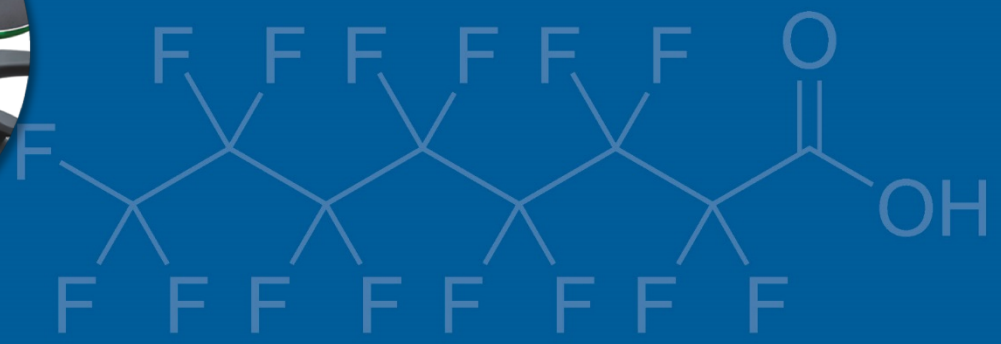


Overview of PFAS

May 30, 2019

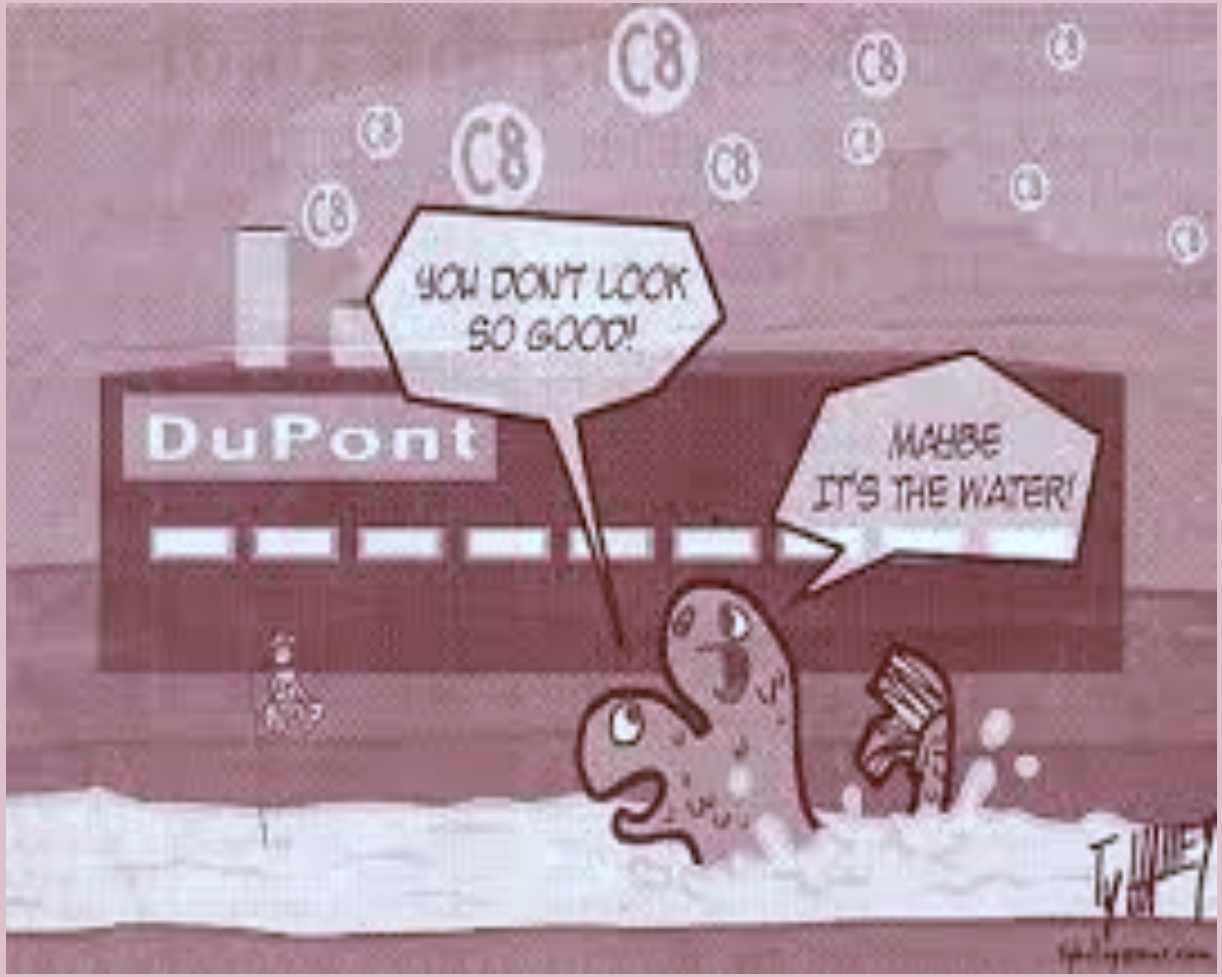
E2TECH ENVIRONMENTAL & ENERGY TECHNOLOGY COUNCIL OF MAINE

PFAS in the News

https://pfasproject.com

Today's Topics

- PFAS Naming Conventions
- Physical/Chemical Properties of PFAS
- Sources of PFAS and Potentially-affected Sites
- Replacement PFAS Chemistry
- History of PFAS
- Sampling Issues and Quality Control
- Analytical Methods



