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The Analysis of Per and Polyfluorinated Alkyl Substances (PFAS) Challenges and Best Practices

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PFAS - Outline

Introduction to PFASs

What are PFASs? Chemistry Sources, Timeline Exposure, Toxicity and Risk Regulatory Review

Analytical Best Practices

Analytical Methods review Why so much variability? How do we reduce variability? New In Line SPE Capability Future Concerns – TOP Assay Alternative chemicals – GenX Capabilities and Questions?









Briefly - What are PFASs?



Class of synthetic compounds containing thousands of chemicals formed from **carbon** chains with **fluorine** attached to these chains.



The **C-F** bond is the shortest and the strongest bond in nature.



PFOS and PFOA are fully fluorinated and the most common perfluorinated chemicals (PFCs).



Persistent and resistant to degradation Found in soil, air and groundwater..



Chemical Structure Why is it Important?



 $\mathbf{F} = \begin{bmatrix} \mathbf{F} & \mathbf{O} \\ \mathbf{I} & \mathbf{II} \\ \mathbf{F} & \mathbf{C} \\ \mathbf{F} \\ \mathbf{F} \\ \mathbf{n} \end{bmatrix}$

Perfluoroalkyl

Carboxylate



Perfluoroalkyl Sulfonate



Perfluoroalkyl Sulfonamido Amines



Fluorotelomer Sulfonates



Perfluoroalkyl Sulfonamido acetic acid amine

Primary Sources – Point or Direct

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- Released in large quantities from primary manufacturing facilities
- Secondary Manufacturing incorporation of PFC raw materials into industrial and consumer products
- The use of AFFFs to fight fires is a direct pathway to the environment – (Connection to DoD)





Secondary Sources -Indirect



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- Commercial and consumer products have a finite lifetime.
 - Dispose to landfillsWWTP
 - Air emissions
- Trace chemistry transformation mostly degradation byproducts (TOP Assay)





Exposure, Toxicity and Risk







- Major source of non-occupational exposure to humans is from food, water and air.
- Human and wildlife exposure can continue even though the chemicals are no longer in use, due to persistence.
- PFOS and PFOA have half-lives in humans ranging from 2 to 9 years, depending on the study.
- PFOA associated with liver, pancreatic, testicular, and mammary gland tumors in laboratory animals. PFOS causes liver and thyroid cancer in rats
- PFOA and PFOS are likely carcinogenic. Pathways are being studied.

Regulatory Challenges and New Developments



- Lack of regulatory guidance for most matrices and most PFAS compounds
- Wide variety of detection limits and analyte lists
- Lack of published methods
- What is Method 537M?
- What are the ASTM Methods?
- What is the ISO Method 25101?



PFAS – Regulatory Timeline



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When	Who	What Happened
1980s	EU	Groundwater directive to prevent discharge of PFOS
2002	US EPA	Initiated voluntary phase out of PFOS
2002	3M	Discontinued making PFOS (7 other makers complied)
2006	US EPA	Announced 2010 (95%)/15(100%) PFOA Stewardship Program
2008	Canada	Regulated and prohibited PFOS imports to Canada
2009	UN	Stockholm Convention - adds PFOS to Annex B
2010	US EPA	2010 PFOA Stewardship program - must reduce PFOA use by 95%
2015	US EPA	Target elimination of PFOA by Dec. 31,2015.
May 2016	US EPA	PFOS and PFOA life time health limits reduced to 70 ppt each or the total if both are present.
Sept 2016	NJ	DWQI proposed PFOA drinking water MCL of 14 ppt

What started happening in 2016?





/hat's U	p in New	Jersey?	(04/2018)	
State	PFOA ppt	PFOS ppt	Comments	Source
Alabama	70	70		EPA
Alaska	400	400		ADEC
California	Prop 65	Prop 65	Proposed	OEHHA
Connecticut	70	70	PFNA, PFHxA, PFPeA, PFHpA	DPH
Colorado	70	70	PFHpA	
Delaware	70	70		DNR
Georgia	70	70	Proposed	DPH
Illinois	400	200		
lowa	70	70		DNR
Kentucky	400	200		NKWD
Maine	70	70		ME DEP
Maryland	70	70		
Michigan	70	70	HB 5373 proposed 5	MI DEQ
Minnesota	35	27		MDH
New Hampshire	70	70		DES
New Jersey*	14	13		NJDEP
New York	70	70		EPA
North Carolina	2000	NA		DENR
Ohio	400	200		EPA
Oregon	24000	300000	PFHpA, PFNA, PFOSA	
Pennsylvania	70 (May lower to 6)	70		PA DEP
Rhode Island	70	70		
Texas	290	560	PCLs for 16 PFCs	CEQ
Vermont	20	20		VT DOH
West Virginia	400	200		

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Why are PFAS an Analytical Challenge?



