#### ANALYSIS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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8/4/16 1



TOXICANT EXPOSURES IN RHODE ISLAND: Past, Present, and Future



#### Brown University Superfund Research Program



### **INTRODUCTION: PFAS IN THE NEWS**





**Per**fluoroalkyl carboxylates:



Examples: m=2 PFBA m=4 PFHxA **m=6 PFOA**  **Per**fluoroalkane sulfonates:



Examples: m=3 PFBS m=5 PFHxS **m=7 PFOS** 

Per = fully fluorinated alkyl tail.

**Per**fluoroalkyl carboxylates:





**Per**fluoroalkane sulfonates:



Examples: m=3 PFBS m=5 PFHxS **m=7 PFOS** 

Poly = partially fluorinated alkyl tail.

**Poly**fluoroalkyl substances:



**Per**fluoroalkyl carboxylates:



Examples: m=2 PFBA m=4 PFHxA m=6 PFOA

#### **Per**fluoroalkane sulfonates:



Examples: m=3 PFBS m=5 PFHxS **m=7 PFOS** 



**Poly**fluoroalkyl substances:



m=5 6:2 FtS m=7 8:2 FtS

6

# What is a precursor?

**Poly**fluroalkyl substances that can undergo transformation to form **per**fluoroalkyl acids



### **INTRODUCTION: CHEMISTRY AND USES<sup>3</sup>**

#### **PFAS characteristics:**

- Chemically stable
- Thermally stable
- Hydrophobic/lipophobic
- Surfactant properties
- Recalcitrant in environment

 δ +
 δ 

 C F

 • F electronegative, not polarizable

 • C-F bond strength

 • Weak intermolecular interactions









- Fluoropolymer manufacturing (e.g. polytetrafluoroethylene)
- Firefighting foams
- Electroplating, paper coating, stain/ water repellant, textiles, electronics, insecticides/herbicides, adhesives, etc.

### **OVERVIEW**

- Sample preparation
- Sample analysis
- Laboratory QA/QC
- Standard methods
- Commercial labs
- Novel analytical tools
- Summary



### **SAMPLE PREPARATION**



#### Solids extraction:

- Soils, plants, other biological tissue
- No direct analysis of solids
- Use solvent to extract compound off of solid, analyze extract
- Extraction methods vary

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### Solid phase extraction (SPE):

- Load large volume onto cartridge,
- elute off into smaller, cleaner volume
- Concentrates sample
- Not always needed- direct, large volume injection
- Some methods use it, some do not ...

### ANALYSIS: LC-MS/MS OVERVIEW<sup>4</sup>

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



## ANALYSIS: LC-MS/MS OVERVIEW

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





Accepted tool for PFAS analysis

### **ANALYSIS: DATA AND QUANTIFICATION**



Data analysis/quantification:

- Generally, concentrations determined by comparison of compound response to calibration curve
- Exact method of quantifying concentration <u>may differ between</u> <u>labs</u>
- Examples: external calibration, internal standard, isotope dilution

## **QUALITY ASSURANCE/QUALITY CONTROL**

<u>Method blanks</u>: checks for contamination during sample preparation; ~2/30 samples + after elevated samples



<u>Laboratory control</u>: adds known amt. compound to clean matrix; ensures test method is working; ~1/30 samples



<u>Matrix spike</u>: adds known amt. compound to field sample; tests matrix interferences; ~1/30 samples



<u>Duplicate</u>: tests analytical precision; ~1/30 samples



<u>Calibration check</u>: Validates existing calibration; frequency varies e.g. 1/10 samples and at batch end for EPA 537

## **STANDARD METHODS FOR PFAS<sup>5-7</sup>**

Method Name	Method 537	ASTM D7979-16	ASTM D7968-14
	Drinking	Water, influent/effluent	
Matrix	water	wastewater, sludge	Soil
		PFAA, n:3 acid, FTUCA,	PFAA, n:3 acid,
Compound Classes	PFAA, FASAA	FTCA	FTUCA, FTCA
Sample container	Polypropylene	Polypropylene	Polypropylene
Sample volume	250 mL	5 mL	2g, adjust if needed
Extraction	SPE	None	50:50 H₂O: MeOH
Filtering	None	Polypropylene	Polypropylene
Reporting Limits	2.9-14 ng/L	10-300 ng/L	25-750 ng/kg
Holding Times	14 days	28 days	28 days
	5 g/L buffer,		
Preservation	cooled <10°C	Cooled, <6°C	Cooled, <6°C
Quantification	Internal std.	External cal.+ recovery of is	sotope labeled PFAS

- PFAA = perfluoroalkyl acids
- n:3 acid = n:3 saturated acid
- FASAA = perfluoroalkyl sulfonamidoacetic acid
- FTUCA = fluorotelomer unsaturated carboxylic acid
- FTCA = flurotelomer carboxylic acid

## **COMMERCIAL LAB AVAILABILITY**

Laboratory	Method	Matrices	<b>Compound Classes</b>	Aqueous RL*		
		Water, Solid,				
		Air, Tissue,	PFAA, FTS, FASA,			
Axys	Internal	Serum, Urine	FASAA, PAP, FTCA	1-80 ng/L		
	EPA 537 or	Water, Solid,				
Eurofins	direct injection	Tissue, Products	PFAA, FTS, FASAA	2-10 ng/L		
			PFAA, FTS, FASA,			
Test America	Mod EPA 537	Water, Solid	FASAA, FASE	2-100 ng/L		
		Water, Solid,	PFAA, FTS, FASA,			
Vista	Mod EPA 537	Tissue	FASE, FASAA	1-40 ng/L		
* Reporting limit (RL) range encompass all compound classes; RLs for all labs were below EPA HA						
levels for PFOS/PFOA						

- PFAA = perfluoroalkyl acids sulfonamidoethanol FTS = fluorotelomer sulfonates PAP = polyfluoroalkyl phosphate  ${\color{black}\bullet}$ esters
  - FASA = perfluroalkyl sulfonamides ۲
  - FTCA = fluorotelomer carboxylic acid

- FASE = perfluoroalkyl
- FASAA = perfluoroalkyl sulfonamidoacetic acid
- FTUCA = fluorotelomer unsaturated carboxylic acid 18

### **OTHER ANALYTICAL TOOLS: TOP ASSAY<sup>8</sup>**

#### **Total oxidizable precursor assay:**



- <u>Bulk</u> precursor quantification = total amt. precursors present
- Does *not* identify individual precursor compounds present

19

### **OTHER ANALYTICAL TOOLS: PIGE**

#### Particle induced gamma-ray emission (PIGE):



- Spectroscopic measurement of <sup>19</sup>F nuclei
- Measures *total* fluorine- helping to complete PFAS mass balance
- Applicable to soil, products (e.g. paper), geologic formations, etc.

## **SUMMARY**

#### Summary

- Primary tool for detection/quantification: LC-MS/MS
- Sample extraction/preparation techniques vary
- Commercial availability of compound classes/matrices varies
- High potential for background issues  $\rightarrow$  QA/QC!

### In the future

- Diversification of target compounds
- Need for comparison across labs/ methods
- Commercial development of novel techniques (e.g. TOP)



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