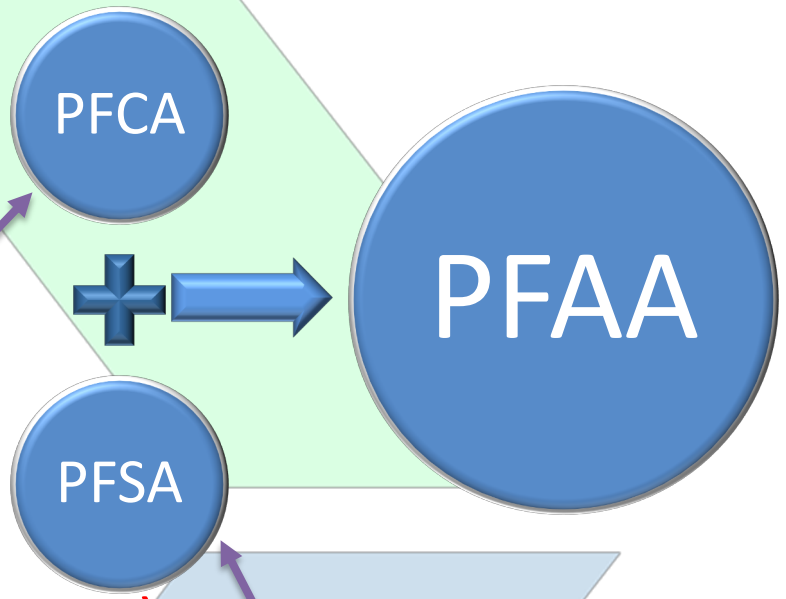
PFAS Naming Conventions

Acronyms

- **PFC** = Per-fluorinated chemical
- **PFAS** = Per- and Poly-fluoroalkyl substances

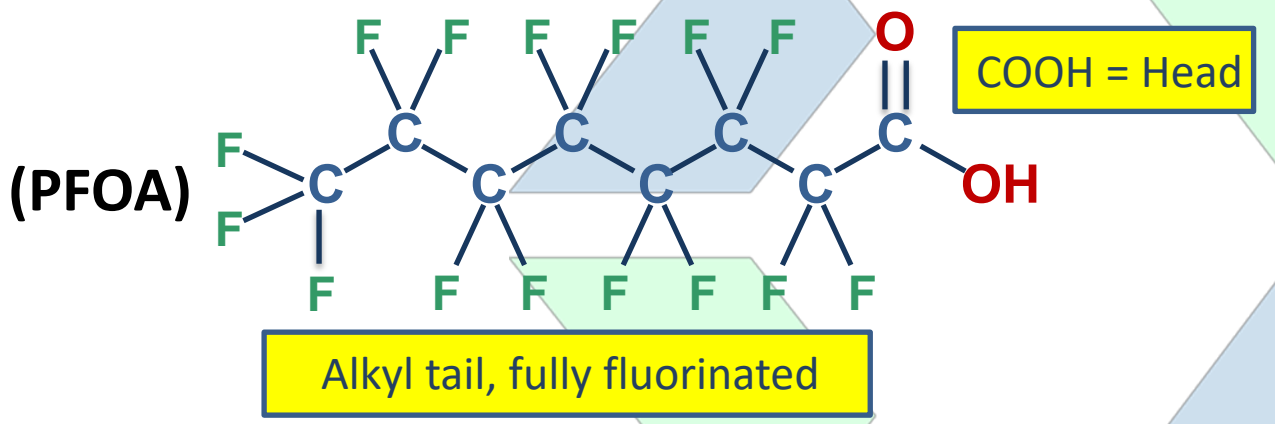
Perfluoroalkyl Substances

- **PFAA** = Perfluoroalkyl acids
- **PFOA** = Perfluorooctanoic acid (perfluorooctanoate)
- **PFOS** = Perfluorooctane sulfonic acid (perfluorooctane sulfonate)
- **PFCA** = Perfluorocarboxylic acids
- **PFSA** = Perfluorosulfonic acids

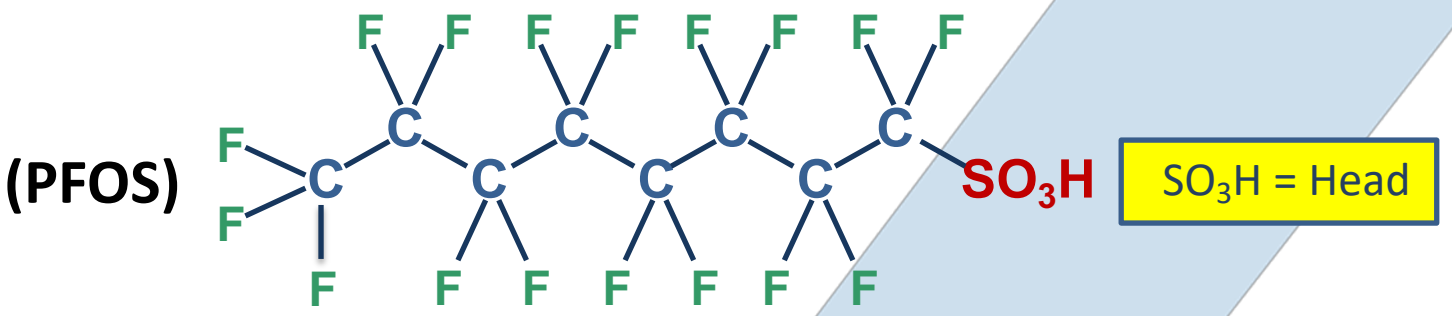


Quick Chemistry Lesson #1

- Remember: PFAS are **Per** and **Poly**fluoroalkyl substances
- **Per-fluoroalkyl substances**: fully fluorinated alkyl tail
  - Perfluoroalkane carboxylates (or carboxylic acids): **PFCAs**



