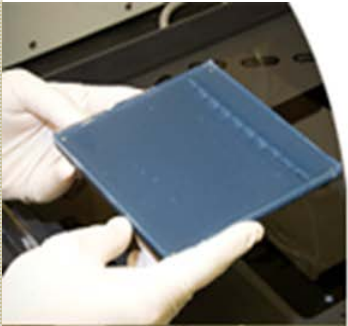




Wisconsin State
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PFAS Analytics at WSLH

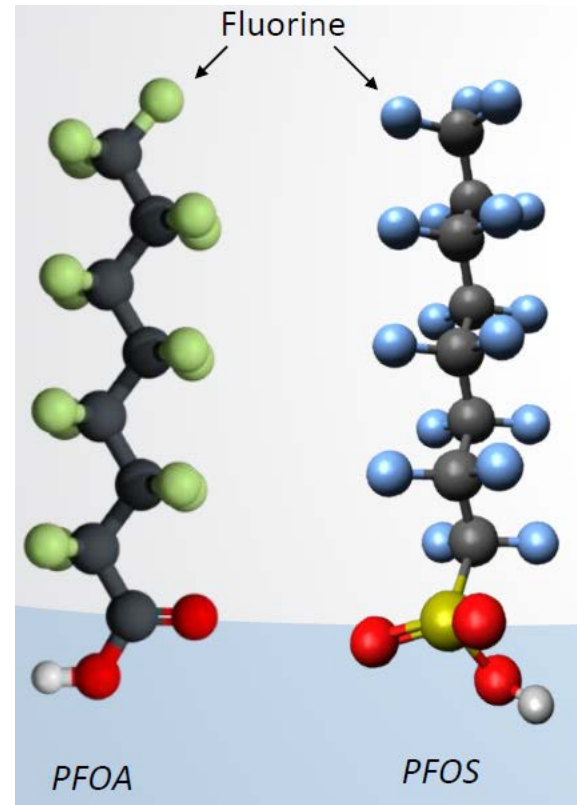
Chen Zhang, PhD, Associate Scientist

04/04/2019



Per-and Polyfluoroalkyl Substances (PFAS)

- **A group of synthetic chemicals**
- **Chains** of carbon (C) atoms surrounded by fluorine (F) atoms
- **Widely used** in industrial processes and in consumer products, surface modifiers, food packaging coatings, and fire-fighting foams
- **Persistent, Bio-accumulative, Toxic**
- **Health advisory** level at 70 ppt for two frequently detected PFAS each:
PFOA (Perfluorooctanoic acid) and
PFOS (Perfluorooctanesulfonic acid)





PFAS Analysis

- Compound lists
- Methods
 - DW: EPA 537.1
 - Others: ISO 21675
 - Others: ASTM D7979
- Technical challenges
- WSLH status



Analyte Lists

- EPA method targets on 18 compounds
- ISO 30 compounds
- ASTM 21 compounds
- Research in WSLH 43 compounds
- Surrogates and internal standards (IS)



EPA 537.1

- Previous EPA 537: 14 compounds
- Current EP537.1 : 18 compounds
- Published
- ADONA, Gen-X and F53-B: trade names for surfactants
- 250 mL DW sample
- Sub-ng/L level analysis
- Test offered

Category	Compound Acronym
Perfluoroalkyl Carboxylic Acid $\text{F}-(\text{CF}_2)_n-\text{C}(=\text{O})\text{OH}$	PFHxA
	PFHpA
	PFOA
	PFNA
	PFDA
	PFUnA
	PFDoA
	PFTrDA
	PFTeDA
	PFBS
Perfluoroalkyl Sulfonic Acid $\text{F}-(\text{CF}_2)_n-\text{SO}_3\text{H}$	PFHxS
	PFOS
Perfluoroalkyl Sulfonamide $\text{F}-(\text{CF}_2)_n-\text{SO}_2\text{NH-R}$	NMeFOSAA
	NEtFOSAA
ADONA	ADONA
Gen-X	HFPO-DA
F-53B	9CI-PF3ONS
F-53B	11CI-PF3OUDS



