



PFAS Testing Methods / Guidance

PFAS Sampling Procedures and Analytical Methods
2023 Specialty Conference & Workshop Series

Narragansett Bay Commission

Providence, Rhode Island

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Topics for Discussion

- Focus
 - Current Status of the Most Commonly Used PFAS Analytical Methods in Comparison to Draft EPA Method 1633
- Regulatory criteria and analytical methods
- Finalized EPA methods
- Laboratory modified “user defined” methods
- Draft Method 1633, compare and contrast





What are the Health Advisory Levels?

- Interim updated Health Advisory for PFOA = 0.004 parts per trillion (ppt)
 - Interim updated Health Advisory for PFOS = 0.02 ppt
 - Final Health Advisory for GenX chemicals = 10 ppt
 - Final Health Advisory for PFBS = 2,000 ppt
- prior HAL was 70 ppt combined PFOA & PFOS

UCMR 5 Reporting Limits

Chemical	Minimum Reporting Level (ppt)	Lifetime Health Advisory Level (ppt)
PFOA	4	0.004 (Interim)
PFOS	4	0.02 (Interim)
GenX Chemicals	5	10 (Final)
PFBS	3	2,000 (Final)

PFOA – implementable in commercial laboratories to the point where analysis to these levels would be widely available using existing instrumentation, at a reasonable cost with a high level of certainty??



An official website of the United States government [Here's how you know](#)

EPA United States Environmental Protection Agency

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Related Topics: [Safe Drinking Water Act](#) CONTACT US

Per- and Polyfluoroalkyl Substances (PFAS)

Proposed PFAS National Primary Drinking Water Regulation

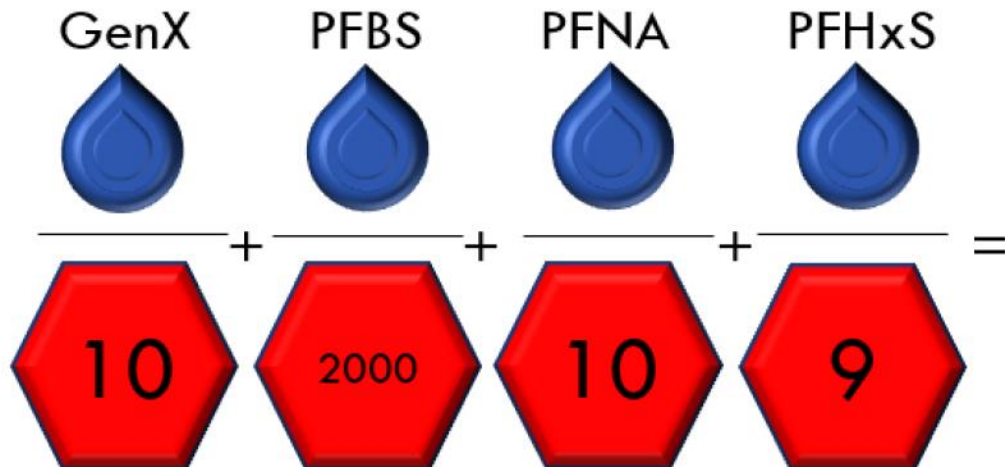
NEW On March 14, 2023, EPA announced the proposed National Primary Drinking Water Regulation (NPDWR) for six PFAS including

Compound	Proposed MCLG	Proposed MCL (enforceable levels)
PFOA	0 ppt*	4.0 ppt*
PFOS	0 ppt*	4.0 ppt*
PFNA		
PFHxS	1.0 (unitless)	1.0 (unitless)
PFBS	Hazard Index	Hazard Index
HFPO-DA (commonly referred to as GenX Chemicals)		

The Hazard Index is a tool used to evaluate potential health risks from exposure to chemical mixtures.

Compound	Proposed HBWC (ppt)
PFHxS	9.0
PFNA	10
PFBS	2000
HFPO-DA (commonly referred to as GenX Chemicals)	10

Implications for sources discharging to surface / groundwater used for drinking water?



If the running annual average HI greater than 1.0, it is a violation of the proposed HI MCL

Hazard Index Value

<https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas>

EPA Takes Important Step to Advance PFAS Strategic Roadmap, Requests Public Input and Data to Inform Potential Future Regulations under CERCLA

April 13, 2023

Contact Information

EPA Press Office (press@epa.gov)

EPA is proposing to add an additional 7 PFAS to the CERCLA HSL beyond PFOA & PFOS

WASHINGTON — Today, the U.S. Environmental Protection Agency (EPA) is issuing an Advance Notice of Proposed Rulemaking (ANPRM) asking the public for input regarding potential future hazardous substance designations of per- and polyfluoroalkyl substances (PFAS) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as “Superfund.”

IMPLICATIONS beyond CERCLA?

PFAS additions to standard site characterization, disposal & state regulatory lists?

Site “re-openers” ?

Bans / limits on biosolids land application?

