# Pushing the Boundaries on Quantitative PFAS Analysis

## ALS Canada

**Presented by: Darlene Stastny**

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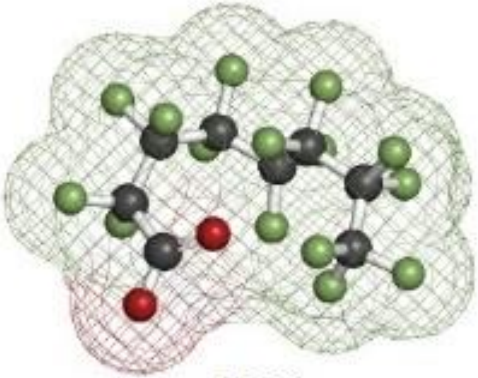
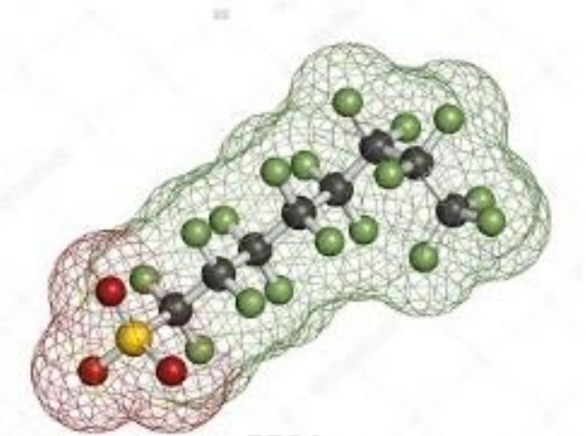
# Outline

- PFAS Chemistry
- Sources and Exposure Concerns
- Canadian Regulations and Guidelines
- Analytical Options for PFAS analysis
- New Analytes of Concern
- Trace Analysis
- Sampling Considerations
- Quality Considerations



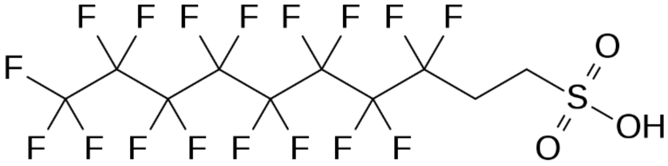
PFOA

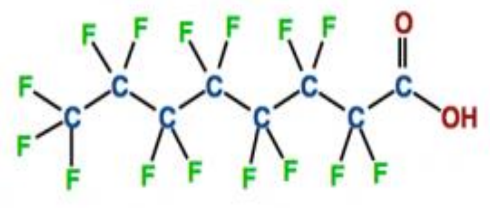


PFOS

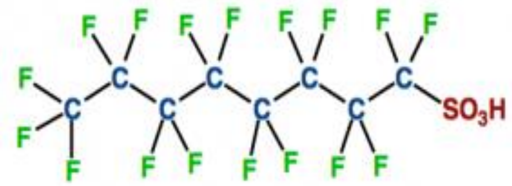
# PFAS Chemistry

- Group of synthetic chemicals containing more than 5000 compounds formed from carbon chains with fluorine attached to these chains.
- PFAS = perfluorinated and polyfluorinated substances
- PERfluorinated - all carbons are saturated with fluorine
- POLYfluorinated– not all carbons are attached to fluorine
- PFOS and PFOA are fully fluorinated and the most common perfluorinated chemicals.





