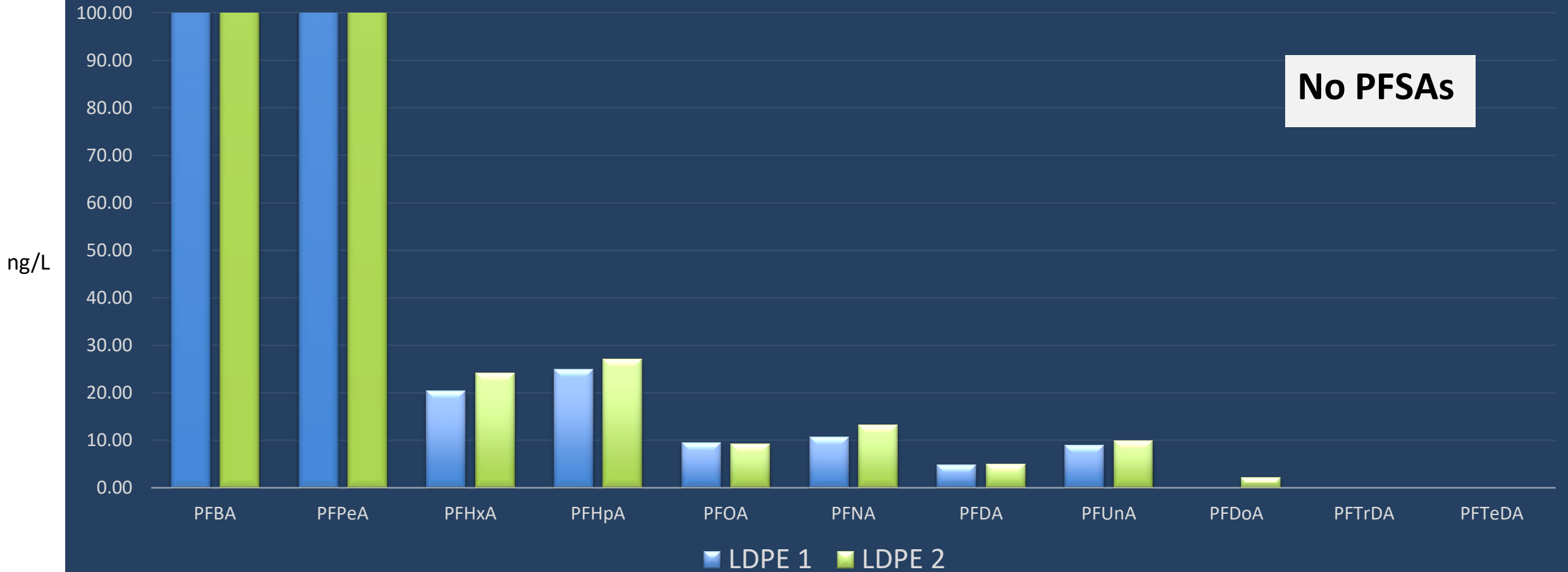
LDPE Tubing



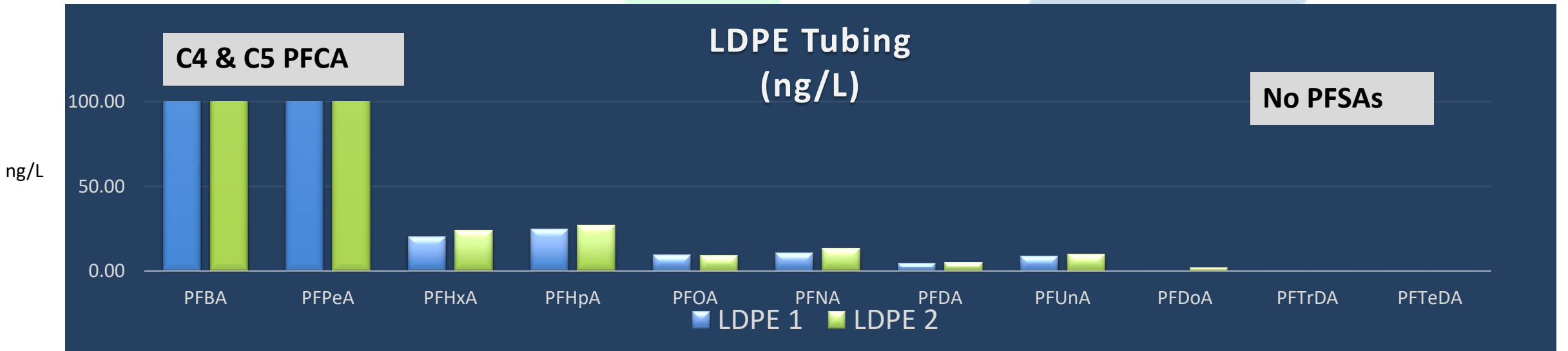
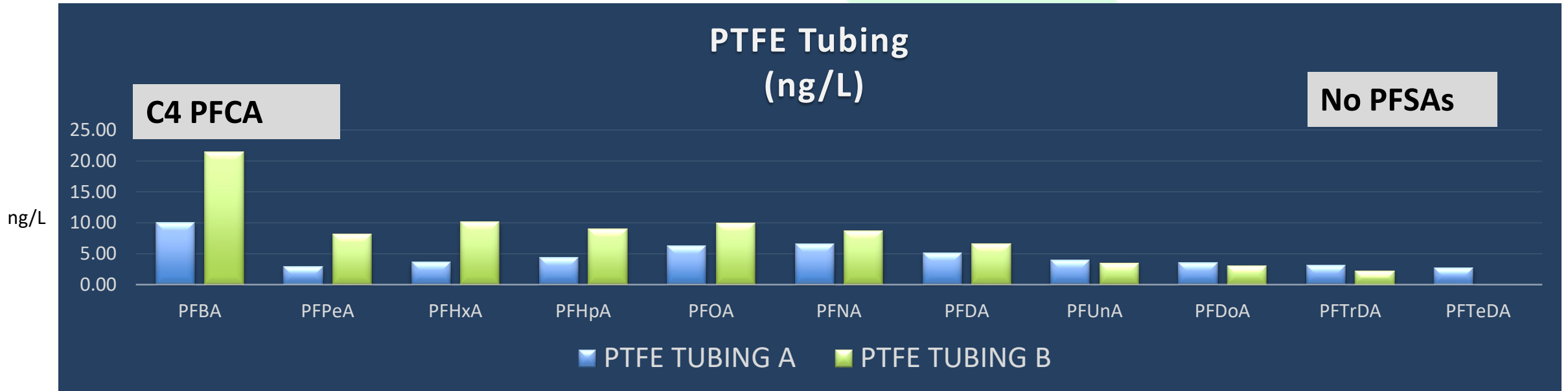
LDPE Tubing (ng/L)