  - Perfluoroalkane sulfonates (or sulfonic acids): **PFSAs**

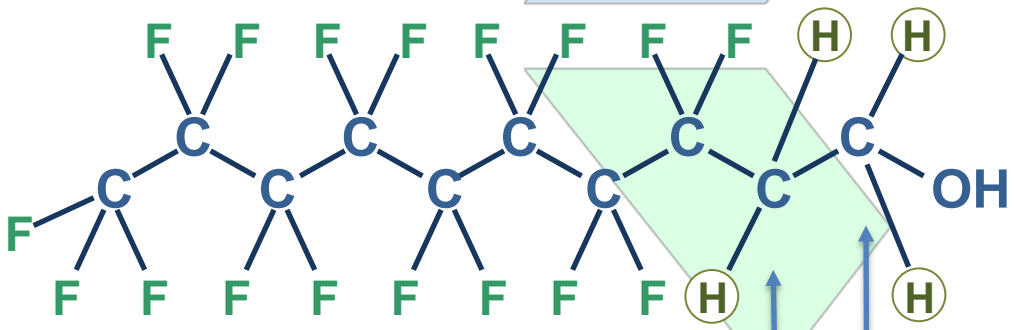


PFAAs

Quick Chemistry Lesson #2

- Remember: PFAS are **Per** and **Poly**fluoroalkyl substances
- **Poly-fluoroalkyl substances**: non-fluorine atom (typically hydrogen or oxygen) attached to at least one carbon atom in the alkane chain

Fluorotelomer Alcohol (8:2 FTOH)

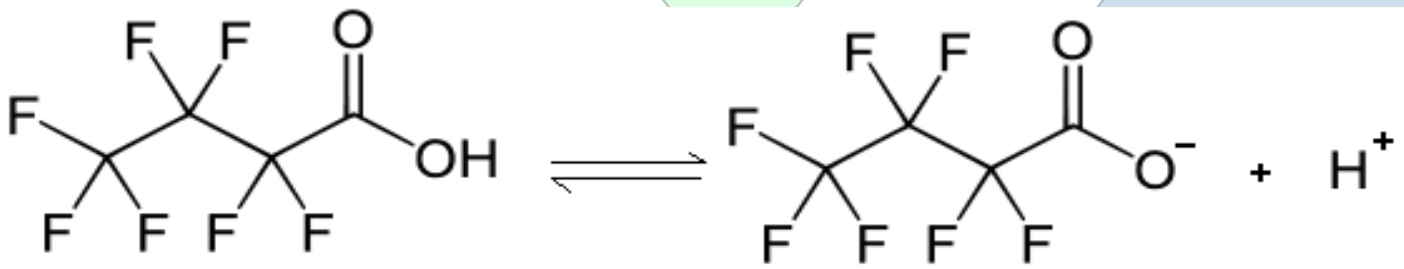


Polyfluoroalkyl substances may also be degraded to perfluoroalkyl substances (e.g., PFOS or PFOA): PRECURSORS

What Are PFAS?

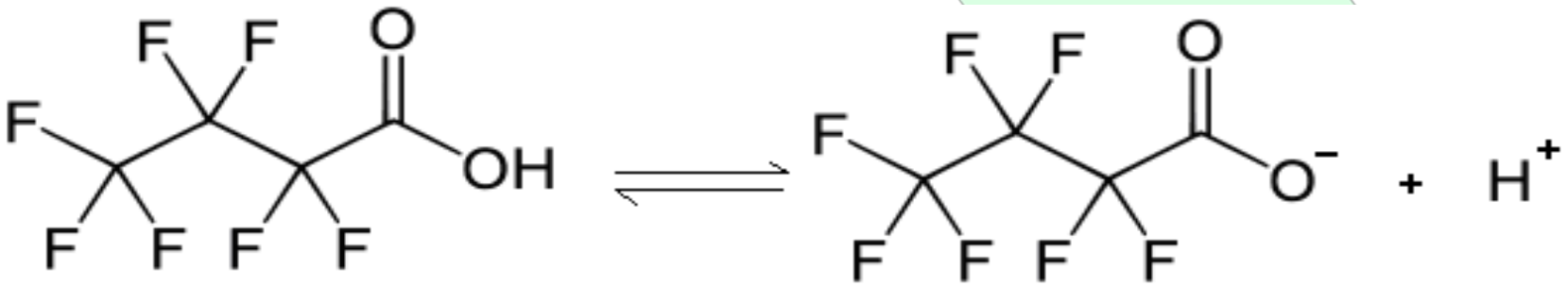
- Poly- and per-fluoroalkyl substances
  - Generic family of chemicals
  - Manmade and do not occur naturally
  - Used since 1940 (Critical for the Manhattan Project)
  - Can be branched or linear
  - Used to make products that resist heat, oils, grease, stains, and water
- Most prevalent and researched: PFOA and PFOS
- PFAS: Acid or anion?