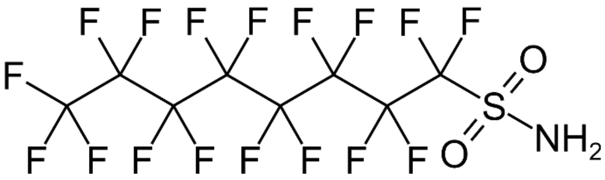
**PFOA** - perfluorooctanoic acid



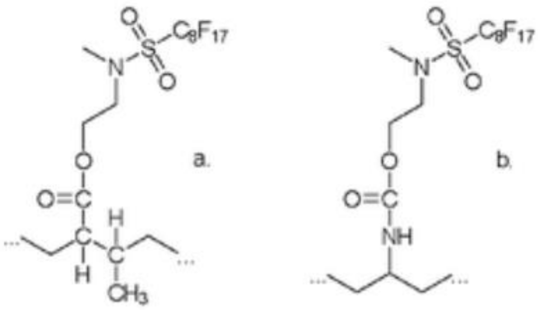
**PFOS** - perfluorooctanesulfonic acid

# PFAS Precursors

- Thousands of compounds are considered PFAS, including complex molecules, many of which are not measured by standard analysis
- These PFAS compounds are know as PFAS Precursors, and are released into the environment along with targeted PFAS compounds – often referred to as precursor pool, or PFAS “dark matter”
- These precursors can transform to PFAS “end-points” Perfluoroalkyl Acids (PFAAs) over time
  - These end point products do not degrade further (ex. PFOS and PFOA)
- Traditional PFAS analysis only targets the key analytes and select precursors, this may or may not greatly underestimate the presence of PFAS in the environment, and have serious implications on remedial efforts.
- Potential for target compounds to “appear” or increase unexpectedly in the future (liability)



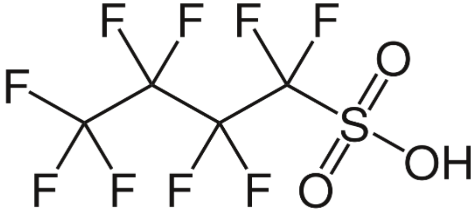
PFOSA



Conceptual representation of example copolymers:
a. ester-linked NMeFOSE methacrylate
b. urethane-linked NMeFOSE

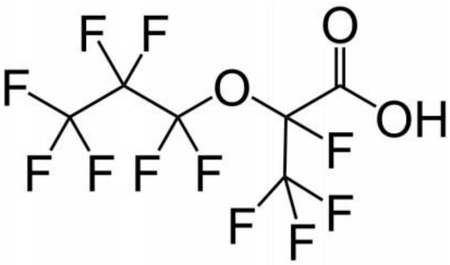
# Alternatives

- Short-chain PFAS
  - PFCAs with < eight carbons
  - PFSAs with <  six or carbons
  - Eliminated by humans more quickly
  - Ex. PFBS as replacement for PFOS



PFBS

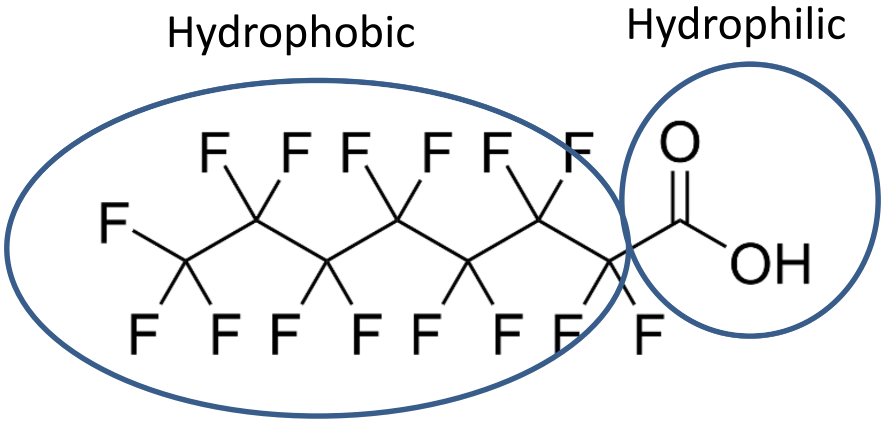
- Replacement Compounds
  - Alternatives such as GenX, and Adona used by manufacturers to replace regulated PFOA



GenX

# Properties and Uses of PFAS

- Beneficial Properties
  - Fire resistant
  - Oil, grease, water and stain repellent
- Common Applications
  - Fire fighting foams (AFF)
  - Cookware
  - Clothing
  - Cosmetics
  - Food Packaging
  - Cleaners
  - Paper, Leather, Textiles
  - Paints
  - Wire insulation



# PFAS Sources

- Direct sources are from manufacturing and waste, spills or use as AFFF (Aqueous Film Forming Foam).
- Indirect sources are from use of household and packaging products. Further contamination through landfill and waste water treatment plants and transformation of precursors.

