



Polyfluoroalkyl Substances (PFAS): Regulation, Research, Risk, Mitigation & Alternatives

A Program Sponsored by the
Massachusetts Chemistry & Technology Alliance (MCTA)

Sampling & Analytical Considerations



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Alpha Analytical



Standard analytical technical challenges:
High sensitivity required, potential for cross contamination

MOVING TARGET

- **Analytical methodologies**
 - What methods, are they applicable?
 - Reference standard availability?
- **Regulatory requirements**
 - Requested target compound lists
 - Compliance guidelines, required reporting limits
- **What's next?**



PFAS Analysis

- **Primary methodology**

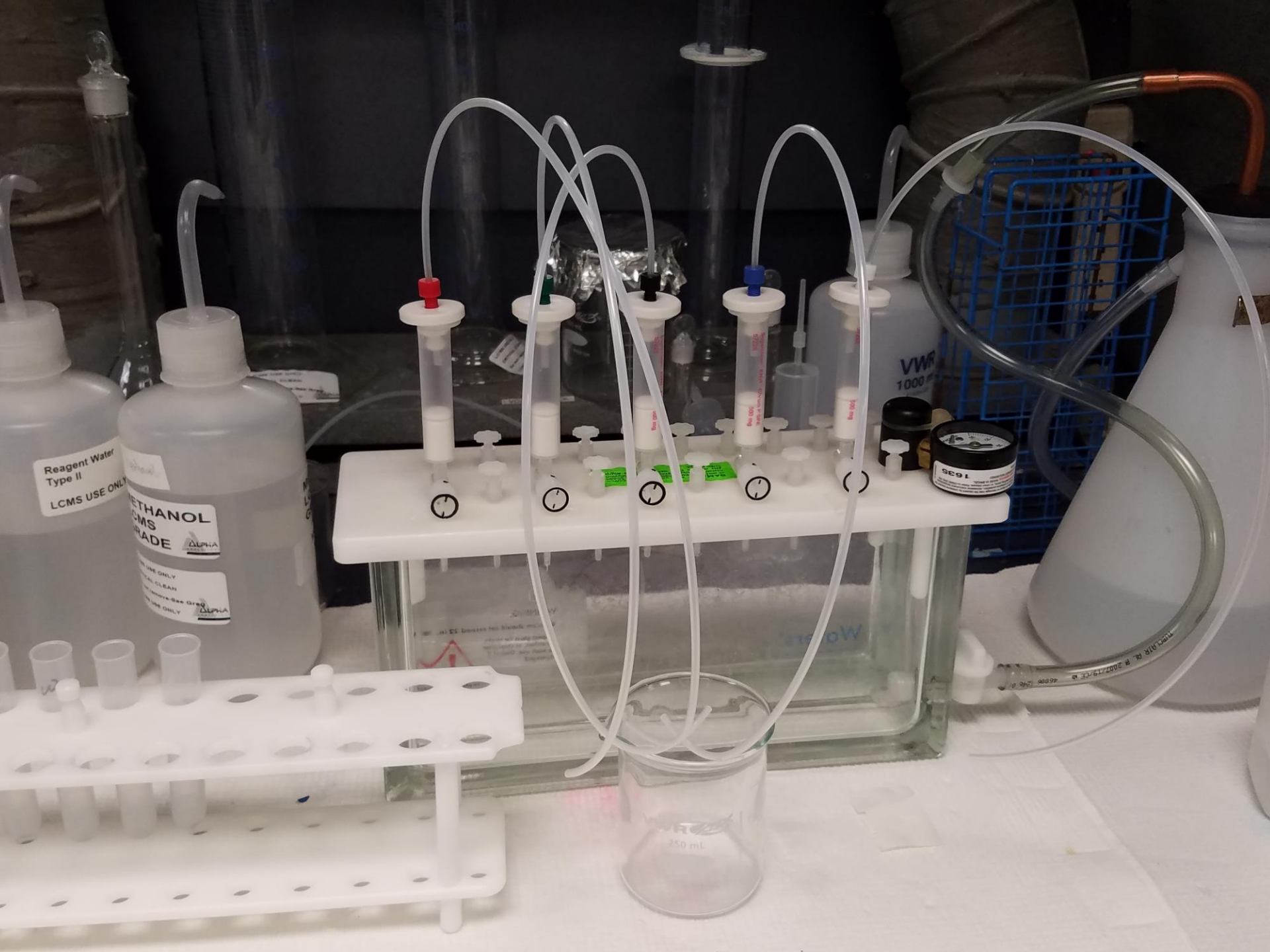
- Method 537 rev1.1 Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) Sept, 2009

- **Sample preparation**

- Solid phase extraction (SPE), *aqueous samples*

- **Analytical Instrumentation**

- Liquid chromatography / tandem mass spectrometry (LC/MS/MS)