C4 & C5 PFCA

No PFSAs



PTFE vs LDPE Tubing



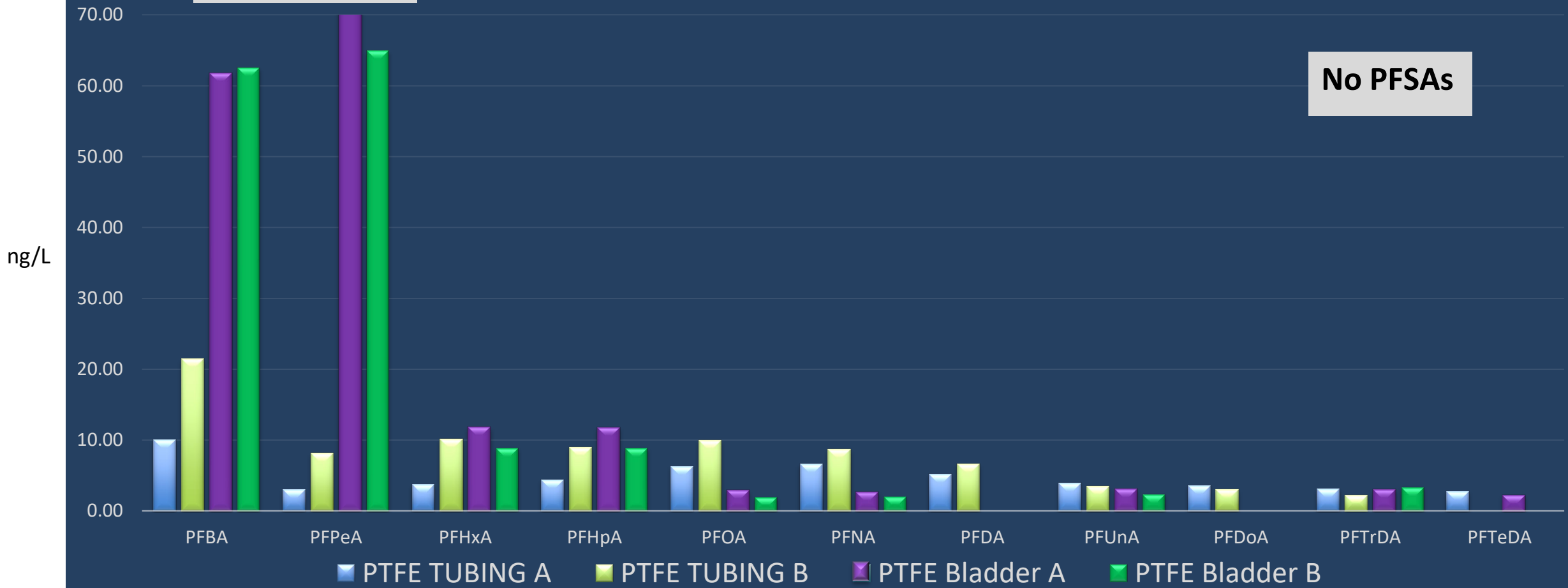
PTFE Tubing & PTFE Bladder



PTFE Tubing and PTFE Bladder (ng/L)