# Human Health Concerns

- Most exposure to PFAS is from the intake of contaminated food and drinking water. Consumer products are a minor portion of the exposure.
- Concerns are mainly <u>chronic toxicity</u>
  - Not biotransformed or metabolized
  - Can be eliminated primarily by urine
- The following potential health risks have been linked to PFAS exposure:
    - Thyroid disease
    - High cholesterol
    - Increased risk of Testicular cancer and
    - Pregnancy-induced hypertension
    - low Infant birth rates
    - Liver damage

# Environmental Concerns

- Stable, persistent and bioaccumulative
  - can travel long distances in the environment, and up the food chain
  - Accumulates in tissues of plants and animals
  - Can bind to particulates and water droplets in the air to be transported long distances

# Federal Guidelines for Drinking Water (HC)

- Health Canada Guidelines for Canadian Drinking Water Quality

| | Maximum acceptable concentration (MAC) (µg/L) |
|---|---|
| PFOA | 0.2 |
| PFOS | 0.6 |

  - When both PFOS and PFOA are found together:
    - Divide concentration of each by its MAC
    - The sum of the results should be less than 1 for water to be considered safe for drinking

# Federal Drinking Water Screening Values (HC)

- Health Canada Drinking Water Screening Values for other PFAS
  - 9 PFAS compounds
  - Based on limited review of existing science
  - Developed based on data using PFOS and PFOA

| | Drinking Water Screening Value (µg/L) |
|---|---|
| PFBA | 30 |
| PFBS | 15 |
| PFHxS | 0.6 |
| PFPeA | 0.2 |
| PFHxA | 0.2 |
| PFHpA | 0.2 |
| PFNA | 0.02 |
| 6:2 FTS | 0.2 |
| 8:2 FTS | 0.2 |

# Federal Soil Screening Values : Soil (HC)

| | Soil Screening Values (mg/kg) | | |
|---|---|---|---|
| | Agricultural / Residential Parkland Use | Commercial Land Use | Industrial (Commercial without Toddler) Land Use |
| PFOS | 2.1 | 3.1 | 30.5 |
| PFOA | 0.70 | 1.05 | 9.94 |
| PFOS + PFOA | $\frac{[PFOS]}{SSV_{PFOS}} + \frac{[PFOA]}{SSV_{PFOA}} \leq 1$ | $\frac{[PFOS]}{SSV_{PFOS}} + \frac{[PFOA]}{SSV_{PFOA}} \leq 1$ | $\frac{[PFOS]}{SSV_{PFOS}} + \frac{[PFOA]}{SSV_{PFOA}} \leq 1$ |
| PFBA | 114 | 173 | 1630 |
| PFBS | 61 | 92 | 872 |
| PFPeA | 0.8 | 1.21 | 11.41 |
| PFHxS | 2.3 | 3.5 | 33 |
| PFHxA | 0.80 | 1.21 | 11.41 |
| PFHpA | 0.80 | 1.21 | 11.41 |
| PFNA | 0.08 | 0.13 | 1.2 |
| 6:2 FTS | 0.80 | 1.21 | 11.41 |
| 8:2 FTS | 0.80 | 1.21 | 11.41 |

# Environmental Quality Guidelines for PFOS

- FEQG for Surface Water, Fish Tissue, Wildlife Diet and Bird Egg

| Water (ug/L) | Fish Tissue (mg/kg ww) | Wildlife Diet (µg/kg ww food) | | Bird Egg (ug/g) |
|---|---|---|---|---|
| | | Mammalian | Avian | |
| 6.8 | 9.4 | 4.6 | 8.2 | 1.9 |

# CCME Guidelines for PFOS

- CCME Guidelines for PFOS in soil and groundwater for the Protection of Environmental and Human Health posted September 23rd 2021