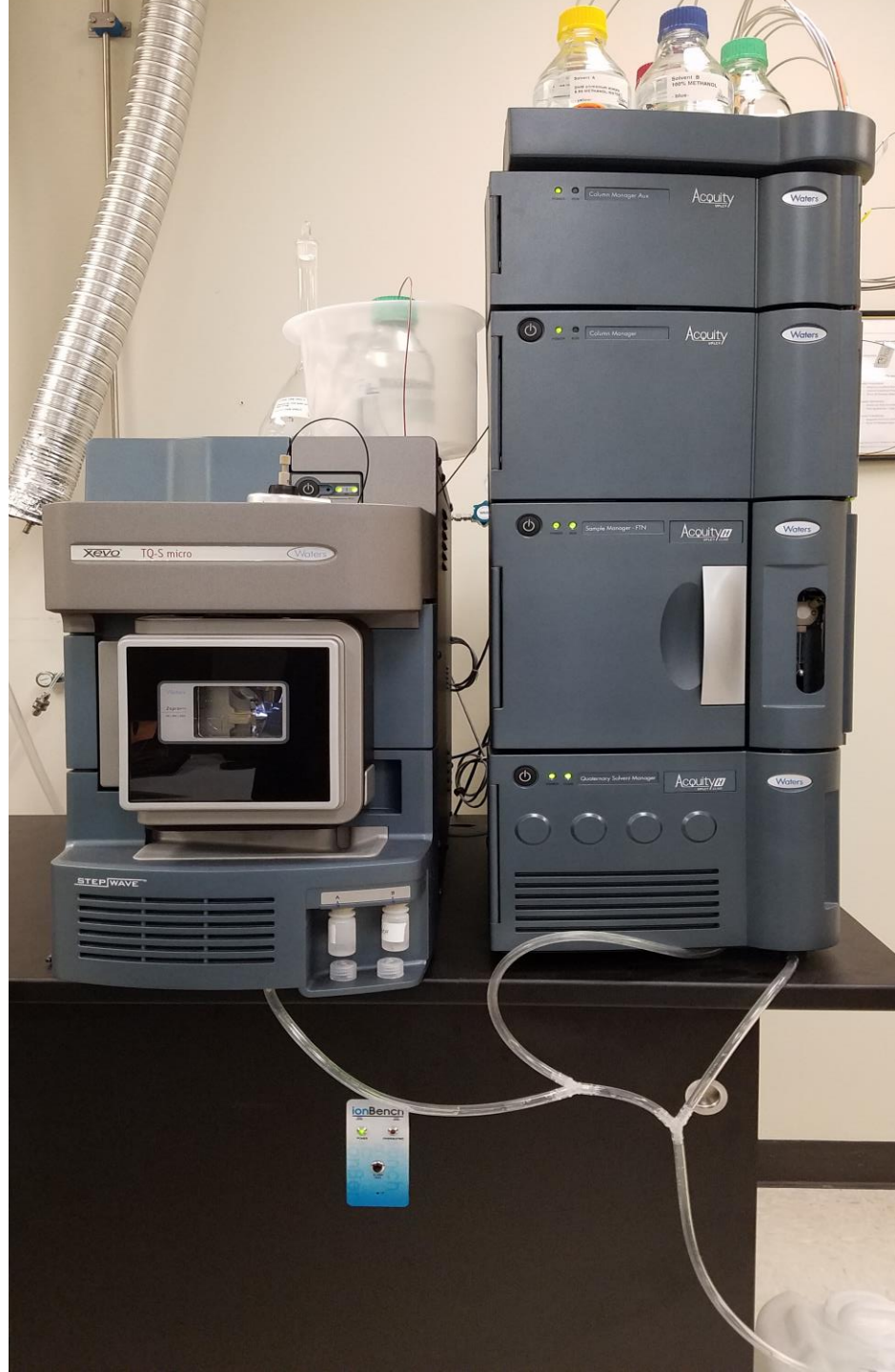
Reagent Water
Type II
LCMS USE ONLY

METHANOL
LCMS GRADE
ALPHA

VWR
1000

9991

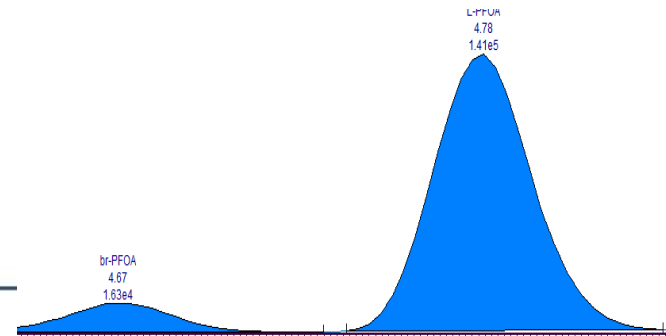
250 mL



Technical Advisory- Laboratory Analysis of
Drinking Water Samples for
Perfluorooctanoic Acid (PFOA) Using EPA
Method 537 Rev. 1.1

815-B-16-021, September 2016

- **PFAS can exist as linear & branched isomers**
 - Method 537 addresses both for PFOS (2009)
- **Branched standards not available at the time for PFOA**
 - Discrepancies in PFOA reporting
 - Addressed in Tech Advisory



Method 537

- **SDWA drinking water method**
 - UCMR 3 method
 - Designed for chlorinated public water supplies
 - Amenable to a specific 14 compd PFAS target list
- **Specific method requirements**
 - Trizma[®] de-chlorinating agent/buffer
 - Field reagent blanks (FRB)
 - Section 3.8: aliquot of reagent water that is placed in a sample container in the laboratory
 - treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures.

Method 537 Section 8.3:

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
 - 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
 - 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.



~~Modified Method 537?~~

- Method 537
 - “as specifically written”
 - Is not amenable to expanded list of compounds or other sample matrices without modification
- Other methodologies
 - “Laboratory proprietary method”
 - LC/MS/MS
 - May use different or multiple SPE cartridges
 - May use isotope dilution approach



Isotope Dilution Approach

- Addition of known amount of isotopically-enriched, compound-specific internal standard
 - PRIOR TO SAMPLE PREPARATION
 - Matrix recovery correction
 - Analysis-specific, analyte-specific concentration normalization
- Provides additional qualitative & quantitative certainty



3 New EPA SW-846 Methods Proposed

- (1) Non-potable water: SW-846 Method 8327 draft, fall 2018
 - LC/MS/MS direct injection AQ method
 - 24 analytes
- (2) Non-potable water: draft method expected 2019
 - LC/MS/MS SPE - isotope dilution
 - 24 analytes
- (3) Solids: draft soil method, expected 2019
 - Will employ an extraction & potentially direct injection

DOD QSM Version

5.1 Table B -15

(pg 1 of 15)

DoD/DOE QSM 5.1
Appendix B
2017

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Aqueous Sample Preparation	Each sample and associated batch QC samples.	<p>Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., AFFF formulations). Inline SPE is acceptable.</p> <p>Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE, with documented project approval.</p>	NA.	NA.	NA.
Soil and Sediment Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	NA.	NA.	NA.
Sample Cleanup Procedure using ENVI-Carb™ or equivalent	Each sample and associated batch QC samples. Not applicable to AFFF formulation samples.	Removal of interferences from matrix.	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix background.

Other Methodologies

- ASTM
- ISO
- TOP Assay
- PIGE
- Time-of-flight high resolution mass spectrometry (qTOF-MS)



- **ASTM 7979-17**

- Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

- **ASTM 7968-17**

- Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

- “This procedure utilizes a quick extraction and is not intended to generate an exhaustive accounting of the content of PFCs in difficult soil matrices.”