NJDEP SPLP PFAS Study

Intention to use SPLP to calculate site specific Site Remediation Standards – Migration to Groundwater (SRS-MGW)

Synthetic Precipitation Leaching Procedure (SPLP) and Soil Remediation Standards for the Migration to Ground Water Exposure Pathway

May 25, 2022



Greg Toffoli, Section Chief
CSRRP, Bureau of Environmental Evaluation & Risk Assessment



- Biases resulting from SPLP apparatus and/or procedure itself?
 - NJDEP study
 - PFOA, PFNA, PFOS & GenX
 - Spiked at 5 different concentrations
 - SPLP & lab user defined PFAS analysis
- Leachate % R averaged in the 90% range
 - Follow up MeOH rinse step little carry over
- Conclusion reached that %Rs indicate no need to modify SPLP method
 - Did not review soil leaching



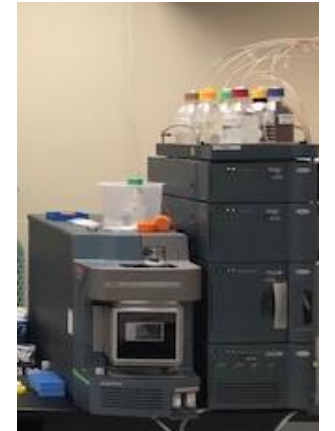
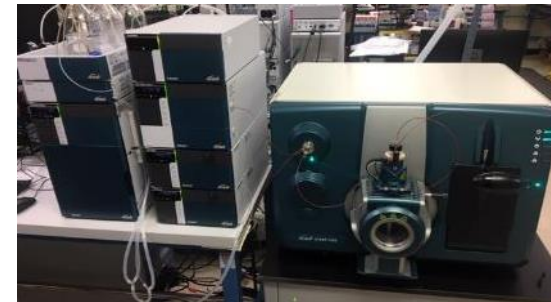
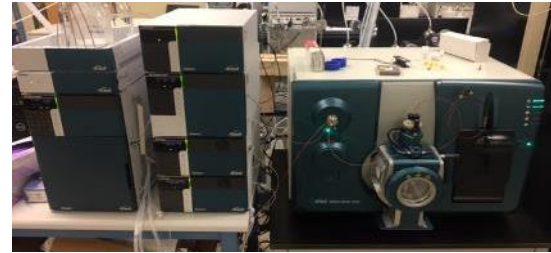
PFAS Method Update: Existing Finalized EPA PFAS Methods



- **Method 537, 2009, 14 cmpds, UCMR3**
 - UPDATED Method 537.1, 2018, 18 cmpds
 - Drinking water samples
- **Method 533, 2019, 25 compounds**
 - Drinking water samples
- **Method 8327, 2021 24 compounds**
 - Aqueous samples

Method 537

- Method 537. Version 1.1 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)

- **Analytical Instrumentation**

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

Method Development for Unregulated Contaminants in Drinking Water: Public Meeting and Webinar