C4 & C5 PFCA

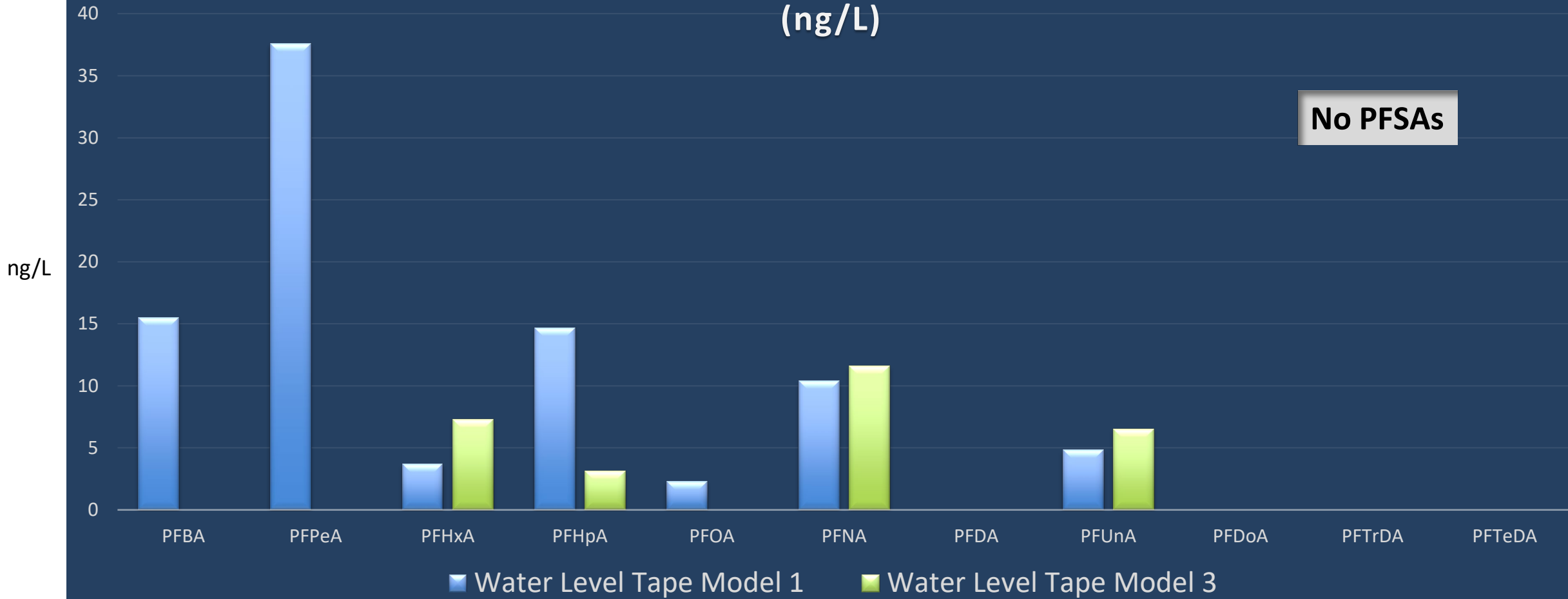
No PFSAs



Water Level Tapes