- International Organization for Standardization
ISO/CD 21675

- Water quality -- Determination of polyfluorinated alkyl substances (PFAS) in water -- Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)
- **Current status** : Under development, round robin planned



TOP (Total Oxidizable Precursor) Assay

- Analysis of individual PFAS compounds may significantly underestimate PFAS mass
 - Precursors
 - **Poly**fluoroalkyl substances that can undergo transformation to form **per**fluoroalkyl acids
- 2 aliquots
 - Analyze 1 normally
 - Treat other aliquot
 - $\text{KS}_2\text{O}_8 + \text{NaOH} / 85^\circ \text{ 6 hrs}$
 - Then analyze
- Total precursors = $\text{PFAS}_{\text{treated}} - \text{PFAS}_{\text{untreated}}$

Acids or Salts – Laboratory Implications

- Terms interchangeable in literature, regulatory guidance & media
- Dissolved in water, PFAS exists in anionic form
 - MS only detects/measures the anion
- Lab reporting acid or anion?
 - Different compounds, different CAS#'s
- EPA Method 537.1 specifies reporting the acid form
 - Form of lab calibration standard?
 - If prepared with salts, concentration must be adjusted to account for difference in mass acid vs. salt





Frequently Asked Questions (FAQs) for Sampling and Analysis of PFAS at WMD Sites

5/17/2017

In NHDES' experience, some analytical laboratories report slightly different forms of PFOS, PFHXS, and PFBS (i.e., perfluorooctanesulfonic acid vs. perfluorooctane sulfonate), which vary slightly from one another in molecular weight, resulting in slight differences in reported concentrations. Confirm with the analytical laboratory that the forms of PFOS, PFHXS, and PFBS being analyzed **and reported** correspond to the CAS No. presented in the table above.



So What Do You Analyze For?

application dependent



- **Industry**

- PFOA / PFOS, UCMR 6 ...
“EMERGING” emerging contaminants?
- Method 537, modified ID method



- **AFFF**

- UCMR 6 to expanded lists
- Generally modified ID method



- **Landfills**

- PFOA / PFOS to expanded list(s)
- Method 537 and / or modified ID

UCMR 3

(Unregulated Contaminants Monitoring Rule)

6 PFAS cmpds included

PFOS	perfluorooctanesulfonic acid
PFOA	perfluorooctanoic acid
PFNA	perfluorononanoic acid
PFHxS	perfluorohexanesulfonic acid
PFHpA	perfluoroheptanoic acid
PFBS	perfluorobutanesulfonic acid

UCMR- Collect data for contaminants suspected to be present in drinking water, but that do not have health-based standards set under the Safe Drinking Water Act (SDWA). Every five years.



EPA Method 537 - List of 14 Compounds

Perfluorooctanoic acid (PFOA)
Perfluorooctane Sulfonate (PFOS)
Perfluorobutanesulfonic acid (PFBS)
Perfluoroheptanoic acid (PFHpA)
Perfluorohexane Sulfonate (PFHxS)
Perfluorononanoic acid (PFNA)
Perfluorohexanoic acid (PFHxA)
Perfluorodecanoic acid (PFDA)
Perfluoroundecanoic acid (PFUdA)
N-methyl perfluorooctanesulfonamidoacetic acid (MeFOSAA)
Perfluorododecanoic acid (PFDoA)
N-ethyl perfluorooctanesulfonamidoacetic acid (EtFOSAA)
Perfluorotridecanoic acid (PRTTrDA)
Perfluorotetradecanoic acid (PFTeDA)



Analyte Name	Acronym
Perfluorotetradecanoic acid*	PFTreA**
Perfluorotridecanoic acid*	PFTriA***
Perfluorododecanoic acid*	PFDoA
Perfluoroundecanoic acid*	PFUnA
Perfluorodecanoic acid*	PFDA
Perfluorononanoic acid*	PFNA
Perfluorooctanoic acid*	PFOA
Perfluoroheptanoic acid*	PFHpA
Perfluorohexanoic acid*	PFHxA
Perfluoropentanoic acid	PFPeA
Perfluorobutanoic acid	PFBA
Perfluorodecanesulfonate	PFDS
Perfluorononanesulfonate	PFNS
Perfluorooctanesulfonate*	PFOS
Perfluoroheptanesulfonate	PFHpS
Perfluorohexanesulfonate*	PFHxS
Perfluoropentansulfonate	PFPeS
Perfluorobutanesulfonate*	PFBS
Perfluorooctanesulfonamide	PFOSA
Fluorotelomer sulfonate 8:2	FtS 8:2
Fluorotelomer sulfonate 6:2	FtS 6:2
Fluorotelomer sulfonate 4:2	FtS 4:2
N-ethyl-N-((heptadecafluorooctyl)sulfonyl)glycine*	NEtFOSAA
N-(Heptadecafluorooctylsulfonyl)-N-methylglycine*	NMeFOSAA

**PFTA
PFTTrDA**

***Method
537**

**proposed list,
new EPA
methods**

Full PFAS Target Analyte List

NYSDEC UPDATE
Oct 2017

For GW, SW, soils, & sediments lab should be directed to report all calibrated PFAS cmpds.

Reported cmpds will include at a minimum (current Oct 2017)



ELAP offers DW cert for PFOA / PFOS. No certification for other matrices but lab should hold PFAS DW cert. "modified" method 537 or ISO 25101

Expected PFOA / PFOS RL 2 ng/L AQ, 3 ug/Kg soil

Perfluoroalkyl sulfonates	Perfluorobutanesulfonic acid	PFBS	375-73-5
	Perfluorohexanesulfonic acid	PFHxS	355-46-4
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanessulfonic acid	PFOS	1763-23-1
	Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroalkyl carboxylates	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	PFHpA	375-85-9
	Perfluorooctanoic acid	PFOA	335-67-1
	Perfluorononanoic acid	PFNA	375-95-1
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUA/PFUdA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTriA/PFTTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTA/PFTeDA	376-06-7	
Fluorinated Telomer Sulfonates	6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2
	8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4
Perfluorooctane-sulfonamides	Perfluorooctanesulfonamide	FOSA	754-91-6
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6