Held June 6, 2018

USEPA, Office of Ground Water and Drinking Water

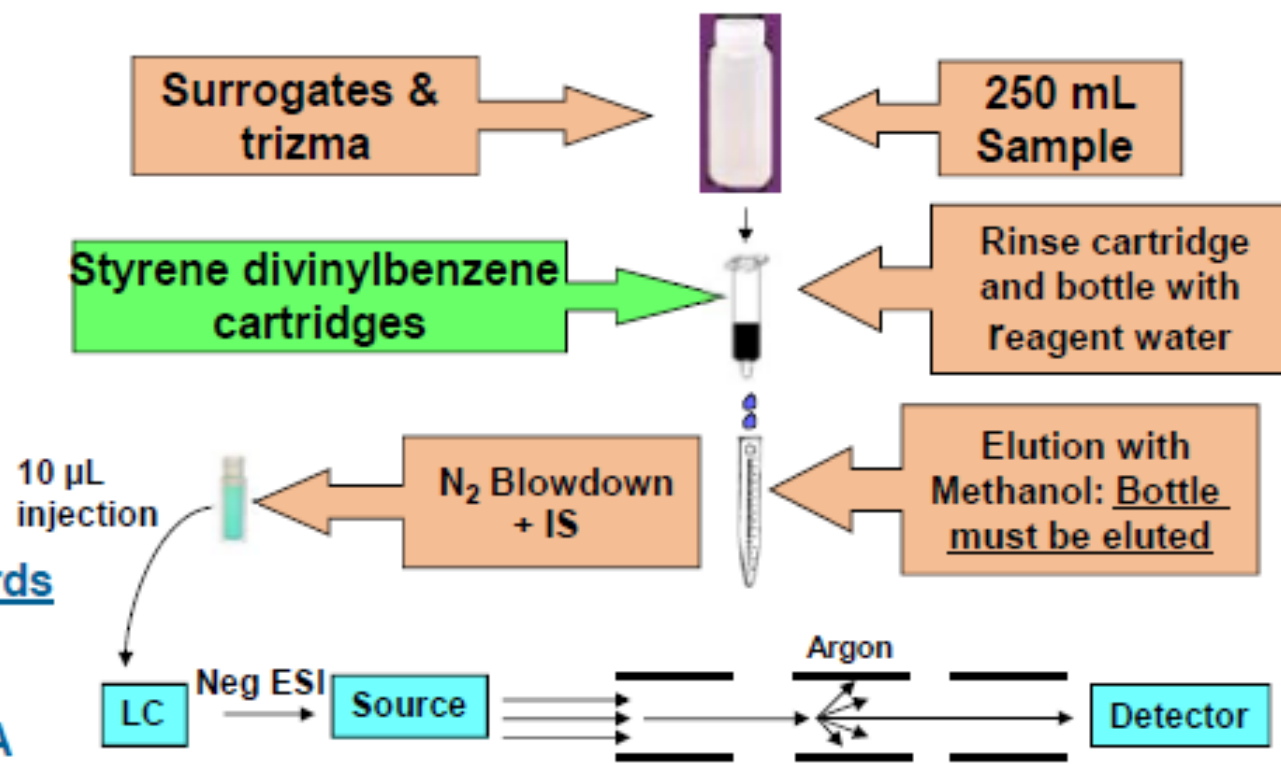


M537 Approach

Preservative
trizma

Surrogates
 $^{13}\text{C}_2$ -PFHxA
 $^{13}\text{C}_2$ -PFDA
 d_5 -NEtFOSAA
 ^{13}C -GenX

Internal Standards
 $^{13}\text{C}_2$ -PFOA
 $^{13}\text{C}_4$ -PFOS
 d_3 -NMeFOSAA



LC/MS/MS - Selected Reaction Monitoring



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)	

UCMR 3 PFAS Compounds



Method Development for Unregulated Contaminants in Drinking Water: Public Meeting and Webinar

Held June 6, 2018
USEPA, Office of Ground Water and Drinking Water

EPA initially intended on adding 7 PFAS compounds to Method 537.

The revised Method 537.1 only included these 4 for a total of 18 PFAS compounds.



Update to Method 537 (in progress)

<u>Potential PFAS additions</u>	<u>Acronym</u>	<u>CAS#</u>
Perfluoro-2-propoxypropanoic acid	* GenX	13252-13-6
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Perfluoro (2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	* 11CI-PF3OUdS	83329-89-9
Potassium 9-chlorohexadecafluoro-3-oxanone-1-sulfonate	* 9CI-PF3ONS	73606-19-6
Sodium dodecafluoro-3H-4,8-dioxanone	* ADONA	958445-44-8

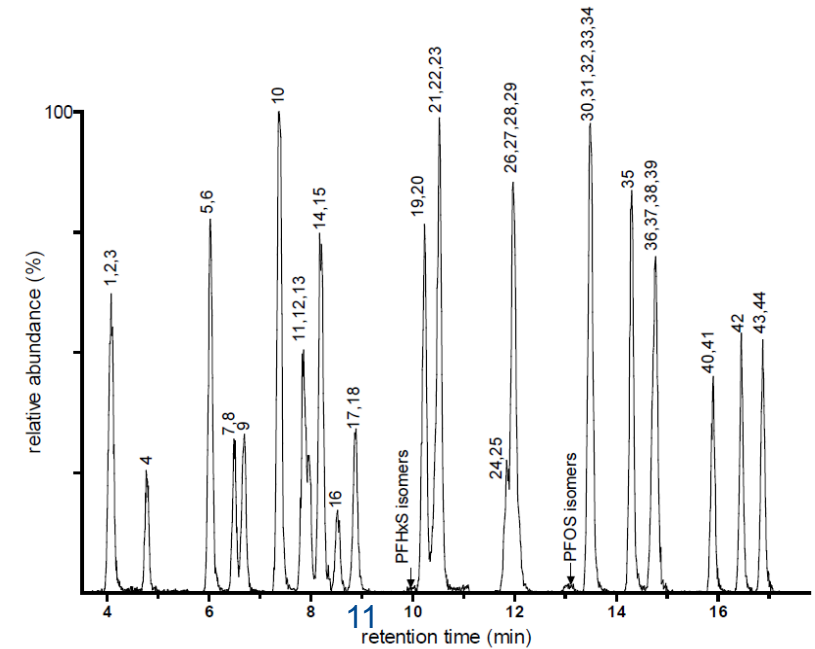
Challenge: Obtain performance data, write method, conduct multi-lab verification and peer review method ASAP