PFOS is present in the environment in the anionic form: perfluorooctane sulfonate.



Perfluorobutanoic acid **Perfluorobutanoate (+ dissociated proton)**

CAS Numbers and PFAS State



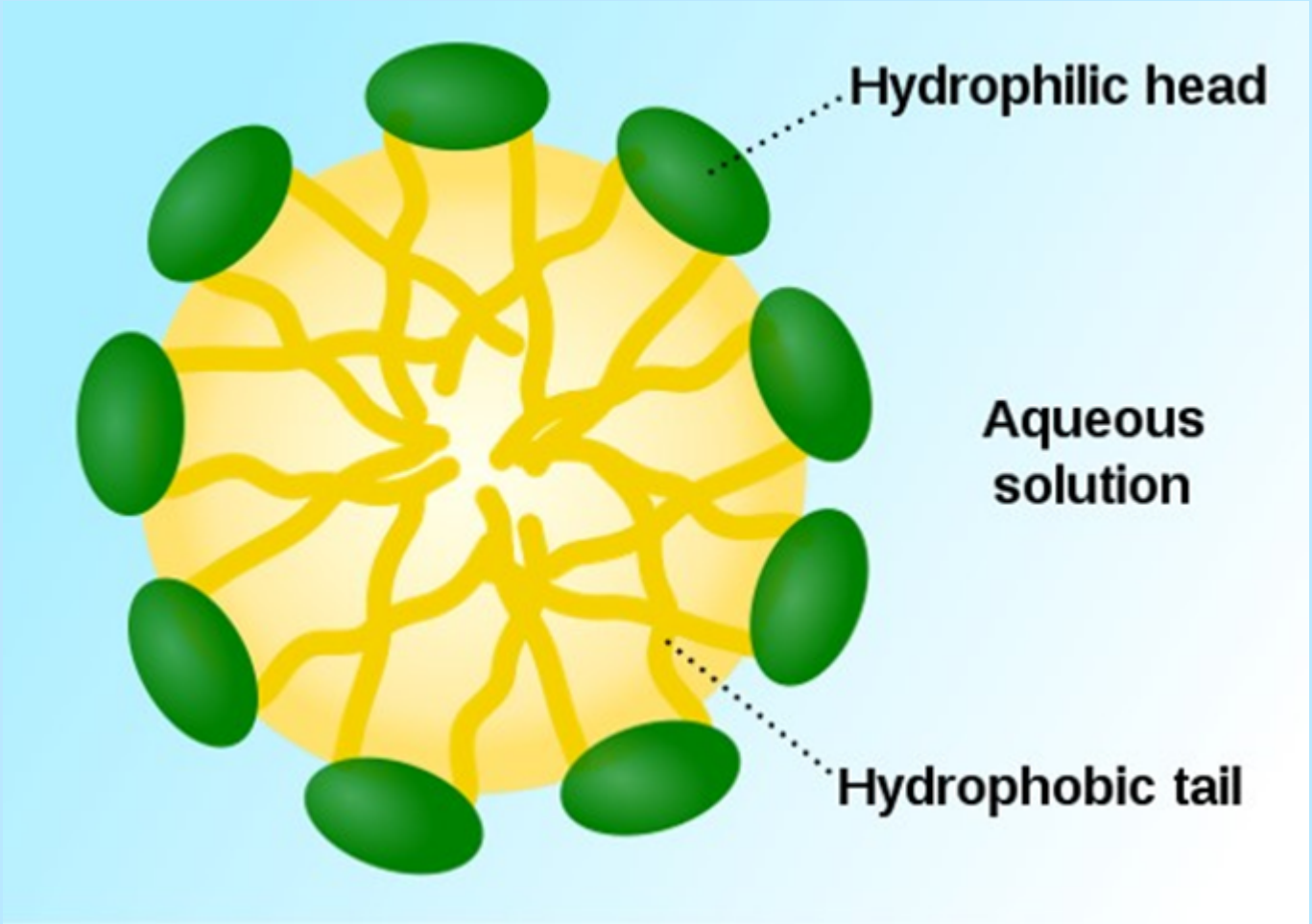
	PFAS State		Structure	CAS No.
PFOA	Anion	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
	Acid	Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
PFOS	Anion	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
	Acid	Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1

Why is this important?

Chemical Properties of Perfluoroalkyl Substances

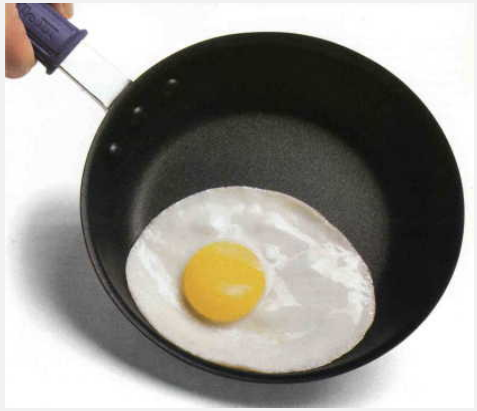
- C-F: Strong bond
- Chemically and thermally stable
- Water soluble and mobile in groundwater
- Surfactant properties
- Recalcitrant in environment

A PFAS Micelle

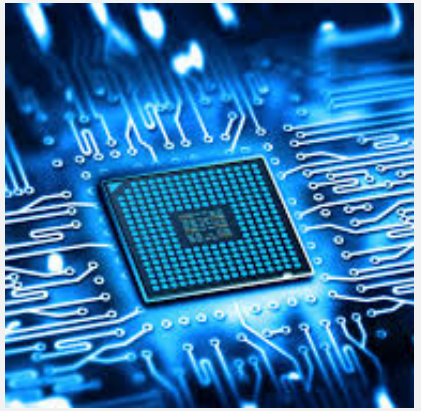


Sources of PFAS and Potentially Affected Sites

Where Are PFAS Used?










