



**The Analysis of
Polyfluorinated Alkyl Substances (PFAS)
including PFOS and PFOA**

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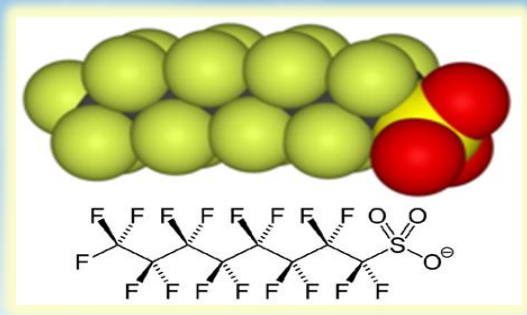
What Are Emerging Contaminants?

- Pose a real or perceived threat to human health or to the environment
- Not currently regulated or have regulations pending
- New source has been identified or a new exposure pathway to humans has been discovered
- New detection method or a new water treatment technology has been developed

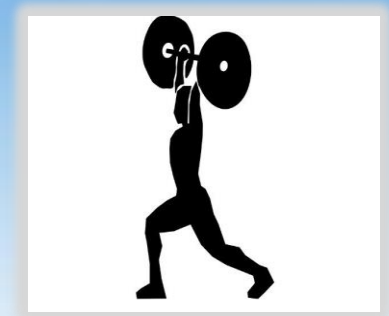


What are PFASs?

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..



Nomenclature

PFAS – Broad term – completely and incompletely fluorinated

PFC – Subset of PFAS completely fluorinated compounds. PFOS and PFOA are PFCs (no hydrogen atoms)

PFAAs – Perfluoroalkyl acids – PFOA and PFOS

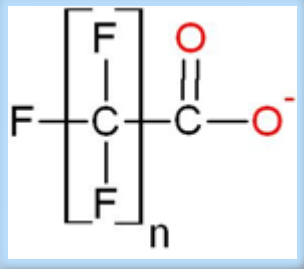
AFFF – Aqueous Film Forming Foam

Fluorochemicals and telomers

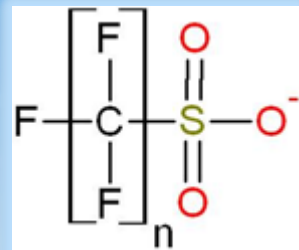


Chemical Structure

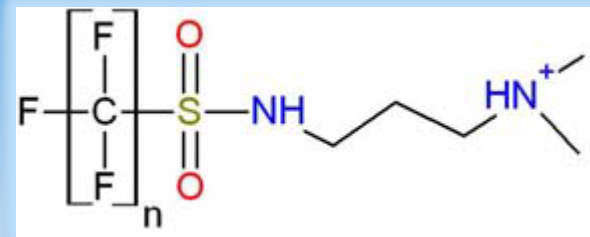
Why is it Important?



**Perfluoroalkyl
Carboxylate**



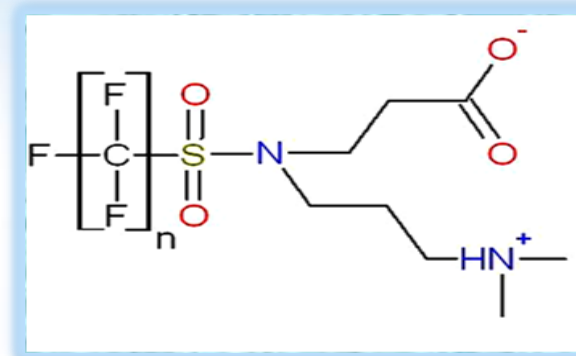
Perfluoroalkyl Sulfonate



**Perfluoroalkyl
Sulfonamido Amines**



Fluorotelomer Sulfonates



**Perfluoroalkyl
Sulfonamido acetic acid
amine**

Primary Sources – Point or Direct

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



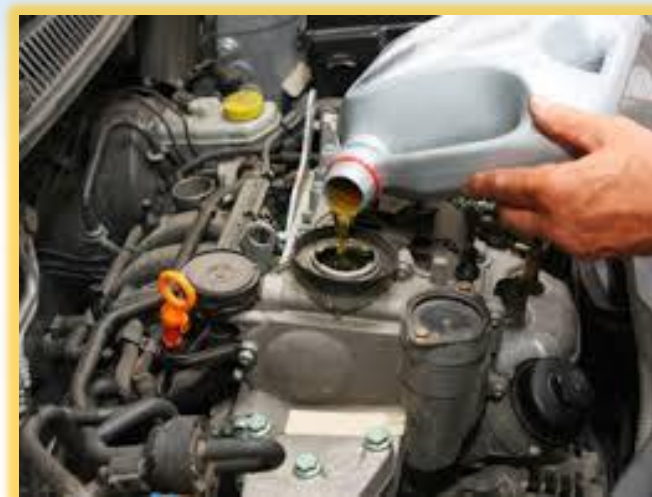
Secondary Sources - Indirect

- Commercial and consumer products have a finite lifetime.
 - Dispose to landfills
 - WWTP
 - Air emissions



PFAS in the Auto Industry

- Low friction bearings and seals
- Used in lubricants, engine oil, transmission and brake fluid
- Applied to upholsteries for water and oil/dirt resistance



Exposure – Occupational and Non - Occupational



- Major source of non-occupational exposure to humans is from food and air
- Fish consumption is a significant pathway of human exposure.
- Human and wildlife exposure can continue even though the chemicals are no longer in use, due to persistence.