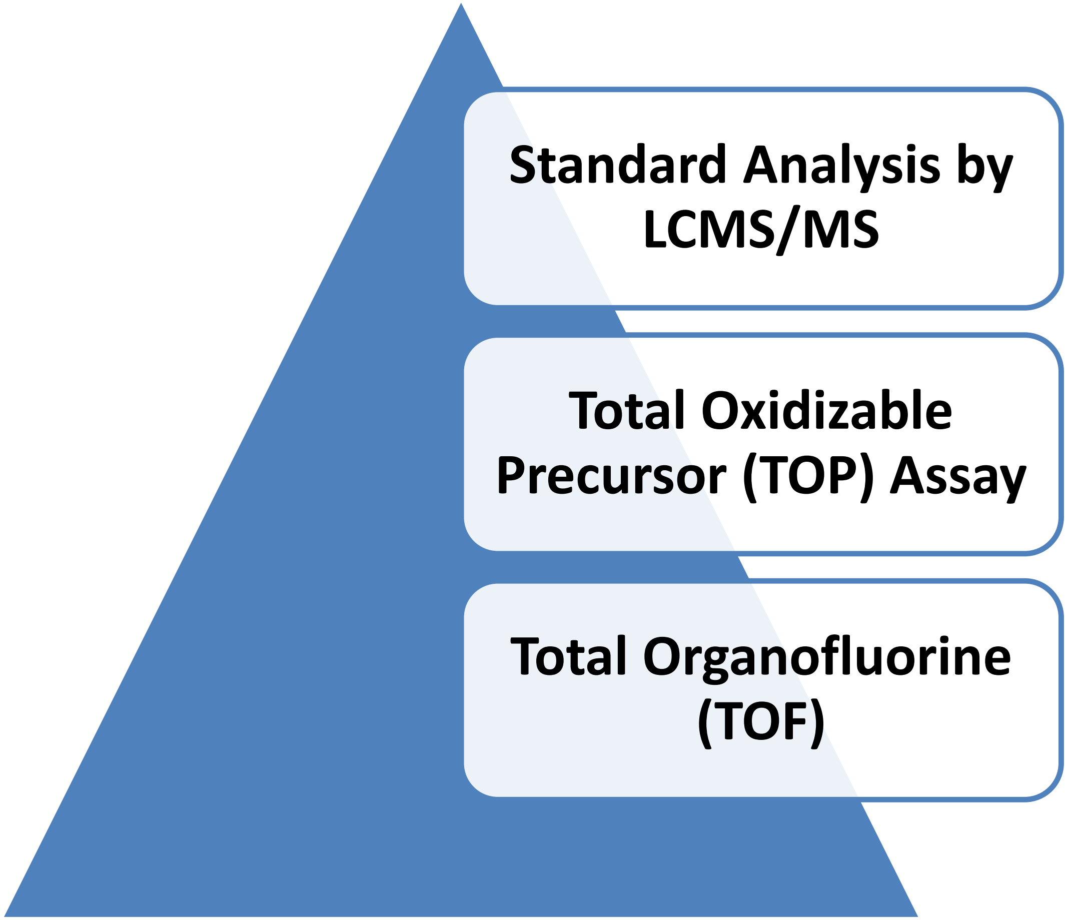
| **Soil Quality Guidelines for PFOS (mg/kg dry weight)** | | | | |
|---|---|---|---|---|
| | Land Use | | | |
| | Agricultural | Residential/ parkland | Commercial | Industrial |
| Final Guideline | **0.01** | **0.01** | **0.01** | **0.01** |

| **Groundwater quality guidelines for PFOS (mg/L) considering ecological and** | | |
|---|---|---|
| | Soil Type | |
| Final Guideline | **0.0006** | **0.0006** |

# Provincial Regulations

- BC
  - Only province with any kind of provincial standard
  - PFOS, PFOA and PFBS regulated in water , PFOS and PFBS are regulated in soil under the Contaminated Sites Regulation
- Ontario
  - MECP released a guidance value for assessing the potable groundwater pathway (2020)
  - Recommend to use value of **70 ng/L** to compare the summed concentration of 11 PFAS parameters

# PFAS Analytical Options



Standard Analysis by LCMS/MS

Total Oxidizable Precursor (TOP) Assay

Total Organofluorine (TOF)

# Option 1 : Standard Analysis by LCMS/MS

- **Water (Routine and low level)**

Two options for reporting limits:

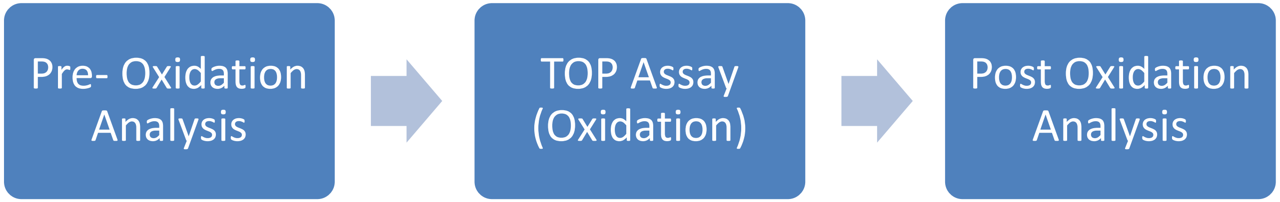
1. Routine reporting limits (0.01-0.1 ug/L) by direct injection using isotope dilution liquid chromatography/tandem mass spectrometry (LC-MS/MS). *only for water*
    - Meets all current guidelines and screening values
2. Low Level reporting limits (0.001-0.05 ug/L) by solid phase extraction (SPE) pre-concentration followed by analysis using isotope dilution liquid chromatography/tandem mass spectrometry (LC-MS/MS).