What Types of Sites Can Be Sources of PFAS?

- Fire training facilities
- Fire stations
- Refineries
- DoD sites/Military bases
- Commercial and private airports
- Landfills (leaching from consumer products)
- Biosolids land application
- Rail yards
- Chemical facilities
- Plating facilities
- Textile/carpet manufacturers
- Residential areas with septic systems

Timeline of PFAS

1938
- PTFE discovered

1949
- PTFE used in products

1956
- Stain-resistant products (PFOS)

1968
- Navy developed AFFF

1978
- Detected in blood of manufacturing workers

2002
- PFOS manufacturing phased out

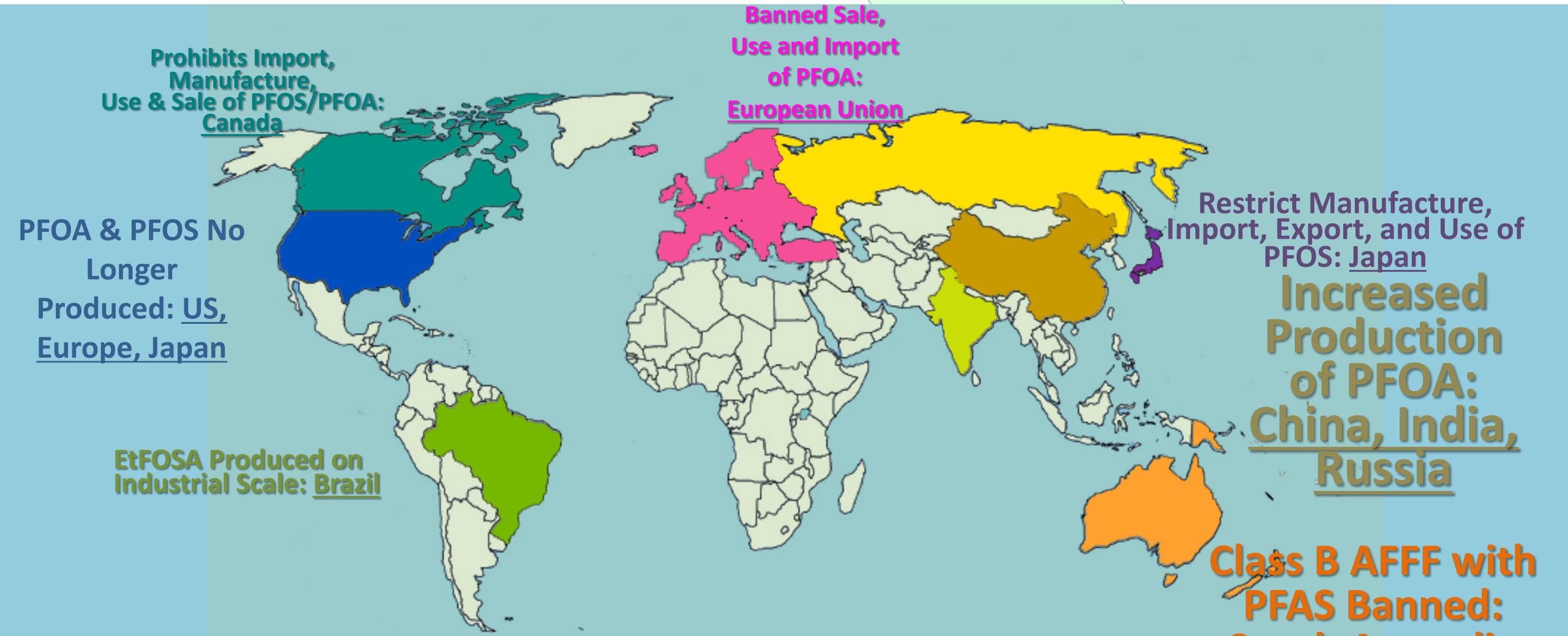
2006
- PFOA phased out
- EPA PFOA Stewardship Program

2009
- Stockholm Convention classifies PFOS as POP

2013-2015
- PFOA phase-out complete
- Sampling of public drinking water wells for PFAAs (UCMR3)

2016
- EPA Health Advisory announced for PFOA/PFOS (70 ppt)

Global Manufacture and Use of PFAS



PFAS Manufactured Globally

Replacement Chemistry

- GenX replaces PFOA
- ADONA replaces PFOA
- 6:2 Fluorotelomers replace PFOS in metals plating
- Telomers replace PFOS and PFHxS in AFFF
- Shorter chain PFAAs replace PFOA: PFBA, PFPeA

PFAS Sampling Issues and Quality Control

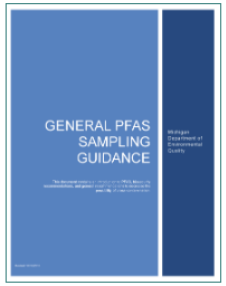
How Do We Sample PFAS?