EPA Method 533

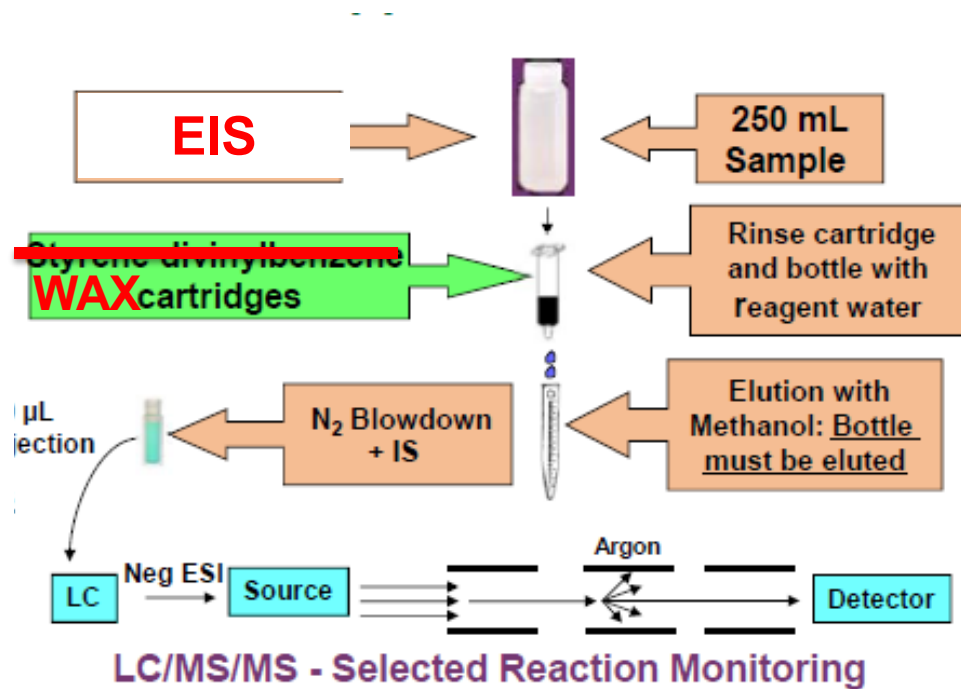


METHOD 533: DETERMINATION OF PER- AND
POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER BY
ISOTOPE DILUTION ANION EXCHANGE SOLID PHASE
EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM
MASS SPECTROMETRY

Figure 1. Example Chromatogram for Reagent Water Fortified with Method Analytes at 80 ng/L^a



Method 533 Procedural Differences from Method 537.1



- Uses extracted internal standard (EIS) isotope dilution approach
 - Isotopically labelled form of the analyte
 - Carbon -13, (¹³C) & deuterium, (²H) EIS
 - Chemically identical analytical performance
 - Spiked prior to all sample prep & extraction / carried through the entire analysis
 - Part of calibration, used for analyte quantification
 - Matrix recovery correction
 - Analyte-specific concentration normalization

Other Significant Method 533 Procedural Difference from Method 537.1

- **Solid Phase Extraction (SPE)**

- Uses WAX SPE cartridge

- Weak anion exchange

- Versus SDVB for Method 537.1

- Styrene divinylbenzene

- Uses ammonium acetate rather than Trizma[®] as a preservative

- Uses 28 day holding time to extraction

- Versus 14 day holding time for Method 537.1



Update to Method 537 (in progress)

<u>Potential PFAS additions</u>	Acronym	CAS#
Perfluoro-2-propoxypropanoic acid	GenX	13252-13-6
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Perfluoro (2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11CI-PF3OUdS	83329-89-9
Potassium 9-chlorohexadecafluoro-3-oxanone-1-sulfonate	9CI-PF3ONS	73606-19-6
Sodium dodecafluoro-3H-4,8-dioxanonate	ADONA	958445-44-8



Analyte	Abbreviation	CASRN	Method 533	Method 537.1
11-Chloroeicosafuoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	x	x
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	x	x
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	x	x
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	x	x
Perfluorobutanesulfonic acid	PFBS	375-73-5	x	x
Perfluorodecanoic acid	PFDA	335-76-2	x	x
Perfluorododecanoic acid	PFDoA	307-55-1	x	x
Perfluoroheptanoic acid	PFHpA	375-85-9	x	x
Perfluorohexanoic acid	PFHxA	307-24-4	x	x
Perfluorohexanesulfonic acid	PFHxS	355-46-4	x	x
Perfluorononanoic acid	PFNA	375-95-1	x	x
Perfluorooctanoic acid	PFOA	335-67-1	x	x
Perfluorooctanesulfonic acid	PFOS	1763-23-1	x	x
Perfluoroundecanoic acid	PFUnA	2058-94-8	x	x
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	x	
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	x	
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	x	
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	x	
Perfluorobutanoic acid	PFBA	375-22-4	x	
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	x	
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	x	
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	x	
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	x	
Perfluoropentanoic acid	PFPeA	2706-90-3	x	
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	x	
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6		x
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9		x
Perfluorotetradecanoic acid	PFTA	376-06-7		x
Perfluorotridecanoic acid	PFTTrDA	72629-94-8		x

Method 533 shifts focus to shorter chain PFAS

Short Chain PFCAs				Long Chain PFCAs			
C4 PFBA	C5 PFHeA	C6 PFHxA	C7 PFHpA	C8 PFOA	C9 PFNA	C10 PFDA	C11 PFUnA

Short Chain PFSAs		Long Chain PFSAs					
C4 PFBS	C5 PFPeS	C6 PFHxS	C7 PFHpS	C8 PFOS	C9 PFNS	C10 PFDS	C11 PFUnS

Method 533: 25 compounds*
Method 537.1: 18 compounds

*** 25 compound Method 533 list does not include all 18 537.1 compounds**

If the 4 cmpds dropped from 533: **PFTTrDA, PFTA, NMeFOSAA & NEtFOSAA** are run by Method 537.1
= 29 compounds combined both methods

DW Methods, UCMR 5

EPA Method 8327 w/ Method 3512 Sample Introduction

An official website of the United States government [Here's how you know](#) ▼

 **EPA** United States Environmental Protection Agency

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Related Topics: [Hazardous Waste Test Methods / SW-846](#) [CONTACT US](#)

SW-846 Test Method 8327: Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

- Not a DW method, amenable to non-potable water
- Does not use SPE sample preparation
- Method was not well received



Laboratory User Defined Methods

- For a long time, EPA finalized methods only existed for aqueous samples
 - *What if you needed to analyze other sample media? Or additional compounds*
- **Laboratory-specific methodology: User Defined Methods**
 - *Labs developed their own modifications*
 - Performance & comparability?
 - Target compound lists, RLs?