Recent State of NH Recommendations

PFAS Sampling Recommendations for Public Water Systems and Private Well Owners

- 1) **Reporting Limits:** Analytical methods with reporting limits of at least 5 nanograms per liter should be utilized.
- 2) **Analytical Methods:** 1) Analytical methods that use isotope dilution conducted by laboratories accredited by the Department of Defense or the National Environmental Laboratory Accreditation Program (NELAP); or 2) EPA Method 537 Rev 1.1 following the provisions of EPA Technical Advisory 815-B-16-021 issued in September 2016 for PFOA by laboratories with NELAP accreditation from NH or another state.
- 3) **Analytes:** The following PFAS were included on the United States Environmental Protection Agency's Unregulated Contaminant Monitoring Rule (UCMR) Round 3 list and as a minimum, ***should be included*** in the requested analysis:

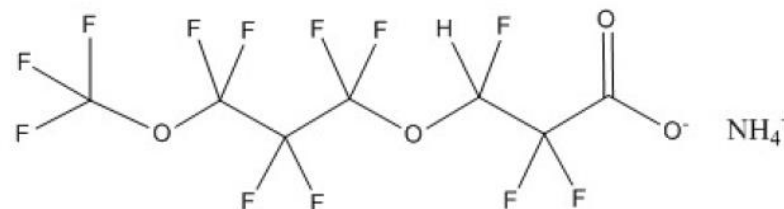
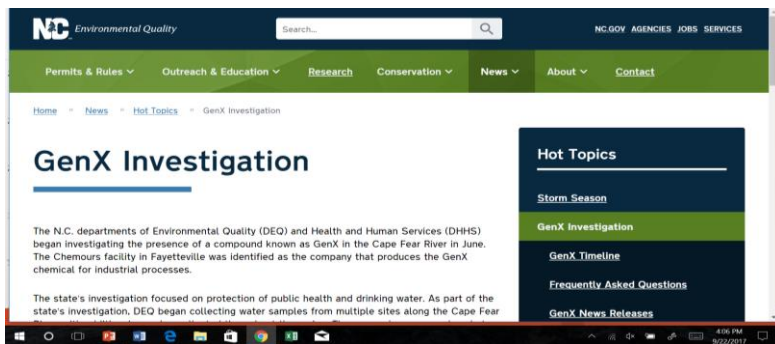
Perfluorooctanesulfonic acid (PFOS)	Perfluorooctanoic acid (PFOA)	Perfluorononanoic acid (PFNA)
Perfluorohexanesulfonic acid (PFHxS)	Perfluoroheptanoic acid (PFHpA)	Perfluorobutanesulfonic acid (PFBS)

The following additional PFAS have been regularly detected in groundwater samples in New Hampshire Drinking Water PFOA Investigation and are also recommended target analytes to include in the PFAS analysis. **537**

Perfluorobutanoic acid (PFBA)	Perfluoropentanoic acid (PFPeA)	Perfluorohexanoic acid (PFHxA)
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Upcoming NHDES Comprehensive Multi-Media Sampling Program

ANALYTE	CAS#	REPORTING LIMIT
8:2 FLUOROTELOMERSULFONATE - 8:2 FTS	39108-34-4	2 ng/L
FLUOROTELOMER SULFONATE 6:2	27619-97-2	2 ng/L
N-METHYL PERFLUOROOCTANESULFONAMIDOACETIC ACID	2355-31-9	2 ng/L
PERFLUOROBUTANESULFONIC ACID	375-73-5	2 ng/L
PERFLUOROBUTANOIC ACID - PFBA	375-22-4	2 ng/L
PERFLUORODECANE SULFONATE - PFDS	335-77-3	2 ng/L
PERFLUORODECANOIC ACID - PFDA	335-76-2	2 ng/L
PERFLUORODODECANOIC ACID - PFDOA	307-55-1	2 ng/L
PERFLUOROHEPTANE SULFONATE - PFHPS	375-92-8	2 ng/L
PERFLUOROHEPTANOIC ACID - PFHPA	375-85-9	2 ng/L
PERFLUOROHEXADECANOIC ACID - PFHXDA	67905-19-5	2 ng/L
PERFLUOROHEXANOIC ACID - PFHXA	307-24-4	2 ng/L
PERFLUOROHEXYLSULFONIC ACID	355-46-4	2 ng/L
PERFLUORONONANOIC ACID - PFNA	375-95-1	2 ng/L
PERFLUORO-N-TRIDECANOIC ACID - PFTRDA	72629-94-8	2 ng/L
PERFLUOROOCTANOIC ACID - PFOA	335-67-1	2 ng/L
PERFLUOROOCTYLSULFONIC ACID	1763-23-1	2 ng/L
PERFLUOROPENTANOIC ACID - PFPEA	2706-90-3	2 ng/L
PERFLUOROTETRADECANOIC ACID - PFTEDA	376-06-7	2 ng/L
PERFLUOROUNDECAOIC ACID - PFUNA	2058-94-8	2 ng/L



Ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA)

California Environmental Contaminant Biomonitoring Program, codified at Health and Safety Code section 105440 et seq.

3/13/2015 Meeting of the Scientific Guidance Panel, Biomonitoring California

Perfluoro-2-propoxypropanoic acid

- FRD-902 and FRD-903
 - 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903)
 - produces 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (FRD-902)

