PFAS Replacement Compounds: "The Next Generation"

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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

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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 sulfonate (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

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When you think PFAS, think…

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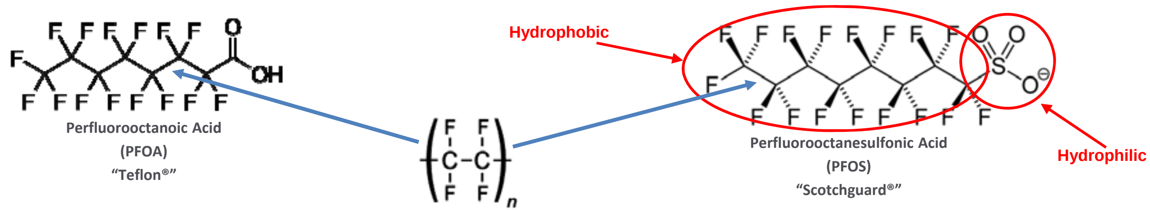
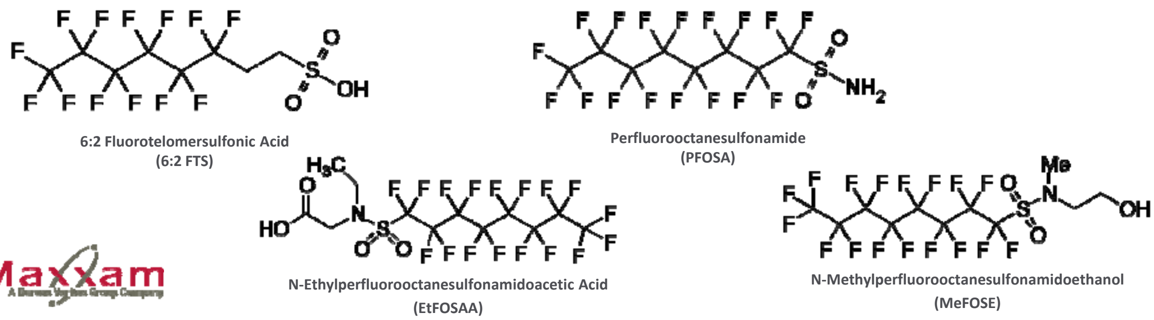
PFAS – Current Target Compounds

PFAS – End Compounds



PFAS - Precursors



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 sulphonates
- January 21, 2015 - related to perfluoroalkyl carboxylates (PFCAs)

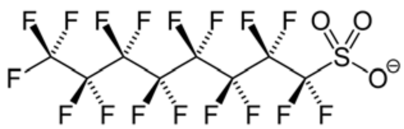
Environment Canada Risk Management

- 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.)

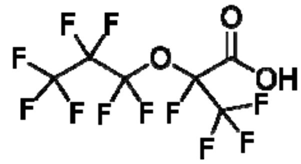
Long Chain PFAS to Short Chain PFAS

≥C7

PFOA

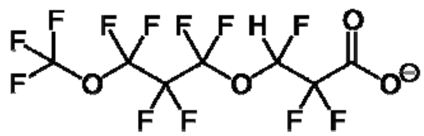


PFOS



"GenX"

PFBS



ADONA

≤C6

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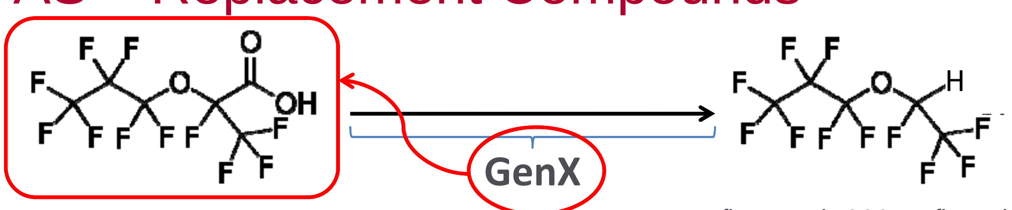
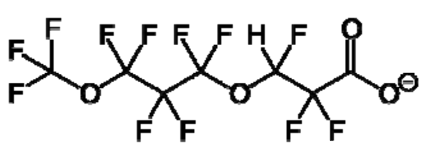
PFAS – Replacement Compounds