- **Soil (low level)**
    - Low level reporting (0.1-0.5 ug/kg) by aqueous Extraction followed by SPE pre-concentration, and analysis by LC-MS/MS

- **Low level Analysis can also be used for Serum and Tissue Samples**

# Option 2:Total Oxidisable Precursor Assay (TOP Assay)

- There are thousands of chemicals that can be classed as PFAS chemicals.
  - Accredited laboratories typically determine around 30-50 of these specific chemicals.
  - The bulk of these chemicals may be tied up in derivatives of PFAS (precursors)
- TOP Assay (Houtz and Sedlak 2012) is designed to expose underlying PFAS not amenable to standard analysis.
- Two data sets are provided: Pre- and Post- Oxidation
- Samples is oxidized to transform any precursor compounds into PFAS end products



Pre- Oxidation Analysis

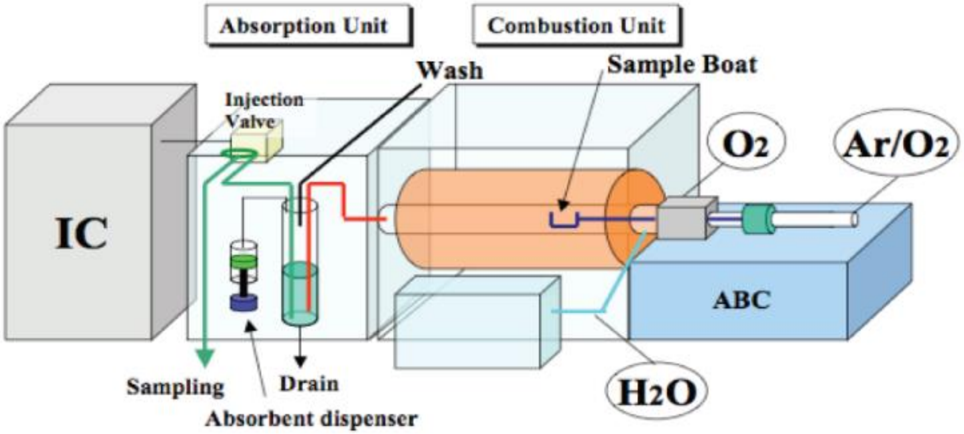
TOP Assay (Oxidation)

Post Oxidation Analysis

- The difference between these data sets will give an idea of precursor levels found in the sample

# Option 3 : Total Organofluorine (TOF)

- Simple way to account for the total mass of PFAS in a sample
- The analysis reports concentration of organic fluorine (weight of fluorine per mL or per gram)
- On average, Fluorine accounts for approximately 65% of the total mass – so TOF concentrations need to be multiplied by ~ 1.5 to estimate the maximum total PFAS content
- Combustion Ion Chromatography (CIC) – higher RLs (0.02 mg/L, 0.1-1 mg/kg)



# PFAS Analysis – Uses and Limitations

- Standard Analysis by LCMS
  - Beneficial Uses: Quantitative data for target analytes for regulatory purposes
  - Limitations:
    - ➢ Limited to the 30-50 target analytes (Does not account for the total “pool” of PFAS)
    - ➢ Does not account for potential PFAS from precursor transformation over time
- TOP Assay
  - Beneficial Uses: Indication of potential PFAS formation over time from precursors, indication of presence of PFAS outside of target analytes
  - Limitations:
    - ➢ Still limited to target analyte list, and compounds that are oxidizable
    - ➢ Higher analytical cost (2 data sets per single sample)
    - ➢ Not fully quantitative
- TOF
  - Beneficial Uses: screening tool for high impact zones, verify the degree to which the TOP assay accounts for potential precursors, lower analytical cost, confirmation of AFFF product “PFAS free”
  - Limitations:
    - ➢ Provides no information of chain length and not selective for PFAS
    - ➢ Not as sensitive a technique (higher DLs) and therefore not suitable for low level screening