F53B trade name

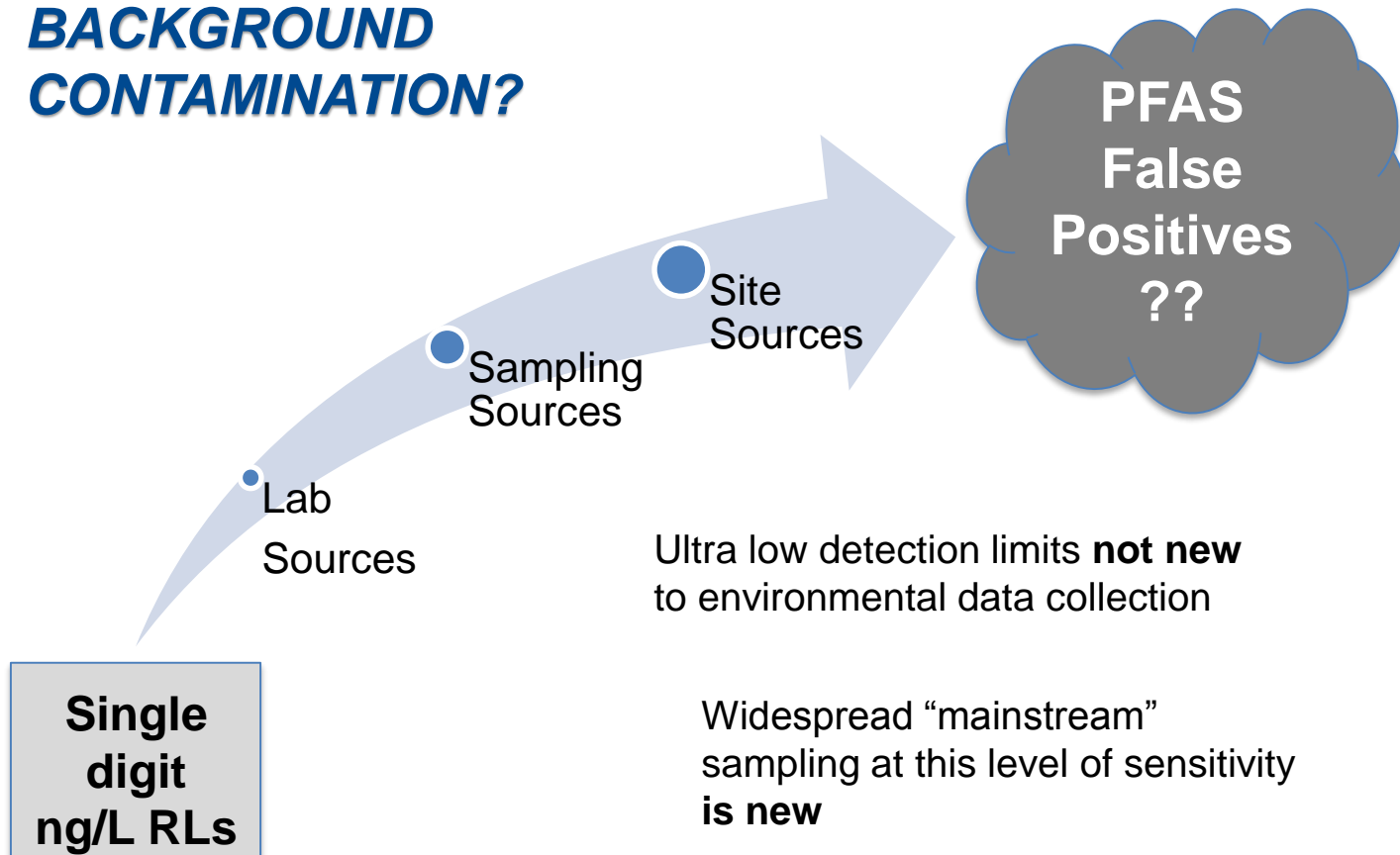
chlorinated polyfluorinated ether sulfonate
PFOS alternative

Environ. Sci. Technol., **2015**, 49 (11), pp 6519–6527

US Navy Inquiry to Laboratories Regarding GenX, ADONA & F53B

- Prompted by a US EPA review initiative of PFOA replacement products.
- Methodology options

BACKGROUND CONTAMINATION?



Ultra low detection limits **not new** to environmental data collection

Widespread “mainstream” sampling at this level of sensitivity **is new**

Ubiquitous nature of PFAS sources coupled with widespread sampling and ng/L RLs? **Unprecedented**



Sampling:

need to address possible sources of contamination

OK

NOT OK

• Field Equipment

- HDPE bottles, silicon tubing, loose paper, aluminum/Masonite clipboards, Alconox / Liquinox[®], nitrile gloves

• Clothing / PPE

- “Well laundered”, preferably cotton

• Personal care products

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

• Field Equipment

- LDPE bottles, Teflon[®] caps, Teflon[®] tubing, waterproof field books, plastic clipboards/binders, Post It[®] notes, chemical (blue ice)

• Clothing / PPE

- No fabric softener, Gor-Tex[®], “dri -fit”, Tyvek[®]

• 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



Potential for PFAS Cross-Contamination from Sampling Equipment and Associated Products



- ***Joint study with TRC***
- ***Objective:***
 - *Can PFAS be transferred from common field and other commercial products during sampling?*
- ***Disclaimer***
 - A first look at “aqueous leachability vector”
 - Snapshot
 - Not an in depth study
 - Obviously a "worst case scenario"
 - Not an assay

