PFAS REPLACEMENT COMPOUNDS

"The Next Generation"

OUTLINE

- PFAS – A quick review
- PFAS Replacement Compounds
- ”Why do we (…or should we) care?”
- Sampling and Analysis
- Regulatory Standards

PFAS – GENERAL CONCEPTS

General

- Anthropogenic (“man made”)
- Encompasses >3,000 substances that contain a carbon and fluorine backbone
- Diverse range of compounds with a variety of chain lengths and end groups
- Ubiquitous (“they’re everywhere”)
- Compounds receiving most attention:
  - *Perfluorooctane sulfonic Acid (PFOS)*
  - *Perfluorooctanoic Acid (PFOA)*
- Next most studied:
  - *Perflurohexanesulfonic Acid (PFHxS)*
  - *Perfluorononanoic Acid (PFNA)*
  - *Perfluorobutanesulfonic Acid (PFBS)*
- Up and comers:
  - *Shorter chain PFAS, i.e., <C4*
  - *PFAS replacement compounds (e.g. GenX*)

Chemical/Physical Properties

- Very stable and persistent – do not degrade
  - *C-F bonds are very strong*
  - *Good stability under heat and chemical stress*
- Low volatility
- Soluble in water
- Readily bind (sorb) to variety of materials (hard to predict partitioning)
- Bioaccumulation
- Some PFAS (e.g. polyfluorinated alkyl substances) can degrade/tranform to other PFAS

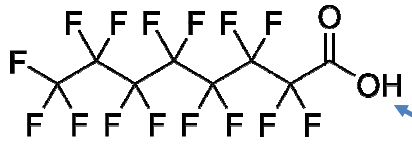
Conventions

- PFAS is an “umbrella term” that includes poly- and perfluorinated compounds
- PFAS is a plural noun
- The trend is to report the sulfonates as the acid, e.g.
  - *PFOS: Perfluorooctanesulfonic acid rather than Perfluorooctane Sulfonate*
- Perfluorinated
  - *All carbons, with the exception of a terminal carbon are attached to fluorine*
  - *Typically saturated*
- Polyfluorinated
  - *Not all carbons are attached to fluorine*
  - *Often represented by “precursor “ compounds*

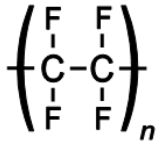
BUREAU VERITAS

PFAS – CURRENT TARGET COMPOUNDS

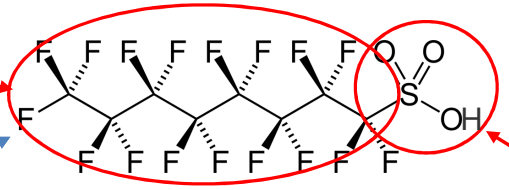
PFAS – End Compounds



Perfluorooctanoic Acid
(PFOA)
"Teflon®"



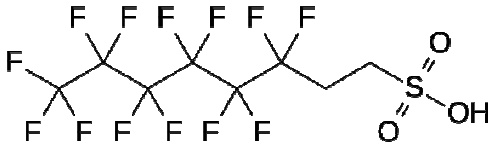
Hydrophobic



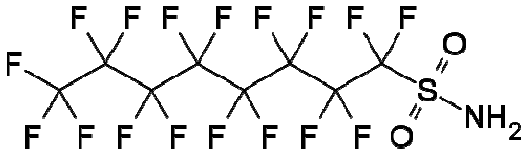
Hydrophilic

Perfluorooctanesulfonic Acid
(PFOS)
"Scotchguard®"

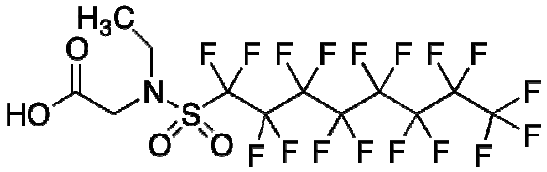
PFAS - Precursors



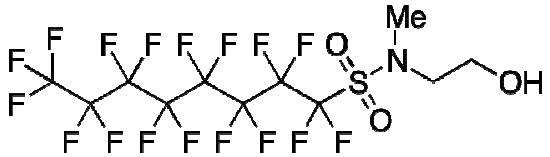
6:2 Fluorotelomersulfonic Acid
(6:2 FTS)



Perfluorooctanesulfonamide
(PFOSA)