Analytical Concerns with Non-Drinking Water Matrices

Aqueous Matrices w/Particulates

- **Particulates will impact SPE performance**
 - Wastewater, "silty" ground water, etc.
- **How are they addressed ? Need a specific SOP**
 - Additional sample prep required
 - Filtering??
 - Centrifuging?
 - How are the solids accounted for?
- **Isotope dilution approach**
 - Samples pre-spiked with extraction internal standards



Soils...Biosolids / Residuals

- Challenging...
- Treat as an AQ or solid sample?
- Samples pre-spiked with extraction internal standards
 - Homogenize
 - Serial extraction
 - Extract clean up
 - Extract concentration



Tissues?

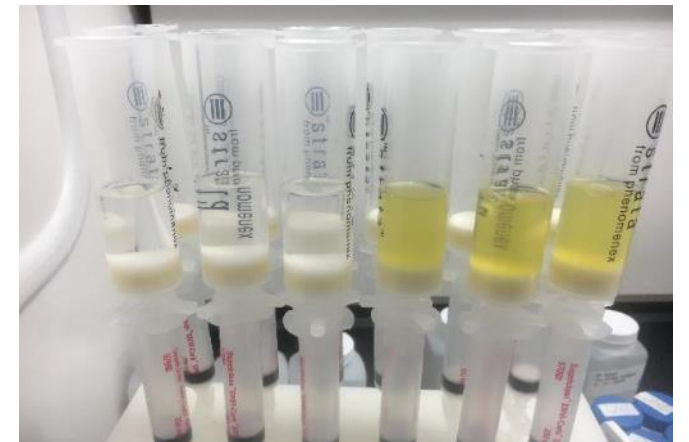
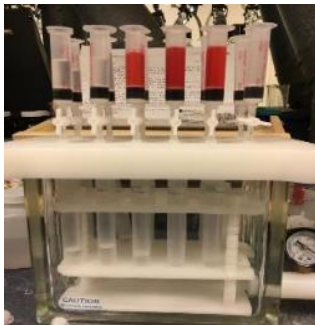
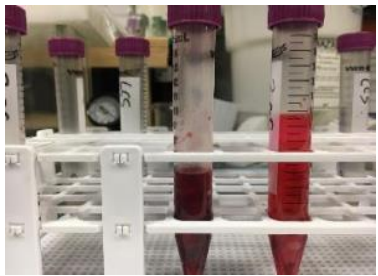
Plant tissue



Fish



Oysters



3 New EPA SW-846 Methods Proposed

- (1) Non-potable water: SW-846 Method 8327 draft, fall 2018
 - LC/MS/MS direct injection, external standard calibration
 - 24 analytes
- (2) Non-potable water: SW-846 Method 8328
 - LC/MS/MS SPE , isotope dilution
 - 24 analytes
- (3) Solids: SW-846 Method 8329 TBD



early 2018 vintage slide



late 2018 vintage slide

Additional EPA Methods?



- SW-846 Method 8328 Target date??
 - Non-potable water plus soils, sediments & biosolids
 - LC/MS/MS SPE, isotope dilution
 - 24 analytes plus HFPO-DA
 - Consistent with DoD QSM 5.1, Table B-15
- EPA 1600 series method?
 - EPA working with DoD
- ~ 40 compounds?



3rd **Draft** Method 1633

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

- ***First EPA Method for solid matrices but...***
 - ***Not multi-lab validated, not finalized yet***
 - ***Certification, regulatory acceptance, uncertainty***

- **DRAFT methods are single lab validated**
- **FINAL Methods are multi-lab validated**
- **3rd revision of draft method, multi-lab validation study ongoing**

Target Compound Lists

Target Analyte Name	Abbreviation	CAS Number	EPA	EPA	EPA	Alpha	draft EPA
Perfluoroalkyl carboxylic acids							
Perfluorobutanoic acid	PFBA	375-22-4		x	x	x	x
Perfluoropentanoic acid	PFPeA	2706-90-3		x	x	x	x
Perfluorohexanoic acid	PFHxA	307-24-4	x	x	x	x	x
Perfluoroheptanoic acid	PFHpA	375-85-9	x	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	x
Perfluorodecanoic acid	PFDA	335-76-2	x	x	x	x	x
Perfluoroundecanoic acid	PFUnA	2058-94-8	x	x	x	x	x
Perfluorododecanoic acid	PFDoA	307-55-1	x	x	x	x	x
Perfluorotridecanoic acid	PFTTrDA	72629-94-8	x		x	x	x
Perfluorotetradecanoic acid	PFTeDA	376-06-7	x		x	x	x
Perfluorohexadecanoic Acid	PFHxDA	67905-19-5				x	
Perfluorooctadecanoic Acid	PFODA	16517-11-6				x	
Perfluoroalkyl sulfonic acids							
perfluoropropanesulfonic acid	PFPrS	423-41-6				x	
Perfluorobutanesulfonic acid	PFBS	375-73-5	x	x	x	x	x
Perfluoropentansulfonic acid	PFPeS	2706-91-4		x	x	x	x
Perfluorohexanesulfonic acid	PFHxS	355-46-4	x	x	x	x	x
Perfluoroheptanesulfonic acid	PFHpS	375-92-8		x	x	x	x
Perfluorooctanesulfonic acid	PFOS	1763-23-1	x	x	x	x	x
Perfluorononanesulfonic acid	PFNS	68259-12-1			x	x	x
Perfluorodecanesulfonic acid	PFDS	335-77-3			x	x	x
Perfluorododecanesulfonic acid	PFDoS	79780-39-5				x	x
Fluorotelomer sulfonic acids							
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4		x	x	x	x
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2		x	x	x	x
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4		x	x	x	x
1H,1H,2H,2H-Perfluorododecanesulfonic Acid	10:2FTS	120226-60-0				x	
Perfluorooctane sulfonamides							
Perfluorooctanesulfonamide	PFOSA	754-91-6			x	x	x
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8				x	x
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2				x	x
Perfluorooctane sulfonamidoacetic acids							
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	x		x	x	x
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	x		x	x	x
Perfluorooctane sulfonamide ethanols							
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7				x	x
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2				x	x
Per- and Polyfluoroether carboxylic acids							
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	x	x		x	x
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	x	x		x	x
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1		x		x	x
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5		x		x	x
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6		x		x	x
Ether sulfonic acids							
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	x	x		x	x
11-Chloroicosasfluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	x	x		x	x
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7		x		x	x
Fluorotelomer carboxylic acids							
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5					x
2H,2H,3H,3H-Perfluorooctanoic acid	5:3FTCA	914637-49-3					x
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4					x
			18	25	24	41	40