- Similar to conventional sampling (e.g., low-flow techniques, direct push, etc.)
- Special care required to prevent cross contamination
- Use of and exclusion of specific sampling equipment and materials

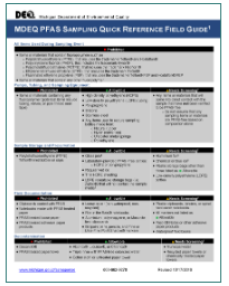
SOP No. RWM-DR-014-ADDENDUM
Effective Date: 03/20/2019
Page 6 of 6

ATTACHMENT A
PFOA SAMPLING AND ANALYSIS PLAN FORM TEMPLATE

Technical Guidance Documents



General PFAS Sampling Guidance
Revised October 16, 2018



PFAS Sampling Quick Reference Field Guide
Revised October 17, 2018

Residential Well PFAS Sampling Guidance
Revised October 11, 2018

Groundwater PFAS Sampling Guidance
Uploaded October 2018

Wastewater PFAS Sampling Guidance
Revised October 11, 2018

Surface Water PFAS Sampling Guidance
Revised November 28, 2018

Soil PFAS Sampling Guidance
Revised November 28, 2018

Fish Tissue PFAS Sampling Guidance
Uploaded January 2019

PFAS Sampling Dos and Don'ts

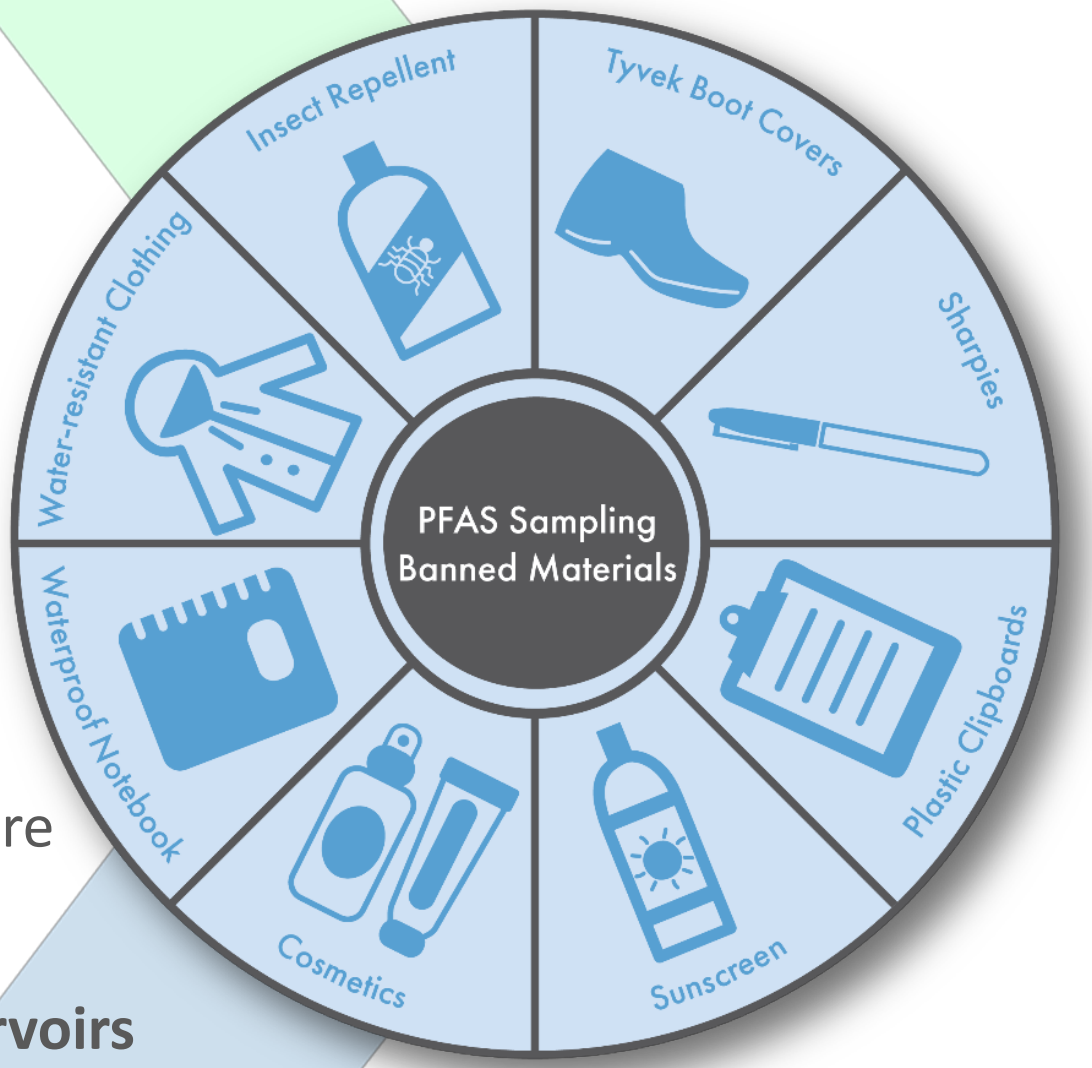
WHAT SHOULD I AVOID?	USE INSTEAD
Passive diffusion bags (PDBs)	
LDPE Hydrasleeves	✓ HDPE Hydrasleeves
Post-It notes during sample handling	
Blue Ice® (chemical ice packs)	✓ Regular ice in Ziploc® bags
Waterproof field books, plastic clipboards and spiral bound notebooks	✓ Field notes recorded on loose paper ✓ Field forms maintained in aluminum or Masonite clipboards
Unnecessary handling of items with nitrile gloves	✓ Personnel collecting and handling samples should wear nitrile gloves at all times while collecting and handling samples or sampling equipment