ISO 21675

Category	Compound Acronym	Methods			Category	Compound Acronym	Methods		
Perfluoroalkyl Carboxylic Acid $\text{F}-(\text{CF}_2)_n-\text{C}(=\text{O})\text{OH}$	PFBA	ASTM	ISO		Perfluorotelomer Acids $\text{F}-(\text{CF}_2)_n-\text{CH}_2-\text{C}(=\text{O})\text{OH}$ $\text{F}-(\text{CF}_2)_n-\text{CH}_2-\text{S}(=\text{O})_2\text{OH}$ $\text{F}-(\text{CF}_2)_n-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	FDEA	ASTM		
	PFPeA	ASTM	ISO			FHEA	ASTM		
	PFHxA	EPA	ASTM	ISO		FOEA	ASTM		
	PFHpA	EPA	ASTM	ISO		FHpPA	ASTM		
	PFOA	EPA	ASTM	ISO		FOUEA	ASTM	ISO	
	PFNA	EPA	ASTM	ISO		FHUEA	ASTM		
	PFDA	EPA	ASTM	ISO		8:2 FTSA	ISO		
	PFUnA	EPA	ASTM	ISO		6:2 FTSA	ISO		
	PFDoA	EPA	ASTM	ISO		4:2 FTSA			
	PFTTrDA	EPA	ASTM	ISO		10:2 FTSA			
	PFTeDA	EPA	ASTM	ISO		8:2 diPAP	ISO		
	PFHxDA			ISO					
	PFOcDA			ISO					
	Perfluoroalkyl Sulfonic Acid $\text{F}-(\text{CF}_2)_n-\text{S}(=\text{O})_2\text{OH}$	PFBS	EPA	ASTM		ISO	Perfluoroalkyl Sulfonamide $\text{F}-(\text{CF}_2)_n-\text{S}(=\text{O})_2\text{NH-R}$	FOSA	ISO
PFPeS					MeFOSA	ISO			
PFHxS		EPA	ASTM	ISO	EtFOSA	ISO			
PFHpS				ISO	NMeFOSAA	EPA		ISO	
PFOS		EPA	ASTM	ISO	NEtFOSAA	EPA		ISO	
PFNS					NMeFOSE				
PFDS				ISO	NEtFOSE				
PFecHS			ASTM						
				ADONA	ADONA	EPA	ISO		
				Gen-X	HFPO-DA	EPA	ISO		
				F-53B	9CI-PF3ONS	EPA	ISO		
				F-53B	11CI-PF3OUdS	EPA			