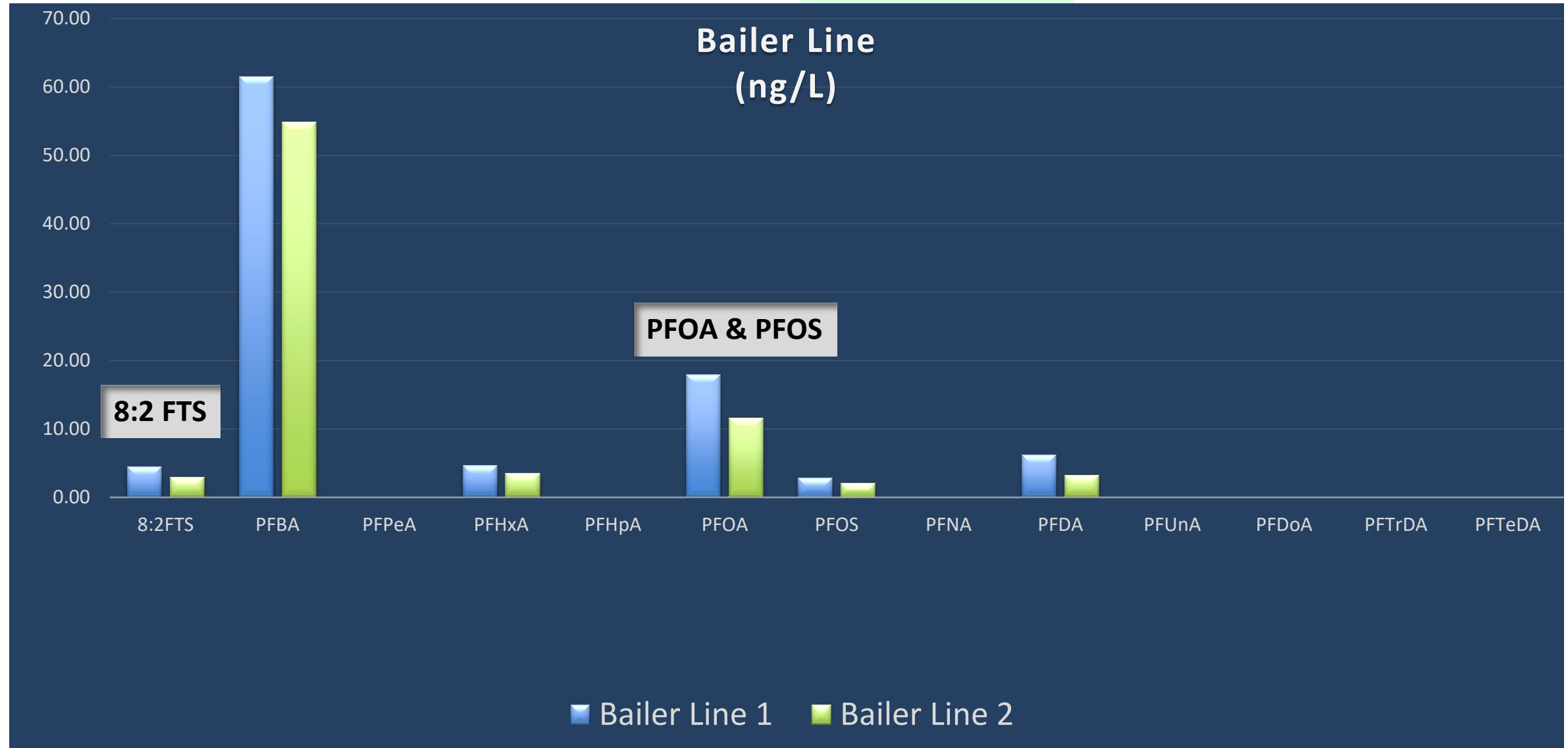


Water Level Tapes (ng/L)