Experimental Design Leaching Step



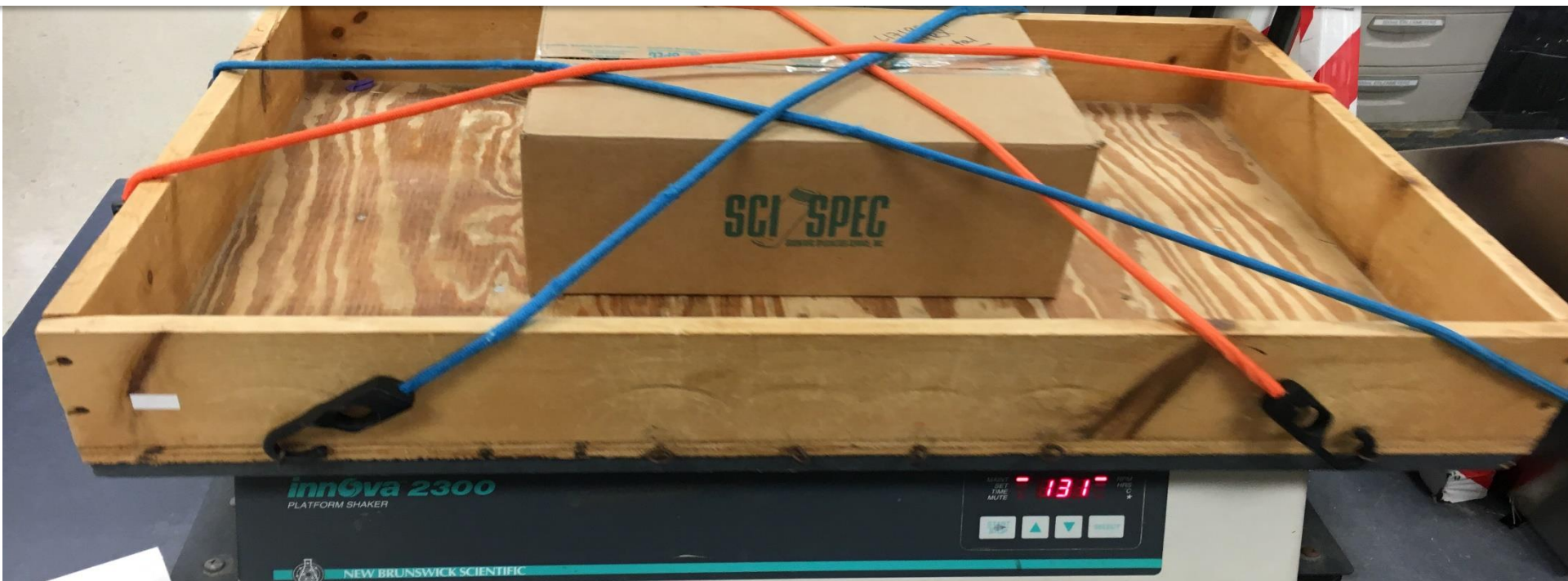
■ Leaching Step

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

■ Analysis Step

- SPE, LC/MS/MS
- 22 compound list





PFAS in Sampling Supplies?



Bentonite



Zip Lock Bag



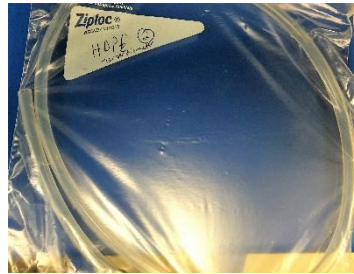
Aluminum Foil



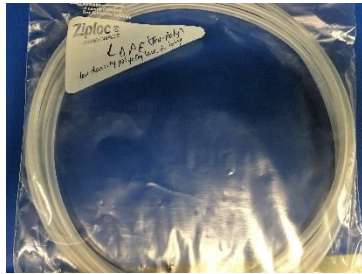
Post-its



Polyethylene Bladder



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



LDPE Tubing :
2 Manufacturers



Silastic Tubing



PTFE
Bladder



Protective
Suit



PTFE
Tubing



Passive Diffusion Bag



Nitrile Gloves



Bailer String



Field Book
(cover & pages)