- All water, 30 compounds
- Unpublished



Research Method at WSLH

Category	Compound Acronym	Methods			Category	Compound Acronym	Methods		
Perfluoroalkyl Carboxylic Acid $\text{F}-(\text{CF}_2)_n-\text{C}(=\text{O})\text{OH}$	PFBA	ASTM	ISO		Perfluorotelomer Acids $\text{F}-(\text{CF}_2)_n-\text{CH}_2-\text{C}(=\text{O})\text{OH}$ $\text{F}-(\text{CF}_2)_n-\text{CH}_2-\text{S}(=\text{O})\text{OH}$ $\text{F}-(\text{CF}_2)_n-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	FDEA	ASTM		
	PFPeA	ASTM	ISO			FHEA	ASTM		
	PFHxA	EPA	ASTM	ISO		FOEA	ASTM		
	PFHpA	EPA	ASTM	ISO		FHpPA	ASTM		
	PFOA	EPA	ASTM	ISO		FOUEA	ASTM	ISO	
	PFNA	EPA	ASTM	ISO		FHUEA	ASTM		
	PFDA	EPA	ASTM	ISO		8:2 FTSA	ISO		
	PFUnA	EPA	ASTM	ISO		6:2 FTSA	ISO		
	PFDoA	EPA	ASTM	ISO		4:2 FTSA			
	PFTTrDA	EPA	ASTM	ISO		10:2 FTSA			
	PFTeDA	EPA	ASTM	ISO		8:2 diPAP	ISO		
	PFHxDA			ISO					
	PFOcDA			ISO					
	Perfluoroalkyl Sulfonic Acid $\text{F}-(\text{CF}_2)_n-\text{S}(=\text{O})_2\text{OH}$	PFBS	EPA	ASTM		ISO	Perfluoroalkyl Sulfonamide $\text{F}-(\text{CF}_2)_n-\text{S}(=\text{O})_2\text{NH-R}$	FOSA	ISO
PFPeS					MeFOSA	ISO			
PFHxS		EPA	ASTM	ISO	EtFOSA	ISO			
PFHpS				ISO	NMeFOSAA	EPA		ISO	
PFOS		EPA	ASTM	ISO	NEtFOSAA	EPA		ISO	
PFNS					NMeFOSE				
PFDS				ISO	NEtFOSE				
PFecHS			ASTM						
					ADONA	ADONA		EPA	ISO
					Gen-X	HFPO-DA		EPA	ISO
				F-53B	9Cl-PF3ONS	EPA	ISO		
				F-53B	11Cl-PF3OUdS	EPA			



Surrogates and Internal Standards

- Sur and IS are used to evaluate system stability/consistency
- Sur/IS are isotope-labeled PFAS compounds
- Sur and IS recovery must be in the range of 70-130%



PFAS Methods

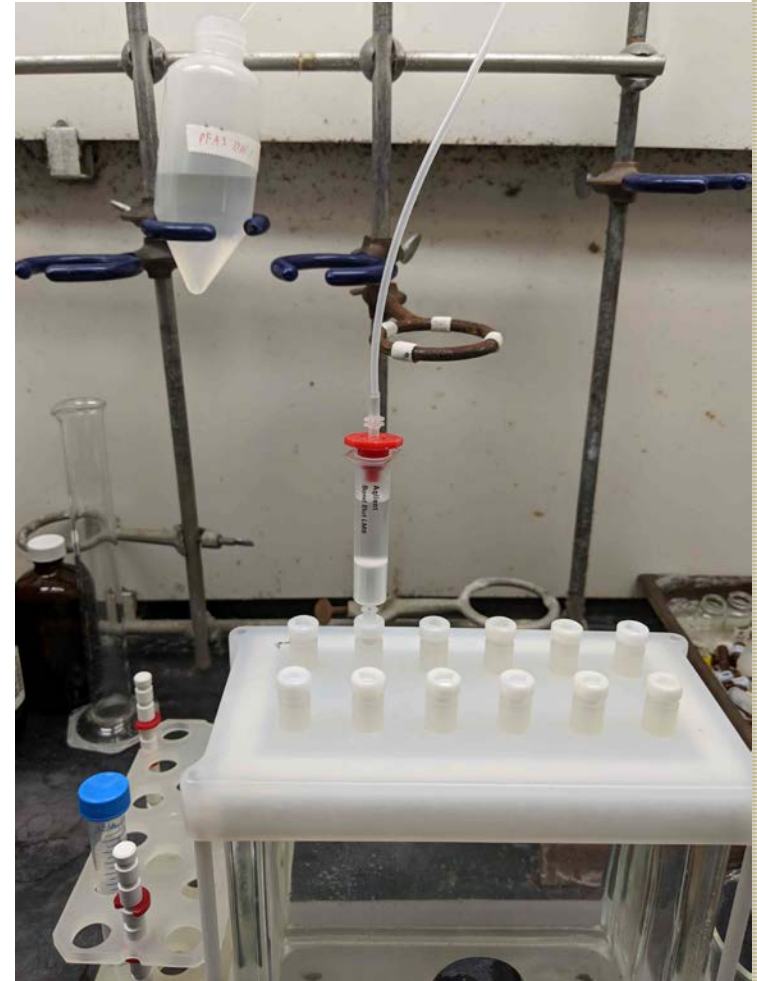
- Solid Phase Extraction (SPE) and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