# Combined Approach

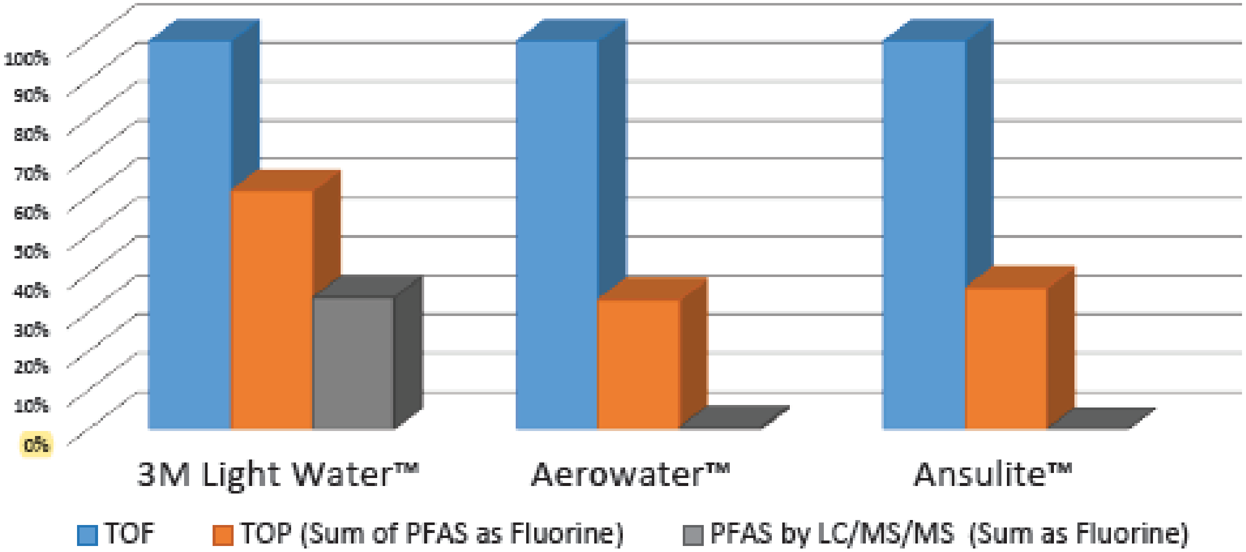


Figure 1. TOF vs TOP vs PFAS (LC/MS/MS) for 3 AFFF Products

# Draft EPA Method 1633 – September 2021

- New draft method targeting 40 compounds in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate and fish tissue
- Fundamental Elements
  - LC/MS/MS with multiple reaction monitoring
  - Whole sample bottle extractions for water
  - Isotope Dilution where labelled PFAS isotopes are available (otherwise labelled internal standards)
  - SPE extraction to achieve lowest required DLs
  - Extensive cleanup to remove interferences
  - Quantification of both linear and branched PFAS isomers where relevant

- Performance criteria will be defined in the final approved version of the method, once multi-laboratory validation studies are complete.