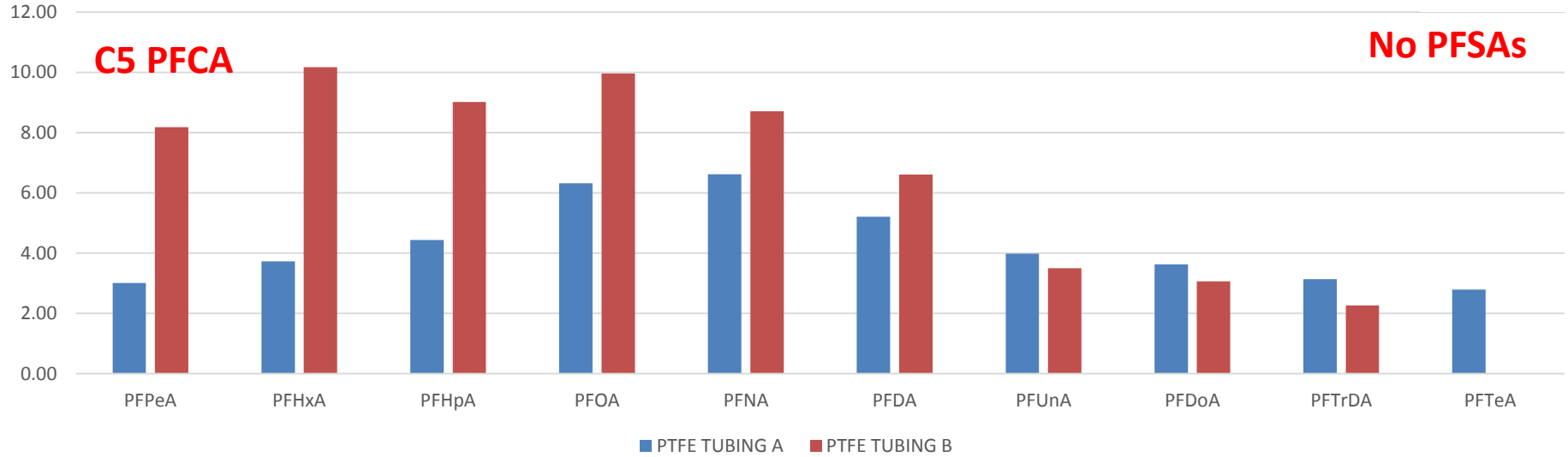


Sample Labels

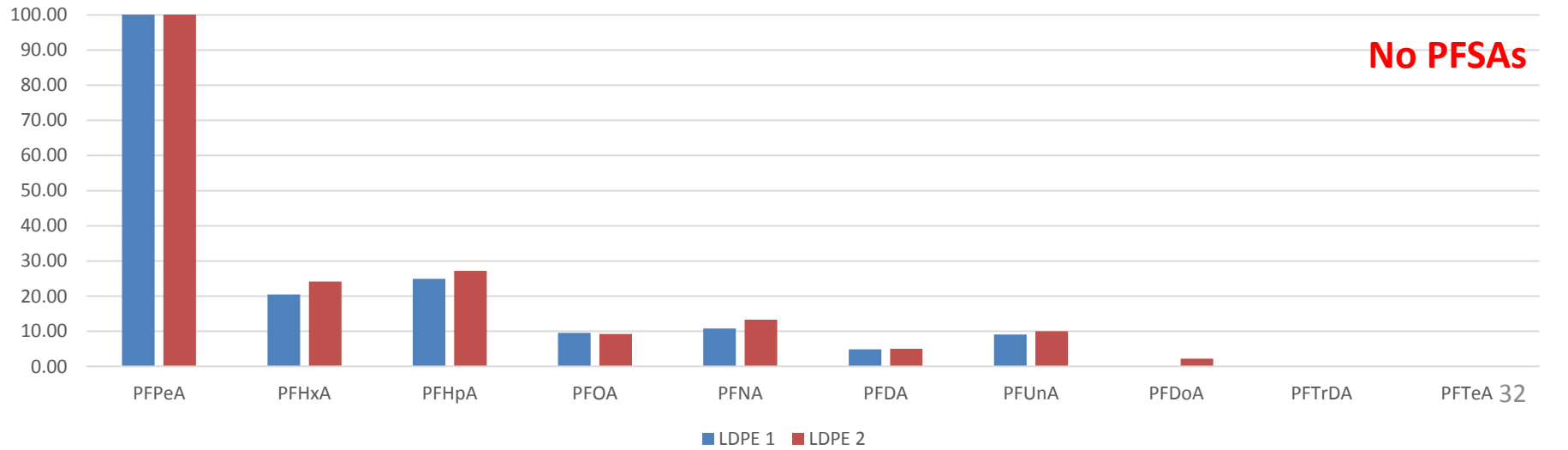
Tubing Results with Detected PFAS



PTFE Tubing (ng/L)

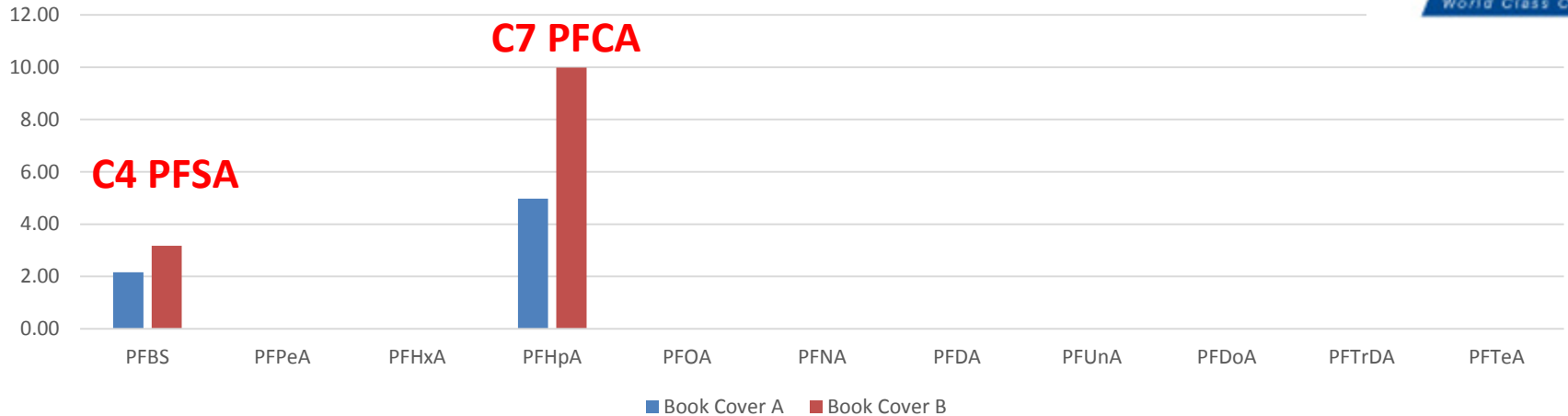


Low Density Polyethylene Tubing (ng/L)

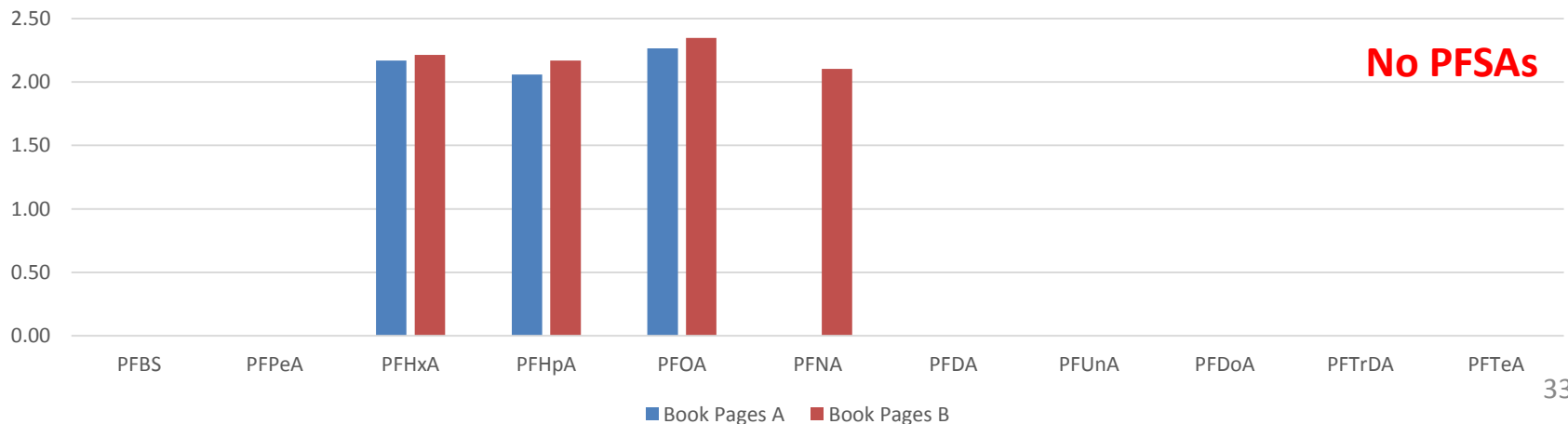


Waterproof Field Logbook

Cover of Field Logbook (ng/L)