Method	Target Matrix	Other Matrices	Expected Date Available	Certification Target
EPA 537.1	Drinking Water		Currently Available	NELAC - 5/2019 DNR
ISO 25101	Non-Potable Water	Soil, Tissue, Sediment	Summer 2019	NELAC DNR
ASTM D7979	Wastewater	Sludge	Late 2019	NELAC DNR
NHANES 6304	Serum		Late 2019	CAP/CLIA



Sample Preparation

- Solid Phase Extraction (SPE) can extract and concentrate PFAS in water
- PFAS binds to the SPE column, and comes out when washing with organic solvent
- Packing material: SDVB resin is used as the





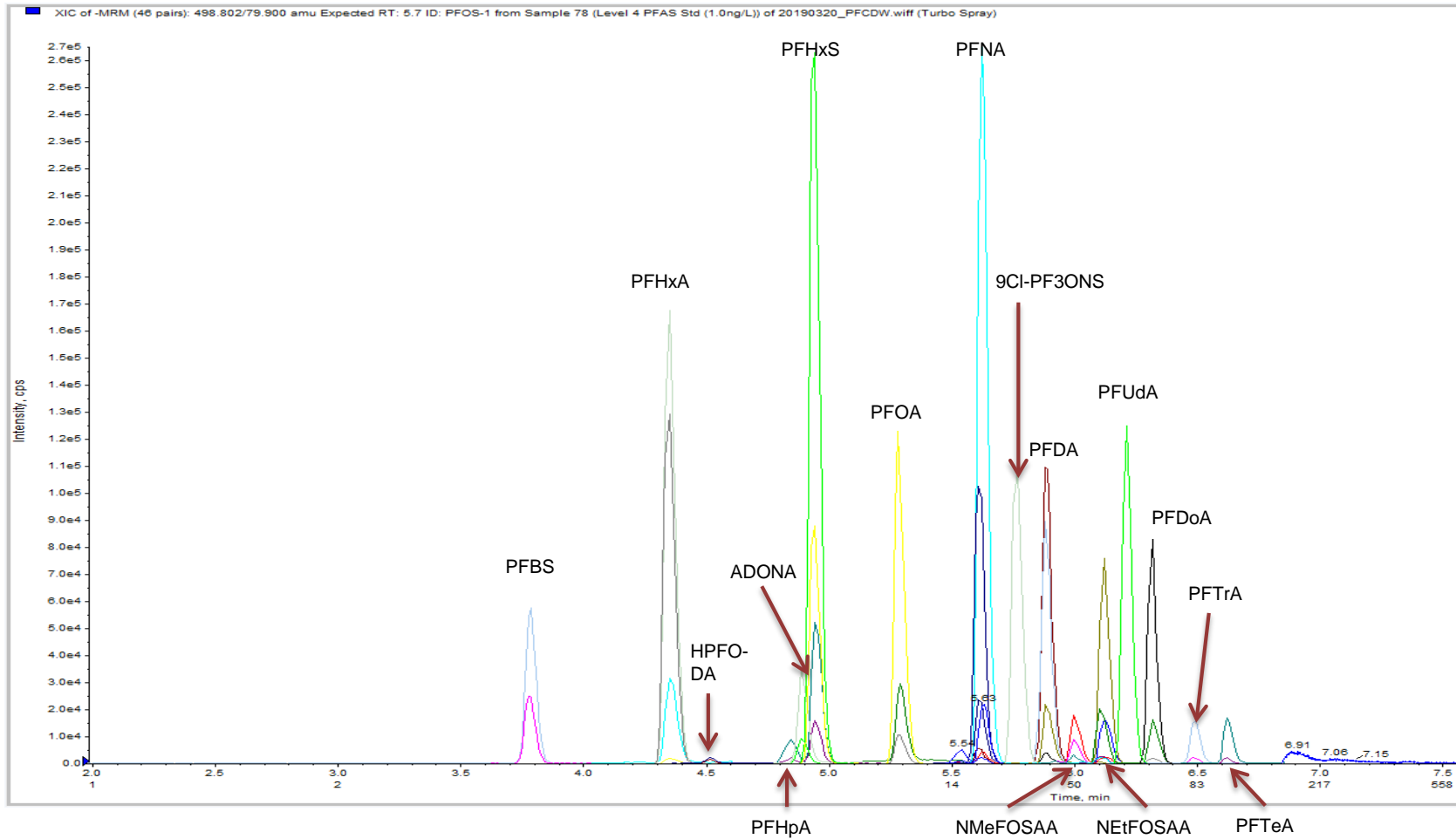
Analytical Instrument

- Waters Aquity Liquid Chromatography (LC)
- Sciex 5500 Mass Spectrometry (MS/MS)
- LC solvent lines they were replaced with PEEK tubing
- PTFE solvent frits were replaced with stainless steel frits to minimize contamination





Example of Chromatography





Detection Limits

Compound Acronym	EPA Detection Limit (ng/L)	WSLH Detection Limit (ng/L)
PFHxA	1.0	0.5
PFHpA	0.7	0.3
PFOA	0.5	0.2
PFNA	0.9	0.2
PFDA	1.6	0.3
PFUnA	1.6	0.4
PFDoA	1.2	0.4
PFTTrDA	0.7	0.3
PFTeDA	1.2	0.3