# Extended Compound Lists

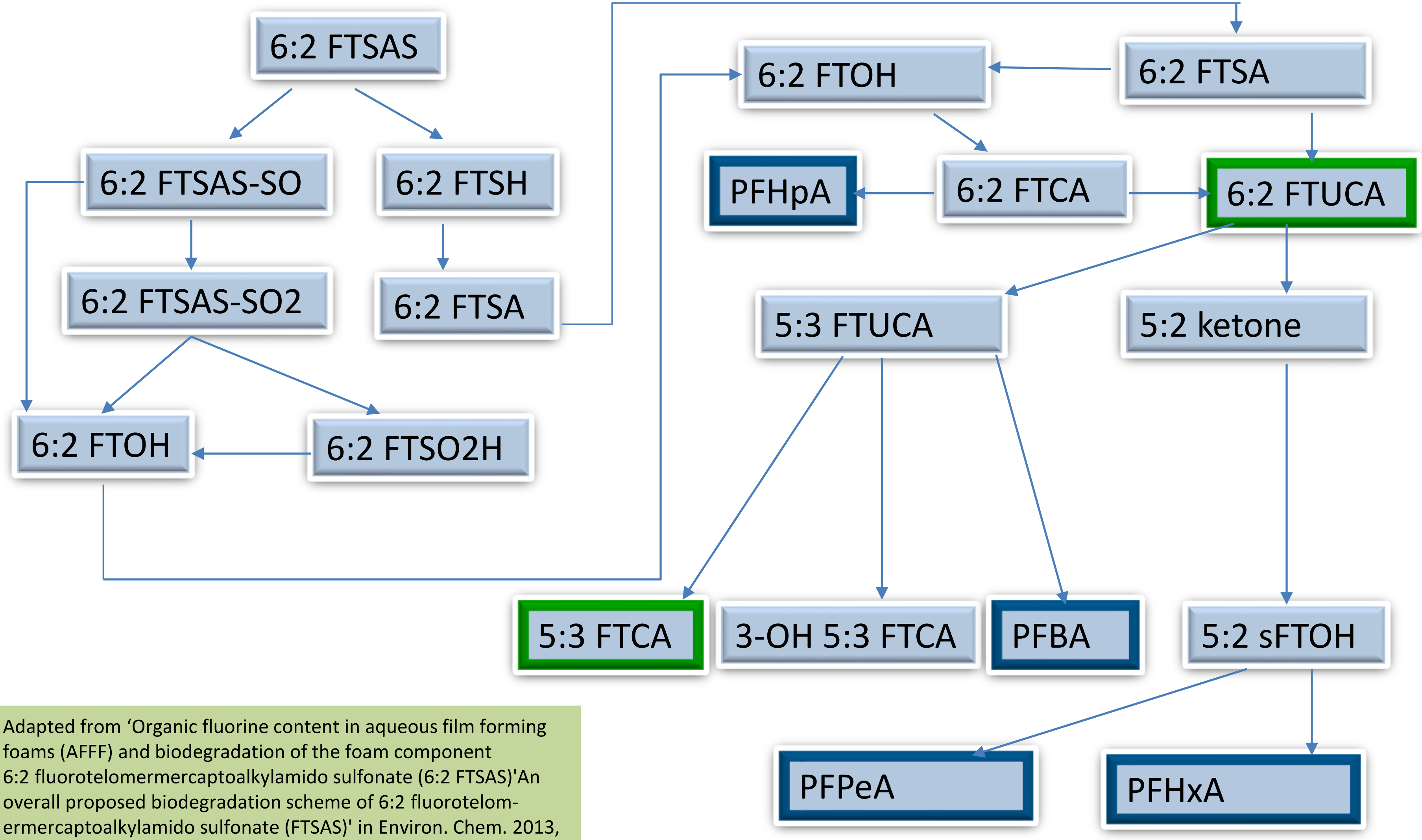
| PFAS Sulfonic Acids | PFAS Carboxylic Acids | Perfluoroalkyl Sulfonamides & Sulfonamido Ethanols (Precursors) | Fluorotelomers | PFAS Replacement Compounds | Other |
|---|---|---|---|---|---|
| **PFBS** | **PFBA** | **PFOSA** | **4:2 FTS** | **ADONA** | **PFMPA** |
| **PFPeS** | **PFPeA** | **NMeFOSA** | **6:2 FTS** | **9Cl-PF3ONS F-53B** | **PFMBA** |
| **PFHxS** | **PFHxA** | **NEtFOSA** | **8:2 FTS** | **11Cl-PF3OUdS F-35B** | **NFDHA** |
| **PFHpS** | **PFHpA** | **NMeFOSE** | **10:2 FTS** | **HFPO-DA “Gen-X”** | **FDUEA** |
| **PFOS** | **PFOA** | **NEtFOSE** | **(3:3 FTCA) FPrPA** | | **FHUEA** |
| **PFNS** | **PFNA** | **NMeFOSAA** | **(5:3 FTCA) FPePA** | | **FOUEA** |
| **PFDS** | **PFDA** | **N-EtFOSAA** | **7:3 FTCA) FHpPA** | | |
| **PFDoS** | **PFUnA** | | **6:2 FTCA** | | |
| **PFUdS** | **PFDoA** | | **8:2 FTCA** | | |
| **PFTrDS** | **PFTrDA** | | **10:2 FTCA** | | |
| **PFEESA** | **PFTeDA** | | | | |
| **PFECHS** | **PFHxDA** | | | | |

# Rationale for New Analytes

## New PFAS Analytes Available in Extended Suites

| Short Name | Name (Acid Form) | CAS# | Rationale for Addition |
|---|---|---|---|
| 3:3 FTCA | 3:3 Fluorotelomer carboxylic acid | 356-02-5 | EPA 1633 - degradation products; major components of legacy landfill leachates. |
| 5:3 FTCA | 5:3 Fluorotelomer carboxylic acid | 914637-49-3 | |
| 7:3 FTCA | 7:3 Fluorotelomer carboxylic acid | 812-70-4 | EPA 1633 - degradation product |
| NFDHA | Perfluoro-3,6-dioxaheptanoic acid | 151772-58-6 | EPA 1633 - food packaging |
| PFEESA | Perfluoro(2-ethoxyethane)sulfonic acid | 113507-82-7 | EPA 1633 - replacement PFAS |
| PFMPA | Perfluoro-3-methoxypropanoic acid | 377-73-1 | EPA 1633 - manufacturing |
| PFMBA | Perfluoro-4-methoxybutanoic acid | 863090-89-5 | EPA 1633 - manufacturing |
| PFecHS | n-Decafluoro-4-(pentafluoroethyl) cyclohexanesulfonic acid | 646-83-3 | aviation hydraulic oils |
| 6:2 FTUCA | 6:2 Fluorotelomer unsaturated carboxylic acid | 70887-88-6 | degradation product |
| 8:2 FTUCA | 8:2 Fluorotelomer unsaturated carboxylic acid | 70887-84-2 | degradation product |
| 10:2 FTUCA | 10:2 Fluorotelomer unsaturated carboxylic acid | 70887-94-4 | degradation product |
| 6:2 FTCA | 6:2 Fluorotelomer carboxylic acid | 53826-12-3 | degradation product |
| 8:2 FTCA | 8:2 Fluorotelomer carboxylic acid | 27854-31-5 | degradation product |
| 10:2 FTCA | 10:2 Fluorotelomer carboxylic acid | 53826-13-4 | degradation product |