Out There



The life of a lab rat

- PFOS and PFOA have half-lives in humans ranging from 2 to 9 years, depending on the study.
- Readily absorbed after oral exposure and accumulate primarily in the serum, kidney and liver.
- PFOA causes liver, pancreatic, testicular, and mammary gland tumors in laboratory animals. PFOS causes liver and thyroid cancer in rats

PFAS – Regulatory Timeline

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%
2013	Canada	Use of AFFF with PFOS > 0.5ppm are prohibited
2013	DuPont	Makes a statement that it does not make, buy or use PFOS
2015	US EPA	Must 100% eliminate the use of PFOA by December 31,2015
May 2016	US EPA	PFOS and PFOA health limits reduced to 70 ppt each or the total if both are present.

Input from Dr. Jimmy Seow Dept. of Environment and Conservation Western Australia.



State Advisory Levels – NEW LEVELS from EPA = 70 ppt

State	PFOA ppb	PFOS ppb	Comments	Source	Year
Alabama	0.4	0.2		EPA	2009
Alaska	3.1	1.3		ADEC	2013
California	0.4	0.2		OEHHA	2010
Georgia	0.4	0.2		EPD	2009
Illinois	0.4	0.2			
Maine	0.06	0.1		ME DEP	2014
Michigan	0.042	0.011		MI DEQ	2013
Minnesota	0.3	0.3	0.7 PFBA	MDH	2009
New Jersey*	0.014	0.014	0.02 PFNA	NJDEP	2016
North Carolina	1	NA		NCSAB	2009
Ohio	0.4	0.2		EPA	2009
Oregon	24	300	PFHpA, PFNA, PFOSA		
Pennsylvania	TBD	TBD		PA DEP	2015
Texas	0.1	0.2	PCLs for 16 PFCs		2013
Vermont	0.02	TBD		VT DOH	2016
Washington	NA	TBD	Listed PFOS as PBT		
West Virginia	0.4	0.2		EPA	2009

Sample Collection Guidance

- Aqueous samples
250 ml High Density Poly Ethylene (HDPE) bottles
unlined (no Teflon) polyethylene screw caps.
- Sampler avoid contact with:
fluoropolymers, aluminum foil, blue ice, pre-wrapped foods or snacks.
- Samples shipped at $<10^{\circ}\text{C}$.
Trizma pres. for drinking water
- Advisory holding time
14 days collection to extraction;
40 days extraction to analysis.

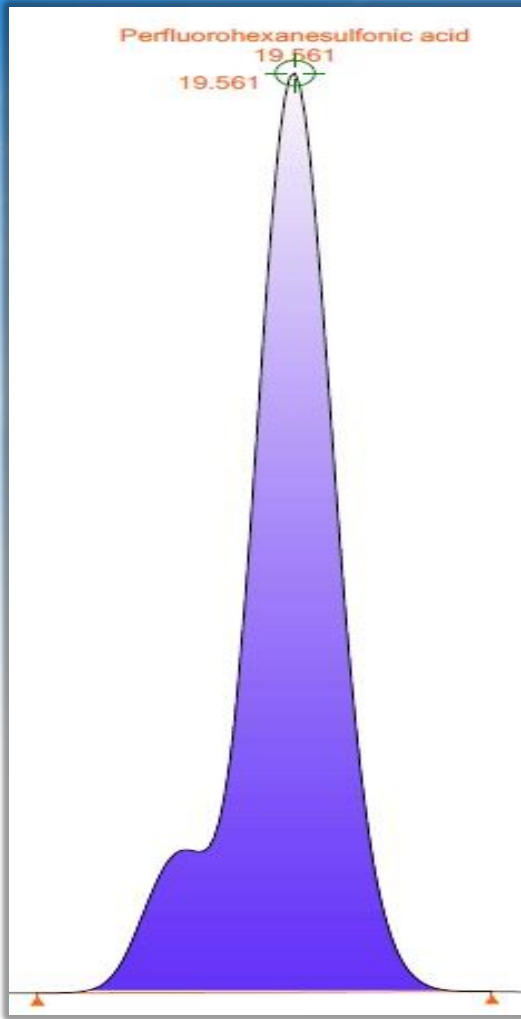


LCMSMS Analytical Methodologies



- Manufacturer's methods were adopted by environmental industry (8321)
- EPA expanded manufacturer's method for drinking water – Method 537
- Laboratories expanded Method 537 to other matrices – Method 537 Mod for ease of use
- ASTM has published D7968-14 and D7979-15 but neither has been validated

Analytical challenges 537m



High cost of analysis, due to expertise, instrumentation, and standards cost

Contamination due to filtration/ sample concentration; PTFE in seals, o-rings, tubing, septa

Limited number of authentic standards for PFAS other than carboxylates, sulfonates, and telomer sulfonates



TestAmerica Capabilities



- TestAmerica Sacramento is EPA approved for Method 537 in drinking water
- Sacramento and Denver both are NELAP and DoD ELAP approved by in-house SOPs (Method 8321 and Modified 537)
- 7 LCMSMS instruments capable of PFAS testing
- > 20 years of experience on a wide variety of matrices including sediments, tissues and consumer products
- Technical expertise required for complex programs

Capabilities for Complex Matrices



Future Concerns

- LC PFASs are being replaced by SC PFASs and little is known about the toxicity
- Legacy methodologies are still in use
- Commercial lab expansions without analytical delineation
- PT samples are not commercially available
- Difficult to obtain true second source analytical standards



Questions???

Thank you for your time.

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