PFAS Sampling Dos and Don'ts

WHAT SHOULD I AVOID?	USE INSTEAD
Equipment with **Teflon®** (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization	✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®
Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids	✓ HDPE or polypropylene containers for sample storage ✓ HDPE or polypropylene caps
Tyvek® suits and waterproof boots	✓ Clothing made of cotton preferred ✓ Boots made with polyurethane and polyvinyl chloride (PVC)
Waterproof labels for sample bottles	✓ Paper labels with clear tape
Sunscreens, insect repellants	✓ Products that are 100% natural, DEET
Sharpies	✓ Ballpoint pens
Aluminum foil	✓ Thin HDPE sheeting

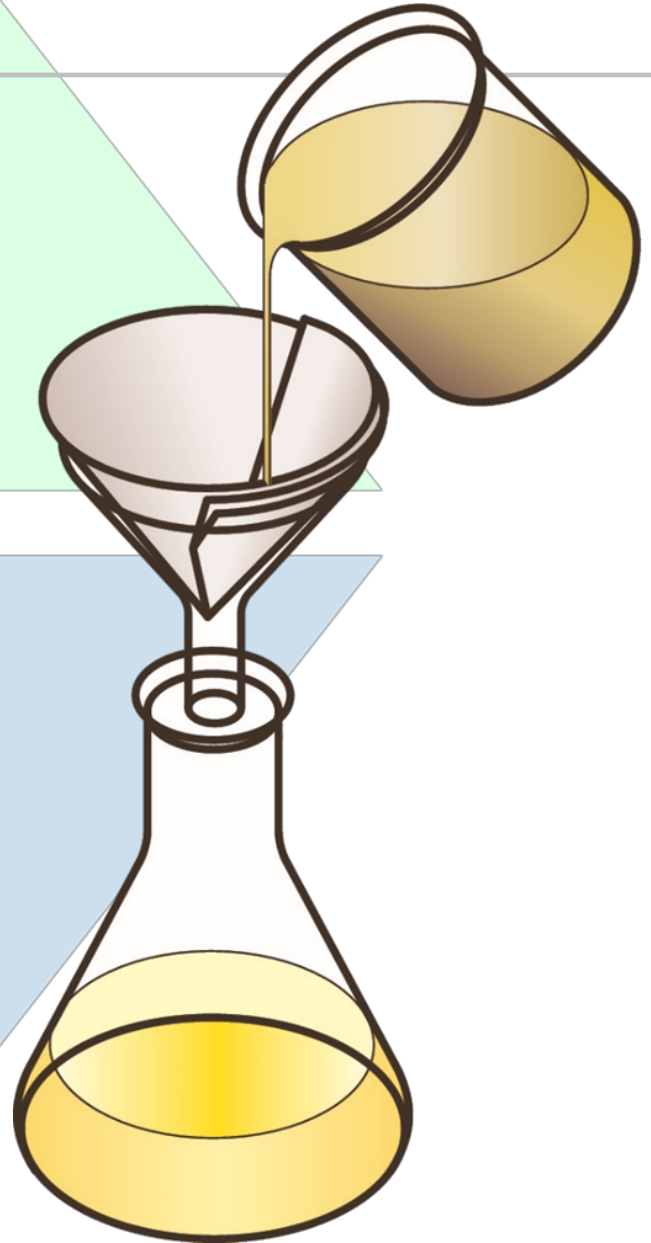
Other Special Considerations

- Field QC
- Decontamination of sampling equipment
- No pre-wrapped food or snacks
- Avoid cosmetics, moisturizers, hand creams on day of sampling.
- Visitors to site must remain at least 30 feet from sampling area.
- Wash hands with water after leaving vehicle before setting up on a well.
- **Partitioning of PFAS to surface in wells and reservoirs**



Filtering of Water Samples

- PFAS may sorb onto glass fiber filters
- Filtered/unfiltered data:
  - Is it PFAS sorbed to soil or sediment in the water sample?
  - Is it PFAS sorbed onto the glass fiber filter?
- Preferred method of dealing with particulates: low flow sampling or use of a centrifuge in the lab
- If filtering is required, do not use glass fiber filters



What Should I Wear?

- No clothing with fabric softeners
- No new clothing
- Avoid boots and other field clothing containing waterproof/resistant material
- Cotton is best

PFAS Analysis: What To Expect

EPA Method 537

The Basics

- Solid-phase extraction
- LC/MS/MS
- Developed for drinking water
- RLs 2-15 ng/L; 0.5-2 ng/g
- Holding time: 14 days/extraction; 28 days/analysis
- Cost: $275-500/sample
- Turnaround time: 2-3 weeks

Methods and Analyte Lists

PFAS Methods

Method	Year	Applicable Matrices	# PFAS Analytes
EPA 537 v 1.1	2009	Drinking Water	14 analytes
EPA 537.1	2018	Drinking Water	18 analytes
ASTM D7979-17	2017	Water, Wastewater	21 analytes
ASTM D7968-17	2017	Soil	21 analytes
ISO 25101	2009	Aqueous	PFOA/PFOS
DoD QSM 5.1	2017	Solid & Aqueous	24+ analytes
DoD QSM 5.2	2018	Solid & Aqueous	24+ analytes
EPA 537 “Modified”	Current	All	24+ analytes