- Globally distributed
- Present at low concentrations and high
- Contamination and analyte loss at all stages of collection and analysis
- Lack of authentic standards
- Unusual physical and chemical properties
- Lack of consensus "best" method for non-DW





How can we mitigate analytical variability?



- Apply tandem mass spectrometry technology
- Implement an isotope dilution quantitation scheme
- Compensate for losses with matrix recovery correction
- Share our knowledge
- Invest resources in multilab validation



Show Branched and Linear Error in PFOS and PFOA



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Study Results - NMI PT



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 24 labs submitted results – 9 Passed
 TestAmerica passed water, soil and fish tissue samples



Sample	Analyte	Sac Lab	Expected
Water A	PFOA	7.91	7.90
	PFOS	3.23	3.00
Water B	PFOA	9.01	10.8
	PFOS	6.81	6.50
Soil A	PFOA	7.00	5.83
	PFOS	290	262
Soil B	PFOA	14.2	12.0
	PFOS	23.5	22.0
Fish A	PFOA	ND	ND
∧_	PFOS	19.9	20.6
Fish B	PFOA	51.4	50.5
	PFOS	49.2	53.7

Sample Collection and Holding Time Studies



"Confusion and clutter are the failure of design, not the attributes of information."



- Samples should be collected in HDPE bottles fitted with unlined (no Teflon) polyethylene screw caps.
- In addition, the sampler should avoid contact with fluoropolymers, aluminum foil, and food wrappers.
- Samples should not be field filtered.
- Samples must be shipped chilled
- Limited HT study data

Managing Artifacts



- The field crew personnel hygiene, clothing, food products, sunscreens and insect repellants
- Sampling equipment avoid fluoropolymer bailers, pump bladders, tubing, valves etc.
- Sample collection wash hands, wear nitrile gloves, do not filter samples, add field QC samples routinely
- Avoid detergents
- > Avoid food or drink on-site
- Limit visitors during sample collection



Managing Loss/Adsorption

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- Many PFAS are surface active, which cause them to stratify, adsorb to surfaces
- Extraction type whole bottle or subsample play a more significant role then material type
- PFAS can adsorb to the filtration equipment. PFAS in the dissolved phase can also adsorb to the filter material
- Unless the samples are analyzed immediately adsorption to glass vials may occur





What are Precursors and Why Do We Care?

- Thousands of precursors used in industrial and consumer products
- Some biotransform to make PFAAs
- Some are fluorotelomers
- Most are ionic, either positive, negative or both
- Fate and transport complex process



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What is the TOP Assay?

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A new PFAS sample preparation technique



How Does it Work in the Environment?





TOP – How Does it Work in the Laboratory?



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PFCA Pattern – Me-FOSA Precursor



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PFCA Pattern – 8:2 FTS



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What Do the Results Mean?

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TOP Assay measures total PFCA

	Precursor	Pre - TOP	Post - TOP	% Oxidation			
FOSA		32.68	ND	100%			
	MeFOSAA	19.38	ND	100%			
	EtFOSAA	18.83	ND	100%			
	6:2 FTS	31.69	ND	100%			
	8:2 FTS	26.37	ND	100%			
	PFCA	Pre – TOP	Post - TOP	Total			
	PFBA	24.94	27.16	109%			
	PFPeA	23.38	28.55	122%			
	PFHxA	26.49	34.87	132%			
	PFHpA	23.10	25.14	109%			
	Y PFOA	23.72	58.71	248%			
		Total 122	Total 174				



What Conclusions Can We Draw? TestAmerica



A lesson in jumping to CONCLUSIONS



PFAA precursors are present in environmental samples and many AFFF products

- Implies treatment strategies must remove precursors and end points
- Presence impacts our treatment strategies and our risk assessments
 - Potentially increases future risk as precursors are biotransformed
- Presence impacts our decisions for AFFF formulations
 - AFFF manufacturers should reduce the content of PFOA etc.

Fluorinated Replacement Chemicals

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- Since 2000, on-going industrial transition to replace LC PFCAs, PFSAs and precursors
- Many alternative chemicals are in use
 below regulatory radar
- Unclear whether they are safe for humans or the environment
- DuPont developed patented GenX technology - enables them to make fluoropolymers without PFOA
- GenX is not a chemical it is a process





Future Concerns



- We need a consensus "best" method.
- Analyte lists are growing for discrete methods, may lead to forensics.
- LC PFASs are being replaced by SC PFASs and little is know about the toxicity
- On-going data variability must be improved
- We need an effective field screening technique.







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Thank you for attending

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Questions



