


PFAS: A Combination Approach for Laboratory Analysis


ALS Canada

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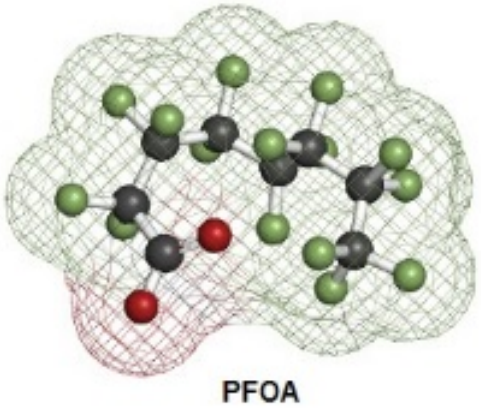
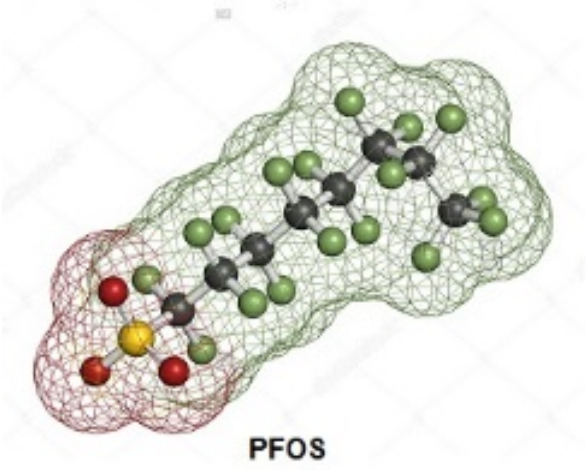
Outline

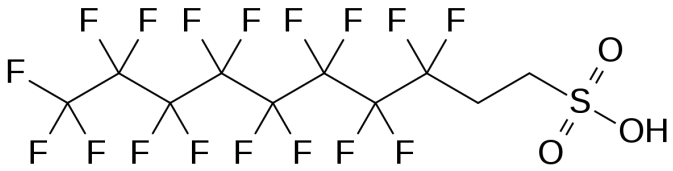
- PFAS Chemistry
- Sources and Exposure Concerns
- Canadian Regulations and Guidelines
- 3 Analytical Options for PFAS analysis
- Sampling considerations
- PFAS in Air

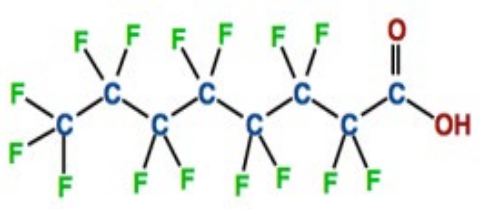

PFOA


PFOS

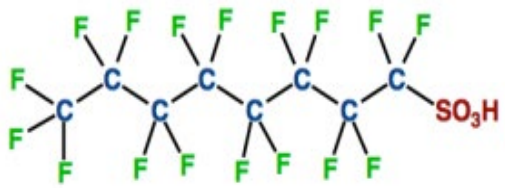
PFAS Chemistry

- 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.





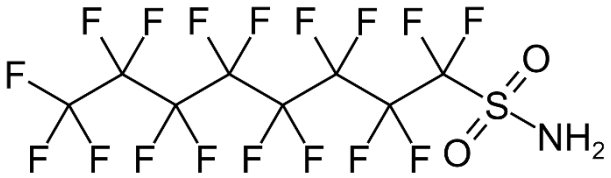
PFOA - perfluorooctanoic acid



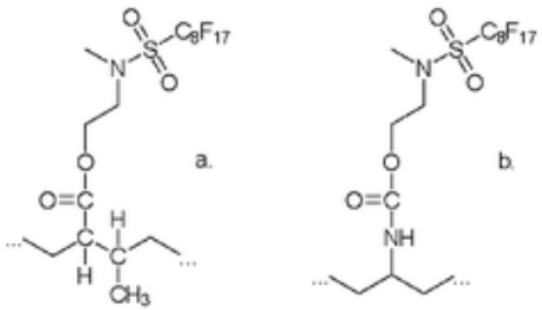
PFOS - perfluorooctanesulfonic acid

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)