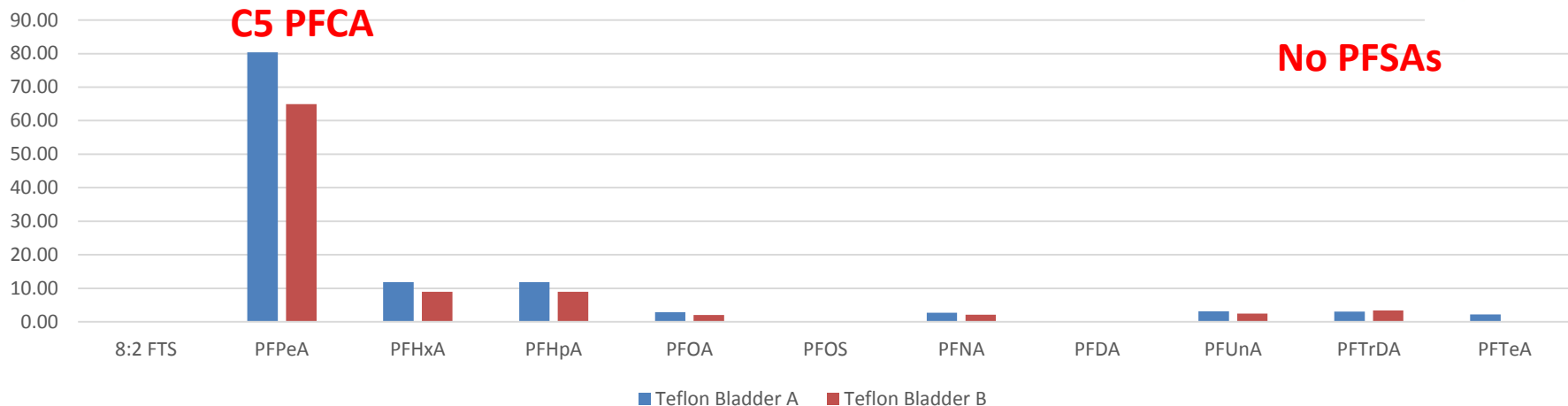


Pages in Field Logbook (ng/L)

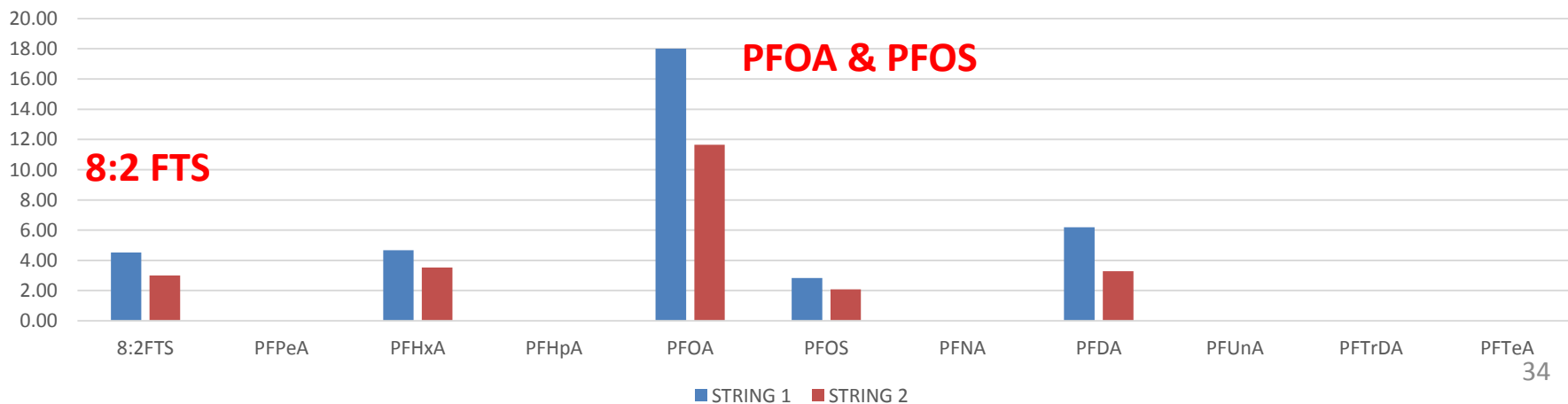


PTFE Bladder/Bailer String

PTFE Bladder in Bladder Pumps (ng/L)



Bailer Line (ng/L)



Analyte	Acronym	# Detections
1H,1H,2H,2H-perfluorohexane sulfonate (4:2)	4:2 FTS	
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2 FTS	
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2 FTS	2
N-methyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	0
N-ethyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	0
Perfluorobutanesulfonic acid	PFBS	3
Perfluorodecanoic acid	PFDA	7
Perfluorododecanoic acid	PFDoA	3
Perfluorodecanesulfonic acid	PFDS	0
Perfluoroheptanoic acid	PFHpA	14
Perfluoroheptanesulfonic acid	PFHpS	0
Perfluorohexanoic acid	PFHxA	13
Perfluorohexanesulfonic acid	PFHxS	2
Perfluorononanoic acid	PFNA	8
Perfluorononanesulfonic acid	PFNS	0
Perfluorooctanoic acid	PFOA	14
Perfluorooctanesulfonic acid	PFOS	4
Perfluoropentanoic acid	PFPeA	9
Perfluoropentanesulfonic acid	PFPeS	0
Perfluorotetradecanoic acid	PFTA	2
Perfluorotridecanoic acid	PFTTrDA	4
Perfluoroundecanoic acid	PFUnA	35 4

No PFAS Detected

Silastic Tubing	Aluminum Foil
Polyethylene Bladder	"sticky notes"
Passive Diffusion Bag	Zip lock bags

Phase 2 Preliminary Data



- Additional HDPE, LDPE & Silastic tubing samples
 - All ND

- PVC pipe
 - All ND

- Plumbers tape
 - Hits of PFOA (24 PPT) & PFPeA (3 PPT)

- Pipe liner
 - Hits of PFBA & PFPeA
 - Not greater than 10 PPT

Bentonite

#1 Coated Bentonite	No PFAS detected
#1 Medium Chips	No PFAS detected
#2 Pellets	PFOA: 2.24 ng/L
#3 Granular	No PFAS detected
#4 3/8" Chips	No PFAS detected
#5 Plug	No PFAS detected

- Candy wrapper

- All ND

- Pizza box

- Hits of PFOA & PFBA

- Not greater than 12 PPT



Wrap Up



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

MOVING TARGET

*Understand regulatory landscape,
have dialog with lab*

Methods, blanks, TCLs, RLs

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