# Potential Degradation Pathway – 6:2 FTSAS



6:2 FTSAS

6:2 FTSAS-SO

6:2 FTSH

6:2 FTSAS-SO2

6:2 FTSA

6:2 FTOH

6:2 FTSO2H

6:2 FTOH

6:2 FTSA

PFHpA

6:2 FTCA

6:2 FTUCA

5:3 FTUCA

5:2 ketone

5:3 FTCA

3-OH 5:3 FTCA

PFBA

5:2 sFTOH

PFPeA

PFHxA

Adapted from ‘Organic fluorine content in aqueous film forming foams (AFFF) and biodegradation of the foam component 6:2 fluorotelomermercaptoalkylamido sulfonate (6:2 FTSAS)'An overall proposed biodegradation scheme of 6:2 fluorotelomermercaptoalkylamido sulfonate (FTSAS)' in Environ. Chem. 2013, Weiner et al.

# Trace Analysis for Water

- Industry seeking LORs down to 0.0001 µg/L
- Designed for water samples that are not expected to contain PFAS at high levels and is therefore not offered for high level contaminated samples or waste waters
- Enhanced internal laboratory segregation and controls
- LORs that maximize data quality, therefore will different from analyte to analyte (0.01 µg/L – 0.0001µg/L)
- Pristine samples for trace level analysis should be separately bagged and marked “TRACE” to segregate in the field and lab and maximize data quality

# Sampling Considerations

Below is a summary of items that **should not be used** by the personnel conducting sampling and acceptable alternatives where applicable

| Not to be used | Acceptable alternative |
|---|---|
| Teflon™ pump or tubing | HDPE or Silicone tubing |
| Decon 90 | Alconox®, Liquinox®, Citrinox® |
| LDPE or glass sample containers | HDPE or polypropylene containers<br>** ensure no Teflon™ liner |
| Chemical Blue Ice packs | Free ice |
| Waterproof field book | Metal clipboard / loose paper |
| Markers | Ball point pen or pencil, sharpie® |
| Water resistant or treated gloves / clothing | Powderless nitrile gloves / cotton clothing |
| Cosmetics, creams, sunscreen and related products | -- |
| pre-packaged food, aluminum foil, fast food wrappers or containers | -- |
| Plastic bags / packaging – screen before use | Polyethylene bags (Ziplock®) |

**This is not a full comprehensive list of all potential sources of PFAS contamination

Resource: Transport Canada PFAS Field Sampling Guidance Document (published in 2017)

# Sampling Considerations (Draft EPA Method)

- Store on ice and submit within 48 hours
- Draft EPA method 1633 indicates that some perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids may potentially degrade into other PFAS compounds beyond 7 days (at ≤6˚C).
- Samples can be frozen to extend hold time up to 90 days
- Samples may need to be extracted as soon as possible if NFDHA is an important analyte

# Quality Considerations

- Focus on maximizing data quality and minimizing false positives
- “clean” and “dirty” sample segregation even more critical with larger analyte suites and every order of magnitude lower in testing becomes more challenging
- Optimum data quality is achieved by not pushing to see the lowest possible detection limits, but by offering a series of methods designed to meet specific needs

# Special Thanks

LABORATORY TESTING SERVICES

www.alsglobal.com

**Katrina Zwambag**
Waterloo Business Manager
+1 519 514 1849
katrina.zwambag@alsglobal.com

**Sandra Cummings**
LC/MS Manager
+1 519 886 6910
sandra.cummings@alsglobal.com

# Questions?

LABORATORY TESTING SERVICES

www.alsglobal.com

**Testing Inquiries**

Darlene Stastny
**M** +1 519 719 4201
darlene.stastny@ALSGlobal.com