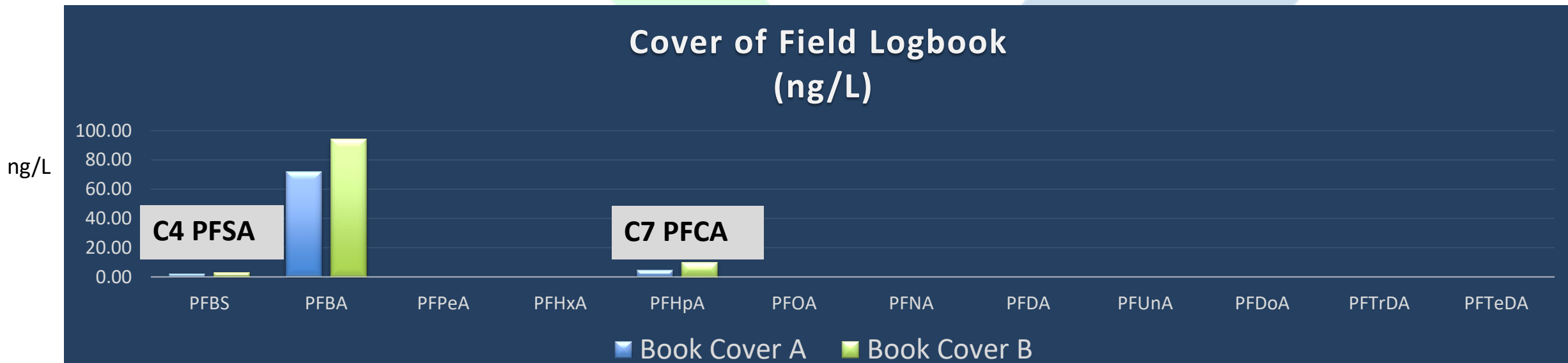
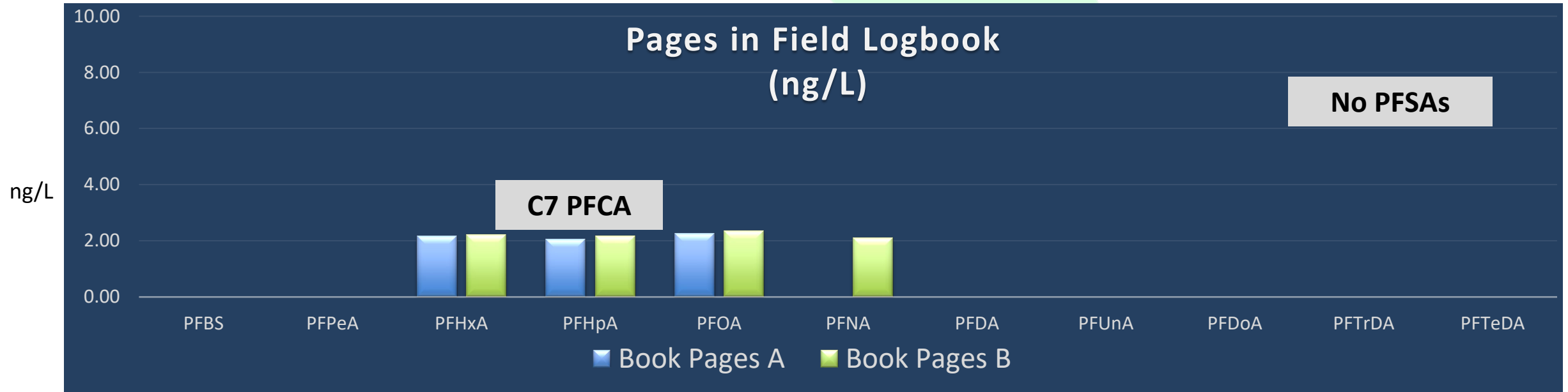