Items of Interest // Comparative Review

AQ Sample Processing

- **Draft Method 1633 rev2**
 - Standard procedure applicable to samples with up to 50 mg suspended solids
 - No filtering
 - Prepare entire sample
 - Homogenize invert 3-4 times
 - Spike w/ EIS
 - *Rev 3 mentions centrifugation*
- **Appendices A & B**
 - Screening & sub sampling



- **User Defined Methods***
 - Not a clear delineation, based on SPE performance
 - No filtering
 - Prepare entire sample
 - Spike w/ EIS
 - Where indicated – centrifugation
 - Resulting AQ and solid fractions
 - » Each extracted? Extract combined?

Overview & Summary- *draft* Method 1633

Sample Extraction

• Aqueous samples

- spiked with isotopically labeled standards, extracted using weak anion exchange (WAX) SPE cartridges with clean up using loose graphitized carbon black (GCB) before analysis.
- 500 mL Aq sample volume ✓

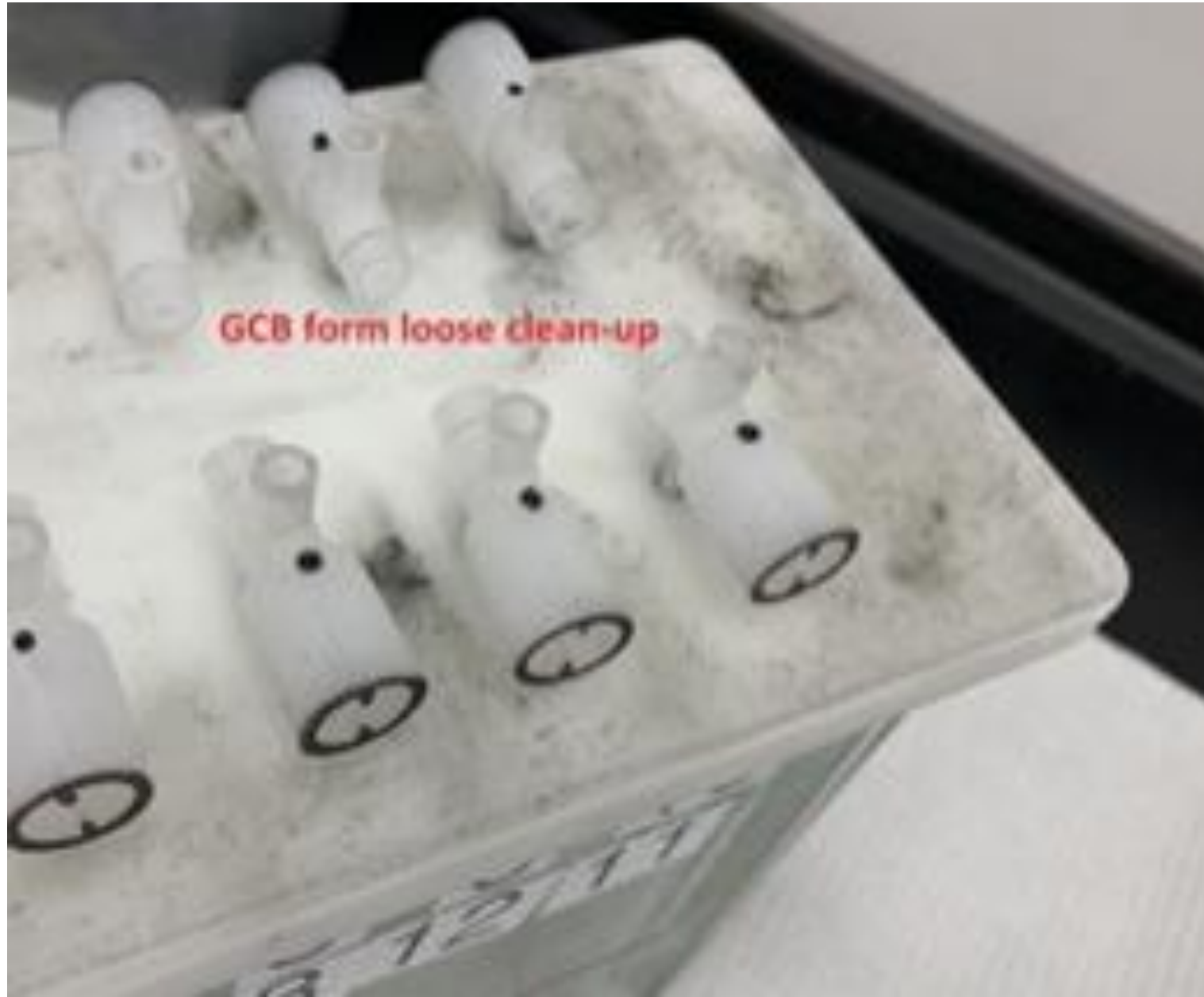
7.1.17 Carbon – EnviCarb® 1-M-USP or equivalent, verified by lot number before use, store at room temperature. Loose carbon allows for better adsorption of interferent organics.

