

# **PFAS Sampling & Analytical Considerations**

#### PFAS: Field Sampling & Cross-Contamination Issues (webinar) Tuesday, June 23, 2020 1:30 PM

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

- Analytical method update
- Cross contamination study results





In the Beginning...

#### Primary methodology

 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)

### EPA Method 537.1 - Target Compound List

	Analyte <sup>a</sup>	Acronym	Chemical Abstract Services Registry Number (CASRN)
*	Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6 <sup>b</sup>
	N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
	N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
	Perfluorobutanesulfonic acid	PFBS	375-73-5
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluoroheptanoic acid	PFHpA	375-85-9
	Perfluorohexanesulfonic acid	PFHxS	355-46-4
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluorononanoic acid	PFNA	375-95-1
	Perfluorooctanesulfonic acid	PFOS	1763-23-1
	Perfluorooctanoic acid	PFOA	335-67-1
	Perfluorotetradecanoic acid	PFTA	376-06-7
	Perfluorotridecanoic acid	PFTrDA	72629-94-8
	Perfluoroundecanoic acid	PFUnA	2058-94-8
*	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9°
*	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9C1-PF3ONS	756426-58-1 <sup>d</sup>
*	4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4 <sup>e</sup>



# 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





Analyte	Abbreviation	CASRN	Method 533	Method 537.1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11CI-PF3OUdS	763051-92-9	x	x
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acd	9CI-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	х
Perfluoroundecanoic acid	PFUnA	2058-94-8	x	x
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	Х	
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	Х	
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	х	
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	Х	
Perfluorobutanoic acid	PFBA	375-22-4	Х	
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	х	
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	Х	
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	X	
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	X	
Perfluoropentanoic acid	PFPeA	2706-90-3	х	
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	Х	
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6		X
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9		х
Perfluorotetradecanoic acid	PFTA	376-06-7		x
Perfluorotridecanoic acid	PFTrDA	72629-94-8		х

# Method 533 shifts focus to shorter chain PFAS

Short	Short Chain PFCAs					Long Chain PFCAs			
C4 PF	BA <b>C5</b>	PFHeA	C6 PFHxA	C7 PFHpA		C8 PFOA	C9 PFNA	C10 PFDA	C11 PFUnA
Short	Short Chain PFSAs			Long Cha	in PFSAs				
C4 PF	BS <b>C5</b>	PFPeS		C6 PFHxS	C7 PFHpS	C8 PFOS	C9 PFNS	C10 PFDS	C11 PFUnS

### Method 533 versus Method 537.1 - Overview

- Method 533
  - Uses extracted internal standard isotope dilution approach
  - Uses WAX SPE cartridge
    - Versus SDVB for Method 537.1
  - 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





# **Isotope Dilution Technique**

- Provides additional qualitative & quantitative certainty
- Matrix recovery correction
  - Analyte-specific sample concentration normalization
- Extracted internal standards
  - Added to sample prior to sample extraction
    - Known amount of isotopically labelled form of the analyte
    - Carbon -13, <sup>13</sup>C & deuterium, <sup>2</sup>H
  - Compound-specific\* internal standard





# Method 537.1 / 533 Limitations

- Written for clean drinking water sample matrix – SO WHAT IF YOU HAVE…
  - Silty groundwater? Wastewater?
  - Soils, biosolids...oysters?
- 537.1 18 specific PFAS ; 533 25 specific PFAS
  SO WHAT IF YOU NEED...
  - Other compounds and/or longer or different list?







- Proscriptive
  - "as specifically written"
- Other methodologies
  - "Laboratory proprietary method"
    - LC/MS/MS
    - May use different or multiple SPE cartridges
- May use isotope dilution technique





"Other Aqueous Matrices"

- Wastewater, "silty" ground water, SPLP, etc.
- Need a specific SOP
  - Additional sample prep
  - Filtering??
  - Centrifuging
- Isotope dilution approach
  - Samples pre-spiked with extraction internal standards!







# Soils & Biosolids

- Isotope dilution recommended
  - Samples pre-spiked with extraction internal stds.
  - SPE clean up cartridge



• Biosolids??





# Other Sample Matrices?

#### Soils prep further modified



### Landfill Waste Stream Study



photo courtesy Sanborn, Head & Associates, Inc.







## Non- Drinking Water EPA PFAS Method?

- Validated Test Method 8327: Per-and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)
- Applicable to other aqueous media beyond drinking water
- Based on EPA Region 5, Chicago Regional Lab method
  - similar to ASTM D7979
    - LC/MS/MS, direct injection, not SPE, external standard calibration

The DoD considers Method 8327 a "screening method" (Alyssa G. Wingard, Senior Chemist, NAVSEA 04X6 Laboratory Quality and Accreditation Office (LQAO); July 2019, email correspondence,

DENIX).



# 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







Sampling Recommendations

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

"OK"

# "NOT 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

### 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

# PFAS in Sampling Supplies: Fact or Fiction?



Field Book (cover & pages)

TRC

Nitrile Gloves

**Bailer** Line

#### **Overview**



- Initially started as an informal inquiry
  - Not an in depth study
- Conservative 24 hour contact time
  - Worst case scenario
- Products chosen at random
  - Generic product names used
- Study was conducted from 2017 through 2018
  - Performed in a series of 7 batches

#### **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









- PFAS not detected in any associated leaching or method blanks
- "Problematic" samples adhesive labels & "level C protective suit"





#### **PTFE Tubing**





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#### **LDPE** Tubing





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**PTFE vs LDPE Tubing** 





### **PTFE Tubing & PTFE Bladder**





#### Water Level Tapes





#### **Bailer Line**





Bailer Line 1 Bailer Line 2

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### **Field Book Pages vs Field Book Cover**





ng/L

# **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

Sampling Plans - Start with standard industry practice for site characterization & sampling... And then make PFAS accommodations

Additional contamination studies

Blanks?