N-Ethylperfluorooctanesulfonamidoacetic Acid
(EtFOSAA)



N-Methylperfluorooctanesulfonamidoethanol
(MeFOSE)

WHY THE NEED FOR PFAS REPLACEMENTS

2010/2015 PFOA Stewardship Program:

- Eight (8) global suppliers agree to:
  - 95% reduction in PFOA (and related precursor) levels in emissions relative to 2000 levels
  - Total elimination of PFOA (and related precursor) levels in emissions

USEPA Significant New Use Rules (SNURs)

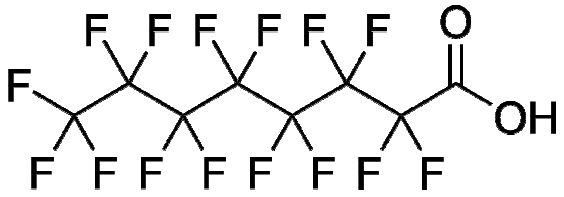
- September 30, 2013 – relating to perfluoroalkyl sulphonic acids (e.g. PFOS)
- January 21, 2015 - related to perfluoroalkyl carboxylic acids (e.g. PFOA)

Environment Canada Risk Management

- Risk management strategies seek to have environmental PFOS concentrations as low as possible, prevent re-introduction to market, and address remaining uses (restrictions, exemptions, BMP etc.)

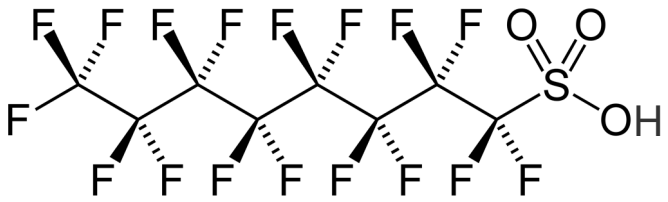
BUREAU VERITAS

LONG CHAIN PFAS TO SHORT CHAIN PFAS

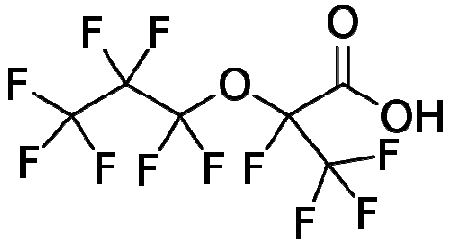


PFOA

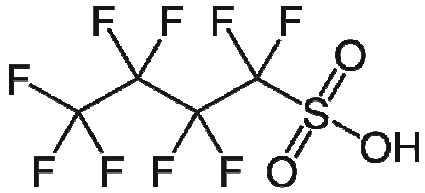
≥C7



PFOS

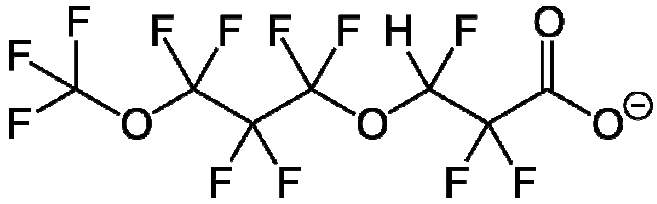


"GenX"



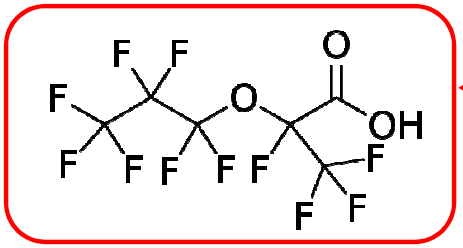
PFBS

≤C6



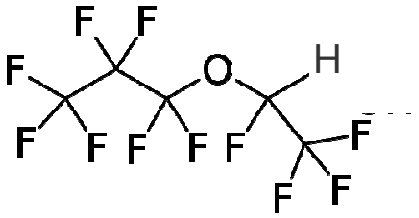
ADONA

PFAS REPLACEMENT COMPOUNDS

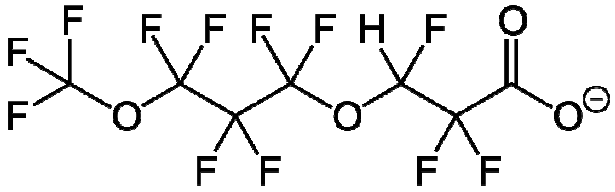


2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid
(FRD-902)