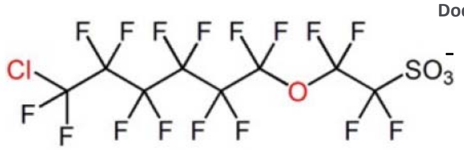


2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid
(FRD-902)

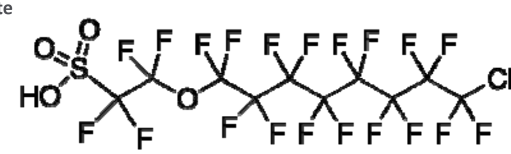
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether
(E1)



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



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



11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic Acid
(F53B minor)

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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.

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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 perfluorooctanesulfonate (PFOS) in the electroplating industry resulting in a high detection frequency, comparable to PFOS
- Wastewater from chrome plating industry contains high concentrations of perfluorooctane sulfonate (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.

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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 (GenX and others have half lives of at least 6 months)
  - Tend to bioaccumulate in a similar fashion to the higher molecular weight compounds they’ve replaced
  - Toxicity is still an unknown
- 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)

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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

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On-site Materials - Common Sense

- Through experience, many environmental stakeholders are adopting a common sense, yet still precautionary approach to the collection of samples for PFAS
- Three main categories of materials associated with sample collection:
  - Prohibited materials
  - Acceptable Materials
  - Materials requiring screening




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Sampling Materials

Prohibited

- Plastic clipboards, binders, spiral
- Waterproof field books
- Water and dirt resistant leather gloves
- Recycled paper
- Markers, fine point Sharpies®
- Plastic bags
- Decon 90
- Chemical or "Blue" ice

Acceptable

- Aluminum field clipboards
- Loose paper
- Powderless nitrile gloves
- Cotton cloth or untreated paper towels
- Ball point pens, pencils
- Polyethylene bags (e.g. Ziplock®)
- Alconox®, Liquinox® or Citrinox®
- Regular ice (sealed polyethylene bags)

Screen/Verify

- Post-it Notes®
- Any special gloves required as specific personal protective equipment (PPE)
- Off-brand markers

Note: This is by no means a comprehensive list of prohibited or acceptable materials. All materials used on site should be evaluated for acceptability or screening prior to use

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Sample Containers and Equipment

Prohibited	Acceptable	Screen
• Teflon® and Teflon® lined caps • Low density polyethylene (LDPE) • Glass Jars • Aluminum Foil	• High Density Polyethylene (HDPE) • High Density Polypropylene (HDPP) • Sample containers provided by the laboratory - Batch proofed and shown to be PFAS free • Stainless Steel • Silicone Materials	• Any sample containers or sampling equipment that will come into direct contact with the samples that have not been verified or certified as being "PFAS-free" • Do not assume that sampling materials are PFAS-free, based on composition alone.

Note: This is by no means a comprehensive list of prohibited or acceptable materials. All materials used on site should be evaluated for acceptability or screening prior to use

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Other On-Site Materials

Prohibited	Acceptable	Screen
Field Clothing/PPE • Any known fluoropolymers that contain PFAS • Clothing washed in fabric softener that may contain PFAS • Chemically treated clothing for insect resistance and UV protection	Sunscreen and Insect Repellants • OFF Deep Woods • Sawyer Permethrin	Field Clothing/PPE • Water resistant and stain treated clothing/PPE • Tyvek suits and clothing that contains "Tyvek" Sunscreen and Insect Repellants Personal Care Products

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Equipment Decontamination

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

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Analytical Method Summary:

- Water methods based on USEPA 537
  - 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

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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

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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

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Summary:

- PFAS Replacements GenX and ADONA will be 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"

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