Current PFAS Reportable by Analytical Laboratories

Analyte	CAS No.	UCMR3 (6)	537 (14)	NYSDEC (21)	ISO 25101 (2)	MDEQ IPP (24)
Perfluorobutanoic acid (PFBA)	375-22-4			X		X
Perfluoropentanoic acid (PFPeA)	2706-90-3			X		X
Perfluorohexanoic acid (PFHxA)	307-24-4		X	X		X
Perfluoroheptanoic acid (PFHpA)	375-85-9	X	X	X		X
Perfluorooctanoic acid (PFOA)	335-67-1	X	X	X	X	X
Perfluorononanoic acid (PFNA)	375-95-1	X	X	X		X
Perfluorodecanoic acid (PFDA)	335-76-2		X	X		X
Perfluoroundecanoic acid (PFUnA)	2058-94-8		X	X		X
Perfluorododecanoic acid (PFDoA)	307-55-1		X	X		X
Perfluorotridecanoic Acid (PFTrA)	72629-94-8		X	X		X
Perfluorotetradecanoic acid (PFTeA)	376-06-7		X	X		X
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5					
Perfluorooctadecanoic acid (PFODA)	16517-11-6					
Perfluorobutanesulfonic acid (PFBS)	375-73-5	X	X	X		X
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4					X
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	X	X	X		X
Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8			X		X
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	X	X	X	X	X
Perfluorononanesulfonic acid (PFNS)	474511-07-4					X
Perfluorodecanesulfonic acid (PFDS)	335-77-3			X		X
Perfluorooctane Sulfonamide (FOSA)	754-91-6			X		X
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)	2355-31-9		X	X		X
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	2991-50-6		X	X		X
6:2 Fluorotelomer sulfonic acid (6:2 FTSA)	27619-97-2			X		X
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	39108-34-4			X		X
4:2 Fluorotelomer sulfonic acid (4:2 FTSA)	757124-72-4					X
10:2 Fluorotelomer sulfonic acid (10:2 FTSA)	120226-60-0					
N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)	24448-09-7					
N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)	1691-99-2					
N-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8					
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2					
HFPO-DA (Gen-X)	62037-80-3		X			
ADONA			X			
F-53B-9Cl			X			
F-53B-11Cl			X			

Analyte lists vary by method, laboratory, and regulatory agency

Determine what list you really need!

Maine DEP Analytical Requirements

Sludge/Biosolids

- PFOA, PFOS, PFBS
- Isotope dilution must be used
- Isotope recovery must be >10% for compounds with screening standard.
- If isotope recovery <10%, samples must be re-extracted and re-analyzed.
- Results must be reported on dry weight basis.
- RLs must be below screening levels in Beneficial use of Solid Wastes
  - PFBS 1.9 mg/kg
  - PFOS 0.0052 mg/kg
  - PFOA 0.0025 mg/kg
- Field blank collected and submitted with each sample set.

LABORATORIES APPROVED BY DEP FOR PFAS ANALYSIS

Typical RLs = 0.0002 – 0.0005 mg/kg

Maine DEP Bureau of Remediation and Waste Management, Division of Technical Services Memorandum, To: Carla Hopkins, Environmental Specialist IV, cc: David Burns, Acting Bureau Director, From: Kelly Perkins, Chemist 3, Date: March 26, 2019, Re: Per- And Polyfluoroalkyl Substances (PFAS) Laboratory Recommendations. Suggests items for discussion with laboratories before analysis of samples.

MAINE DEPARTMENT OF Environmental Protection

Standardized Methods in the Future?

Future Method	Matrix	Calibration	Analytes/RLs	When?
SW-846 8327	Aqueous (non-DW)	Direct injection; External standard	24 PFAS; RL 10 ng/L	Out for public comment soon
SW-846 8328	Aqueous and solids	Isotope dilution	24 PFAS in 8327 plus Gen-X; RL 10 ng/L	Spring 2019; EPA collaborating with DoD
SW-846 8329	Solid prep method	NA	NA	Not definite
New Drinking Water Method	Drinking Water	SPE; Internal standard	Shorter chain PFAS	June 2019; EPA ORD & Office of Water

Every Lab is Different

- **UNDERSTAND WHAT YOUR LAB IS DOING!**
- **EVALUATE THE RESULTS!**

- Is the lab procedure appropriate for the matrix?
- How are solids extracted?
- What quantitation standards are used?
- What quantitation technique is used?
- How are interferences eliminated/minimized?
- Are branched isomers included in the results?
- What are the criteria for a positive detection?
- What concentrations are typically contributed by the lab?

Plug for ITRC PFAS Team

- Includes >350 members: industry, academia, DOD, regulatory, consulting, analytical labs and vendors
- Seven PFAS Fact Sheets:
  - AFFF Introduction
  - History and Use
  - Naming Conventions and Chemical Properties
  - Regulations and Guidance
  - Fate and Transport
  - Site Characterization, Sampling, Lab Methods
  - Remediation Technologies and Methods
- 2019/2020 – Technical Guidance Document

Questions?

Elizabeth Denly, ASQ CMQ/OE

Program Director – PFAS Group

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Thank you