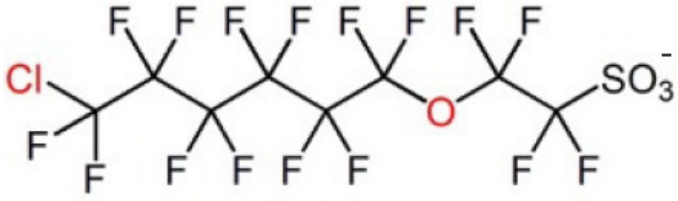
GenX



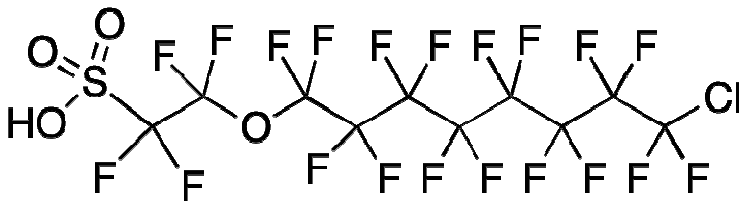
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether
(E1)



Dodecafluoro-3H-4,8-dioxanoate
(ADONA)



9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate
(F53B major)



11-Chlororeicosafluoro-3-oxaundecane-1-sulfonic acid
(F53B minor)

GenX (Chemours) and ADONA (3M)

- Processing aids in the polymerization of polytetrafluoroethylene (PTFE) among other fluoropolymers
  (In English: *Trade names for man-made chemicals used in manufacturing non-stick coatings and for other purposes*)
- Potential by-products produced during other manufacturing processes, suggesting their presence in the environment before being used as a PFAS replacements
- GenX is particularly notorious because of on-going release into the Cape Fear River by the Chemours facility in Fayetteville, NC
- GenX and ADONA are probably more likely to be detected in water where fluoropolymers are manufactured
- For this reason, these two compounds are less likely to be detected where chemicals containing PFAS are actually used.

F53B

- F-53B is a trade name for a 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES)
- Used widely as an alternative to perfluorooctanesulfonic acid (PFOS) in the electroplating industry resulting in a high detection frequency, comparable to PFOS
- Wastewater from chrome plating industry contains high concentrations of perfluorooctane sulfonic acid (PFOS) and F53B
- F53B has been used in China by several producers as a replacement PFAS since the late 1970s as wetting agents and mist-suppressing agents in decorative plating and non-decorative hard plating
- Suggested that it is “uniquely” used in China.

WHY SHOULD WE CARE?

- Marketed by manufacturers that lower molecular weight PFAS (i.e. replacements) are less persistent, bioaccumulative and exert a decreased toxic effect
- Emerging evidence appears to suggest…perhaps *"not so much"*
  - *PFAS replacements are persistent*
  - *Tend to bioaccumulate in a similar fashion to the higher molecular weight compounds they've replaced*
  - *While toxicity information is limited, it is being suggested[1,2] that GenX and replacement compounds are equally if not more toxic than PFOA, the compound they are replacing*
- From a practical perspective:
  - *Lower molecular weight replacements are more soluble*
  - *Harder to remove lower molecular weight PFAS from water*
  - *Increased solubility = increased mobility (risk vs. hazard)*

[1] **Sheng et. al., *Arch. Toxicol.* (2017) 92 (1), pp 359-369**
[2] **Gomis et. al., *Environ. Int.* (2018) 113, pp 1-9**

BUREAU VERITAS

FIELD SAMPLING

- Strict/rigorous sampling protocols
- Sampling and field quality assurance plans must address the potential for cross contamination and/or false positives
- Adsorption of PFAS onto surfaces can be rapid resulting in potential low bias in data
  - *Surface-to-Volume ratio is important*
  - *Minimize transfers of samples*
- Water for blanks MUST be PFAS free
- Close relationship with the laboratory
- Have a solid and defensible field QA program

EQUIPMENT DECONTAMINATION

- Decontaminate field sampling equipment between uses if you are not using PFAS-free disposable equipment
- If using specific equipment for decontamination (e.g. pressure washers), confirm that equipment is free of PFAS-bearing parts
- Scrubbed sampling equipment should undergo a “final” rinse with laboratory certified PFAS-free water
- Blank samples should be collected from rinse water to confirm that it is PFAS-free