Note: The single-laboratory validation laboratory achieved better performance with loose carbon than carbon cartridges. Loose carbon will be used for the multi-laboratory validation to set statistically based method criteria. Once the method is multi-laboratory validated, laboratories will have the flexibility to use carbon cartridges, as long as all method QC criteria are met.

• Soil samples

- Spiked w/isotopically labeled standards, sequentially extracted 3 times with slightly basic methanol
 - 60 minutes total, first 2 extractions using shaker table
 - GCB & WAX SPE clean up
- % solids determination prior to extraction ✓
 - Impact on TAT?





Overview & Summary- *draft* Method 1633

Sample Extraction

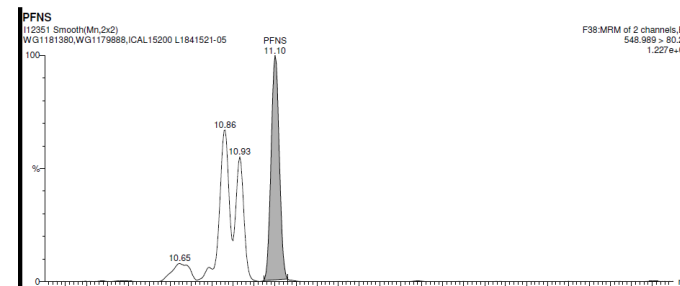
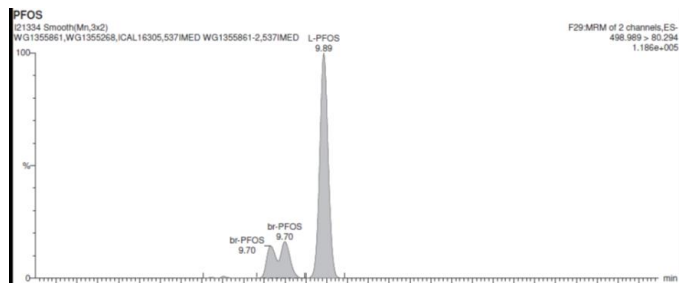
- Tissue samples

- Spiked with isotopically labeled standards
 - Loose GCB added & sequentially extracted 3 times
 - Slightly basic methanol, 16 hours on shaker table ✓
 - 10 mLs acetonitrile, 30 minutes on shaker table
 - 5 mLs slightly basic methanol (0.05M KOH/MeOH)
- Evaporation step (minimal to lessen extract MeOH / water ratio)
- WAX SPE clean up



Overview & Summary- *draft* Method 1633 rev2

Instrumental Analysis – Linear & Branched Isomers



QUANTITATIVE STANDARDS containing a mixture of branched and linear isomers must be used if they are commercially available. Currently, these include **PFOS, PFHxS, NMeFOSAA, and NEtFOSAA.**

QUALITATIVE STANDARDS that contain mixtures of the branched and linear isomers of the method analytes and that are used for comparison against suspected branched isomer peaks in field samples.