No PFSA's

Bailer Line



Field Book Pages vs Field Book Cover



PFCAs vs PFSA's vs Polyfluoroalkyl Substances



PFCAs	PFSA's	Polyfluoroalkyl Substances
PTFE Tubing	Bailer Line	PTFE-lined Tubing
PTFE-lined Tubing	Sample Labels	Bailer Line
LDPE Tubing	Nitrile Gloves	
Bailer Line	Field Book Cover	
Sample Labels		
Pizza Box		
Water Level Tapes		
Silastic Tubing		
Nitrile Gloves		
Field Book Pages		
Field Book Cover		
PTFE Bladder		

Miscellaneous, Fall 2018, 2ng/L RL

Analyte	Bubble Wrap	Garbage Bag A	Garbage Bag B	Pizza Box A	Pizza Box B	"Protein Bar" Wrapper A	"Protein Bar" Wrapper B
4:2FTS	ND	ND	ND	ND	ND	ND	ND
6:2FTS	ND	ND	ND	ND	ND	ND	ND
8:2FTS	ND	ND	ND	ND	ND	ND	ND
FOSA	ND	ND	ND	ND	ND	ND	ND
NEtFOSAA	ND	ND	ND	ND	ND	ND	ND
NMeFOSAA	ND	ND	ND	ND	ND	ND	ND
PFBA	ND	ND	ND	6.83	12.29	ND	ND
PFBS	ND	ND	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND	ND	ND
PFDS	ND	ND	ND	ND	ND	ND	ND
PFHpA	ND	ND	ND	ND	ND	ND	ND
PFHpS	ND	ND	ND	ND	ND	ND	ND
PFHxA	ND	ND	ND	ND	ND	ND	ND
PFHxS	ND	ND	ND	ND	ND	ND	ND
PFNA	ND	ND	ND	ND	ND	ND	ND
PFNS	ND	ND	ND	ND	ND	ND	ND
PFOA	ND	ND	ND	4.78	3.79	ND	ND
PFOS	ND	ND	ND	ND	ND	ND	ND
PFPeA	ND	ND	ND	ND	ND	ND	ND
PFPeS	ND	ND	ND	ND	ND	ND	ND
PFTA	ND	ND	ND	ND	ND	ND	ND
PFTrDA	ND	ND	ND	ND	ND	ND	ND

No PFAS Detected



Silicone Tubing	Aluminum Foil
Polyethylene Bladder	Adhesive Notes
Passive Diffusion Bag	Resealable Plastic Storage Bags
Bubble Wrap	Bentonite
Protein Bar Wrapper	

Wrap Up



STAY CURRENT

Go to the source for regulatory compliance

Understand the potential for PFAS to be in the sampling materials you are using

Use equipment blanks*