ANALYTICAL METHOD SUMMARY

- Water methods based on USEPA 537/533
  - *SPE weak anion exchange extraction*
  - *LC/MS/MS*
- Soil methods based on ASTM D7968-17
  - *Solvent extraction/SPE weak anion exchange extraction*
  - *LC/MS/MS*
- Industry accepted best practices:
  - *LC/MS/MS*
  - *Isotope Dilution required for quantitation*
  - *No Blank correction*

REPORTING

Compound	Water				Soil	
	RDL[(1)] (µg/L)	MDL (µg/L)	RDL[(1)] (low) (µg/L)	MDL (low) (µg/L)	RDL[(1)] (µg/kg)	MDL (µg/kg)
Perfluorobutanesulfonic Acid	0.02	0.0051	0.002	0.00037	1.0	0.14
Dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	0.04	0.0048	0.004	0.00094	2.0	0.20
2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid (HFPO-DA or “GenX”)	0.04	0.0045	0.004	0.0015	2.0	0.33
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate (F53B major)	0.04	0.0093	0.004	0.00049	2.0	0.19
11-Chlororeicosafluoro-3-oxaundecane-1-sulfonate (F53B minor)	0.04	0.0053	0.004	0.00080	2.0	0.20

BUREAU VERITAS

REGULATORY LIMITS[1] (WATER)

Jurisdiction		PFOA (µg/L)	PFOS (µg/L)	PFBA (µg/L)	PFBS (µg/L)	PFHxS (µg/L)	PFPeA (µg/L)	PFHxA (µg/L)	PFHpA (µg/L)	PFNA (µg/L)	GenX (µg/L)
Drinking Water											
Health Canada[(2)]	Screening Value	**0.2**	**0.6**	**30**	**15**	**0.6**	**0.2**	**0.2**	**0.2**	**0.02**	N/V
British Columbia	BC CSR	**0.2**	**0.3**	N/V	**80**	N/V	N/V	N/V	N/V	N/V	N/V
U.S.A - EPA	Health Advisory	**0.07**	**0.07**	N/V	N/V	N/V	N/V	N/V	N/V	N/V	N/V
U.S.A. – Minnesota	HBV	**0.035**	**0.027**	**7**	**3**	**0.027**	N/V	N/V	N/V	N/V	N/V
U.S.A. – New Jersey	MCL	**0.014**	**0.013**	N/V	N/V	N/V	N/V	N/V	N/V	**0.013**	N/V
U.S.A. – N. Carolina	IMAC	**2**	N/V	N/V	N/V	N/V	N/V	N/V	N/V	N/V	**0.14**
Europe – UK	HBV	**10**	**0.3**	N/V	N/V	N/V	N/V	N/V	N/V	N/V	N/V
Australia	HBV	**0.56**	**0.07**	N/V	N/V	0.07	N/V	N/V	N/V	N/V	N/V

[(1)] Sources: ITRC PFAS Regulations, Guidance and Advisories Fact Sheet (June 2018)

[(2)] Protection of Human Health - $[PFOS]/SV_{PFOS} + [PFOA]/SV_{PFOA} \leq 1$

[(3)] Highlighted values have not yet been promulgated

BUREAU VERITAS

SUMMARY

- PFAS Replacements GenX and ADONA are a growing concern in North America
- F53B…depends on how extensively it was used in the North American marketplace (suggestion is that F53B used uniquely in Chinese electroplating facilities)
- US DoD is focusing attention on all three: GenX, ADONA and F53B
- Good PFAS sampling practices are a “must”
  - *Attention to sources of contamination*
  - *PFAS-free water*
  - *Solid field quality assurance program*
- The laboratory analyses are becoming increasingly complex as new compounds are being added to the lists, requiring:
  - *Synthesis of labelled analogues (standards)*
  - *Multiple injections onto the LC/MS/MS per test*
- What were once “provisional guidance values” are becoming “regulated standards”

BUREAU VERITAS

CONTACTS

Stephanie Pollen, BSc
Project Manager
Ultra Trace Analysis
spollen@maxxam.ca
(905) 817-5830

Adam Robinson
Supervisor
LC and LC/MS/MS Methods
arobinson@maxxam.ca
(905) 817-5700 ext. 4057

Terry Obal, PhD, CChem
Chief Science Advisor
tobal@maxxam.ca
(905) 288-2174

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