



### Analytical Methodology Review of Per-and Polyfluoroalkyl Substances (PFAS)

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### EPA to Convene National Leadership Summit to Take Action on PFAS

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**WASHINGTON** (March 19, 2018) -- Today, in a letter sent to governors of 56 states and territories, the U.S. Environmental Protection Agency (EPA) announced plans to host a National Leadership Summit in Washington, D.C. to take action on Per- and Polyfluoroalkyl Substances (PFAS). PFAS is a category of manmade chemicals that have been widely used to make products because of their stain-resistant, waterproof and/or nonstick properties.

"EPA's leadership summit will bring together stakeholders from across the country to build on the steps we are already taking and to identify immediate actions to protect public health," said **EPA Administrator Scott** 







#### 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.

USEPA has compiled an online resource for PFAS that includes topics such as policy and guidance, chemistry and behavior, occurrence, toxicology,

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

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

# PFAS 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?







## ANALYTICAL METHODOLOGIES





#### **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)





EPA United States Environmental Protection Agency

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)

4.67

- Standards not available at the time for PFOA
  - Discrepancies in PFOA reporting



Addressed in Tech Advisory





- 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





#### 3 New EPA SW-846 Methods Proposed

- (1) LC/MS/MS direct injection AQ method
  10 ng/L reporting limit, screening or determinative
- (2) LC/MS/MS isotope dilution AQ method
- (3) LC/MS/MS soil method
  - Will employ an extraction & potentially direct injection

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.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., AFFF formulations). Inline SPE is acceptable. Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE, with documented project approval.	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.			

**DOD QSM Version 5.1** 

Table B -15 (pg 1 of 15)

#### **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."



0/50 water/MeOH





International Organization for Standardization

- 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)





#### TOP (Total Oxidizable Precursor) Assay

- Analysis of individual PFAS compounds using LC/MS/MS may significantly underestimate PFAS mass
  - Precursors
    - Polyfluoroalkyl substances that can undergo transformation to form perfluoroalkyl acids

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- 2 aliquots
  - Analyze 1 normally
  - Treat other aliquot
    - $KS_2O_8$  + NaOH / 85  $^{\circ}$  6 hrs
    - Then analyze
- Total precursors = PFAS<sub>treated</sub> PFAS<sub>untreated</sub>

#### Acids or Salts – Laboratory Implications

- Terms interchangeable in literature, regulatory guidance & media
  - (PFOA) perfluorooctanoic acid (ACID form)
  - (PFOS) perfluorooctane sulfonate (ANION form)
- 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?



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#### So What Do You Analyze For?

#### application & regulatory dependent



#### Industry

- PFOA / PFOS, UCMR 6 ...
  - "EMERGING" emerging contaminants?
- Method 537, modified ID, R&D





#### • AFFF



- UCMR 6 to expanded lists
- Generally modified ID method
- Landfills
  - PFOA / PFOS to expanded list(s)
  - Method 537 and / or modified ID

#### **6 PFAS cmpds included**

PFOS 🗡 EPA HAL	perfluorooctanesulfonic acid	
PFOA 🗡 EPA HAL	perfluorooctanoic acid	
PFNA 🔭 NJ GWQC	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 (PRTrDA)
Perfluorotetradecanoic acid (PFTeDA)





Analyte Name	Acronym	
Perfluorotetradecanoic acid*	PFTreA**	PFTA
Perfluorotridecanoic acid*	PFTriA***	PFTrDA
Perfluorododecanoic acid*	PFDoA	
Perfluoroundecanoic acid*	PFUnA	*Mathad
Perfluorodecanoic acid*	PFDA	<b>E</b> 27
Perfluorononanoic acid*	PFNA	537
Perfluorooctanoic acid*	PFOA	
Perfluoroheptanoic acid*	PFHpA	
Perfluorohexanoic acid*	PFHxA	
Perfluoropentanoic acid	PFPeA	proposed
Perfluorobutanoic acid	PFBA	list, new
Perfluorodecanesulfonate	PFDS	EPA
Perfluorononanesulfonate	PFNS	methous
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*	<b>NEtFOSAA</b>	
N-(Heptadecafluorooctylsulfonyl)-N-methylglycine*	<b>NMeFOSAA</b>	



#### **GenX Investigation**

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#### Perfluoro-2-propoxypropanoic acid

The N.C. departments of Environmental Quality (DEQ) and Health and Human Services (DHHS) began investigating the presence of a compound known as GenX in the Cape Fear River in June. The Chemours facility in Fayetteville was identified as the company that produces the GenX chemical for industrial processes.

The state's investigation focused on protection of public health and drinking water. As part of the state's investigation, DEQ began collecting water samples from multiple sites along the Cape Fear



What is GenX? GenX is a trade name for a man-made and unregulated chemical used in manufacturing nonstick coatings and for other purposes. Chemours' facility in Fayetteville began producing GenX commercially in 2009 as a replacement for PFOA. The same chemical is also produced as a byproduct during other manufacturing processes and it may have been present in the environment for many years before being produced <sup>22</sup> commercially as GenX.

 $\mathbf{\hat{\mathbf{A}}}$ 



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



#### minimization of lab contamination

the usual safeguards "PFAS kit" lots of blanks





### Sampling:

addressing possible sources of contamination

(example recommendations)

#### OK

- Field Equipment
  - HDPE bottles, silicon tubing, loose paper, aluminum/Masonite clipboards, Alconox / Liquinox<sup>@</sup>, nitrile gloves

#### Clothing / PPE

"Well laundered", preferably cotton

#### Personal care products

 None, see "allowable" sun screens & insect repellants

### 

- Field Equipment
  - LDPE bottles, Teflon<sup>@</sup> caps, Teflon<sup>@</sup> tubing, waterproof field books, plastic clipboards/binders, Post It <sup>@</sup> notes, chemical (blue ice)

#### Clothing / PPE

 No fabric softener, Gor-Tex<sup>@</sup>, "dri -fit", Tyvek <sup>@</sup>

#### 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, Clothing, and Personal Care Products

#### 33rd Annual International Conference on Soils, Sediments, Water, and Energy, October 16-19, 2017, Amherst, MA

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#### **Product List**





Bag



Aluminum Foil



Note Pad



Polyethylene Bladder





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

Bag



LDPE Tubing : 2 Manufacturers



Silastic Tubing



Teflon Bladder







Field Book (cover & pages)

A MAGANIA









Nitrile Gloves



**Bailer String** 

#### Observations

- Obviously a "worst case scenario"
- Inconsistencies / some surprises
  - Not all PTFE leached
  - HDPE
  - LDPE (PFPeA!)
- Field sourced materials
  - Bailer line, field book, PTFE bladder pump, sample labels leached
  - PPE, sample label matrix challenges





		#
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	<b>NEtFOSAA</b>	0
N-ethyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	0
Perfluorobutanesulfonic acid	PFBS	3
Perfluorodecanoic acid	PFDA	
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	PFTrDA	4
Perfluoroundecanoic acid	PFUnA	<sup>29</sup> <b>4</b>



### Wrap Up

### Understand regulatory landscape, have dialog with lab

### **MOVING TARGET!**





 - "what we find in the environment often depends on what we look for and how hard we look"

#### **USGS** website

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