PFBS	1.8	0.5
PFHxS	1.4	0.1
PFOS	1.1	0.2
NMeFOSAA	2.4	0.3
NEtFOSAA	2.8	0.2
ADONA	0.9	0.3
HFPO-DA	1.9	0.5
9Cl-PF3ONS	1.4	0.2
11Cl-PF3OUdS	1.5	0.3



Technical Challenges

- Availability of commercial standards
- Background contaminations
- Short Chain PFAS
 - High mobility
 - Low recovery
- Decomposition of PFAS
- Linear and branched isomers



WSLH Status

- Drinking Water - currently offer analysis, seeking NELAC accreditation seeking DNR accreditation when available
- Surface Water and Tissue - will seek NELAC accreditation in the fall, seeking DNR accreditation when available
- Waste - will seek NELAC accreditation in the fall, seeking DNR accreditation when available
- Sediment and Serum - will seek NELAC accreditation in the fall, will seek DNR accreditation when available



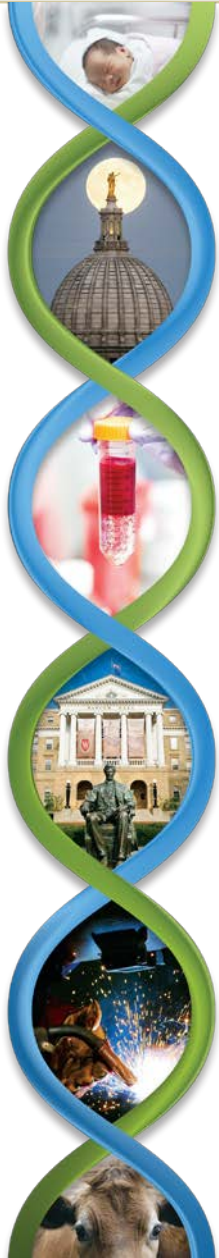
Lets work on it together!

Environmental Monitoring: Erin Mani

Human Biomonitoring: Noel Stanton

Research: Drs. Chen Zhang & Martin Shafer

EHD Division: David Webb





Technical Challenges

- Linear and branched isomers
- Will report total isomers