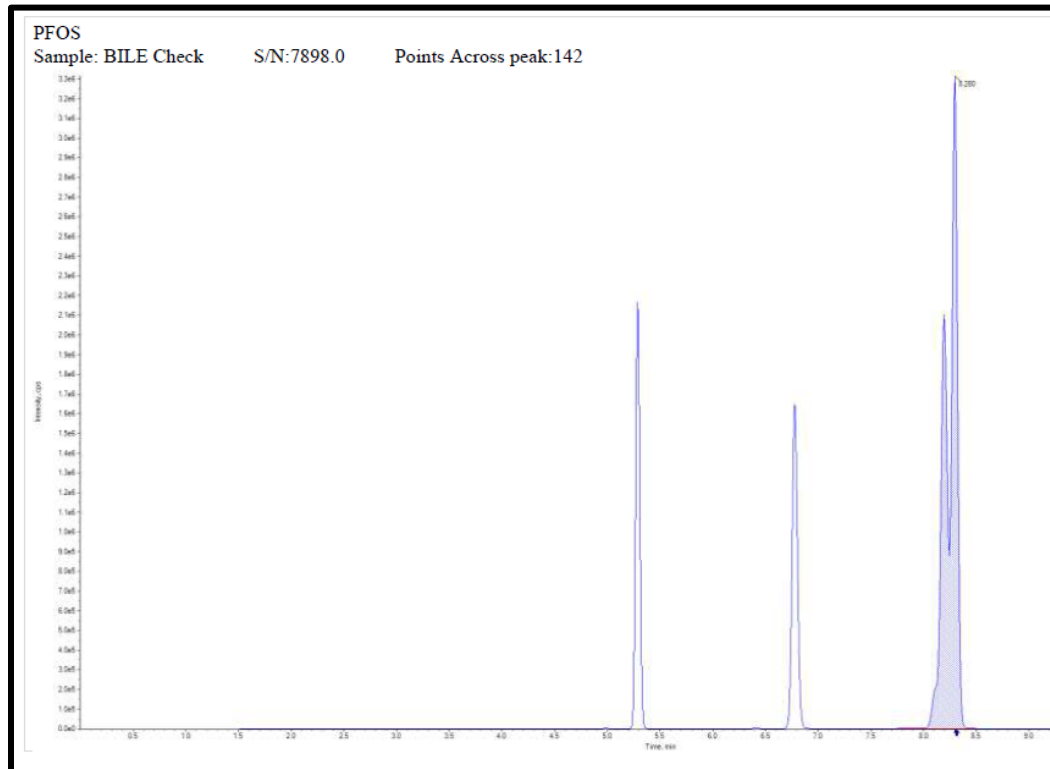
PFOA qualitative standard previously available

- Draft Method 1633 adds qualitative branched isomer standards for 6 additional PFAS (*note: linear/branched not reported separately*) **PFNA, PFOSA, NMeFOSA, NEtFOSA, NEtFOSE, and NMeFOSE** 11 / 40 PFAS can be reported as the total of Linear & Branched

Overview & Summary- *draft* Method 1633 rev2

Instrumental Analysis - Bile Salt Interference Check

- Bile salt interference check(s) added to Draft Method 1633
 - Potential PFOS interferent in tissue samples primarily



taurodeoxycholic acid (TDCA) ***Acetonitrile mobile phase***

10.2.2.5 When establishing the chromatographic conditions, it is important to consider the potential interference of bile salts during analyses of tissue samples. Inject **the bile salt interference check** standard containing TDCA (**see Section 7.5 if the mobile phase is not acetonitrile**) during the retention time calibration process and adjust the conditions to ensure that TDCA (**or TCDCA and TUDCA**) **does** not coelute with any of the target analytes, EIS, or NIS standards. Analytical conditions must be set to allow a separation of at least 1 minute between the bile salts **and the retention time window of** PFOS

Must also include if acetonitrile is not the mobile phase and tissues are being analyzed

taurochenodeoxycholic acid (TCDCA)
tauroursodeoxycholic acid (TUDCA)

Holding Time Comparison

Sample Media	537.1 sample	537.1 extract	533 sample	533 extract	8327 sample	8327 extract	1633 rev2 draft sample	1633 rev2 draft extract
drinking water	14 days	28 days	28 days	28 days	X	X	X	X
aqueous	X	X	X	X	14 days*	30 days*	0-6C 28 days** <= -20C 90 days DARK	DARK 0-4C 90 days *****
soils, sediments	X	X	X	X	X	X	0-6C 90 days*** <= 20C 90 days***DARK	DARK 0-4C 90 days *****
biosolids	X	X	X	X	X	X	0-6C 90 days**** <= -20C 90days****DARK	DARK 0-4C 90 days *****
tissue	X	X	X	X	X	X	Once received by the laboratory, the samples must be maintained protected from light at ≤ -20 °C until prepared. Store unused samples in HDPE containers or wrapped in aluminum foil at ≤ -20 °C.	0-4C 90 days ***** maintained protected from the light

* Formal holding times have not yet been established for these

** With the caveat that issues were observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days. These issues are more likely to elevate the observed concentrations of other PFAS compounds via the transformation of these precursors if they are present in the sample.

*** with the caveat that samples may need to be extracted as soon as possible if NFDHA is an important analyte.

**** EPA recommends that samples be frozen if they need to be stored for more than a few days before extraction.

***** with the caveat that issues were observed for some ether sulfonates after 28 days. These issues may elevate the observed concentrations of the ether sulfonates in the extract over time.

Method 1633 Comparability with User Defined?

- **Disclaimer: new method, not a lot of commercial samples run yet**
 - Little comparison data available, there are potential procedural differences
 - *That said, routine, relatively clean matrices / “usual suspect” PFAS **should** be comparable*
- **Obvious questions**
 - Target compound lists, Reporting limits
- **More complex matrices?**
 - Comparability concerns w/draft 1633 vs. lab user defined methods possible
 - However, the specific inconsistencies will differ depending on the lab’s user defined SOP and the sample being analyzed
 - Interferences due to matrix, AQ particulates, non-target PFAS and linear to branched isomer pattern, etc. could impact each method differently



Wrap up

Draft Method 1633 Summary

- Aq samples w/particulates
 - Still a “grey area”
- Bile salt interference check for tissues
- Branched isomers standards for 6 additional PFAS compounds
- Holding time differences

- **Obvious benefit from having a final, standardized method for all environmental media**



Questions?

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