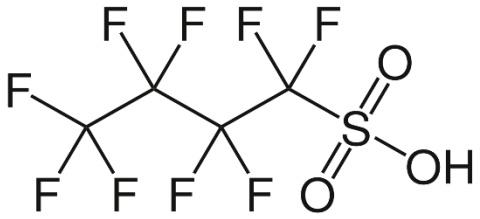
PFOSA



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

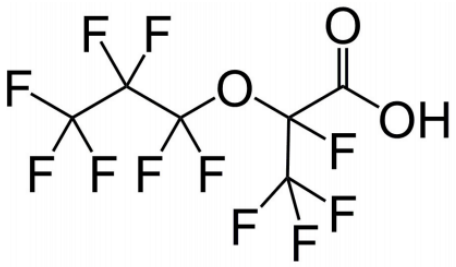
Alternatives

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



PFBS

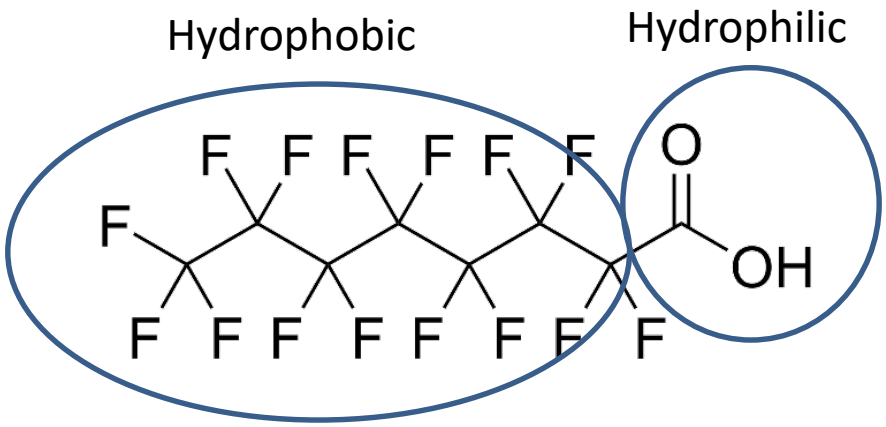
- Replacement Compounds
  - Alternatives such as GenX, and Adona used by manufacturers to replace regulated PFOA



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 chronic toxicity
  - 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
    - 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

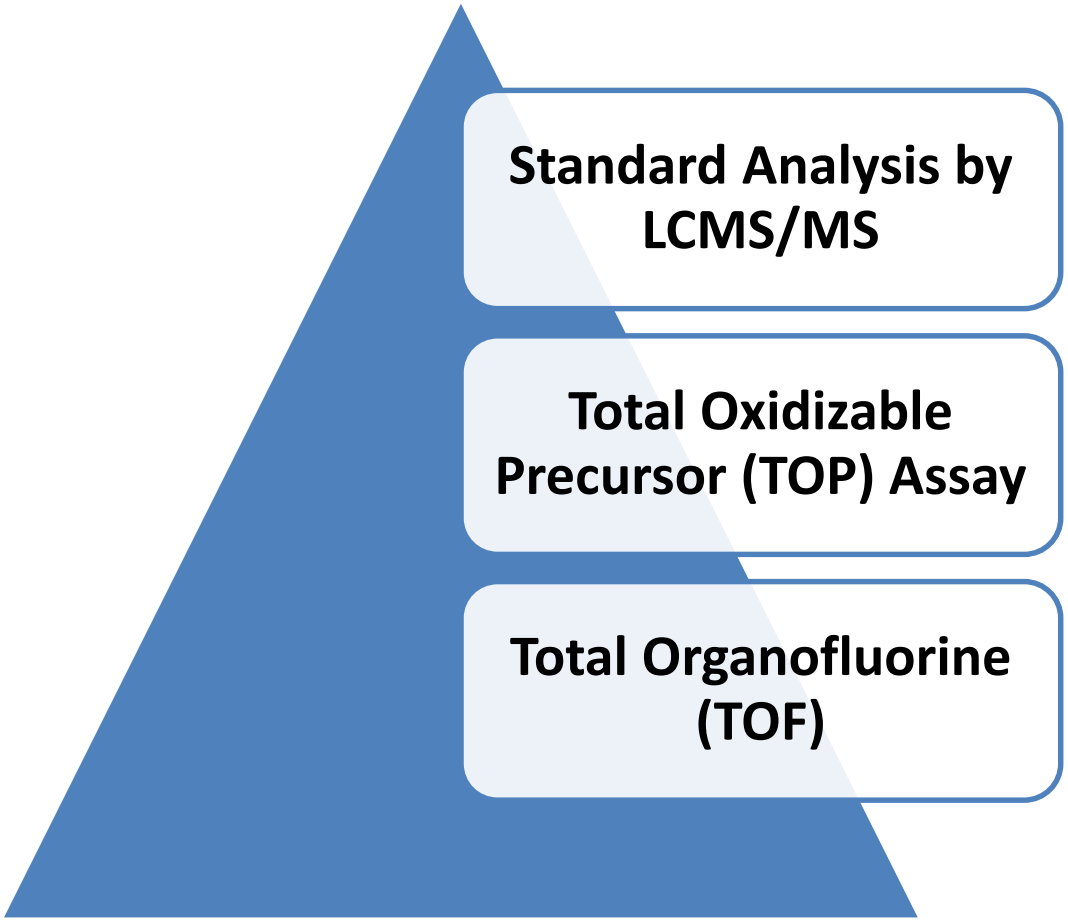
Water (ug/L)	Fish Tissue (mg/kg ww)	Wildlife Diet (µg/kg ww food)		Bird Egg (ug/g)
		Mammalian	Avian	
6.8	9.4	4.6	8.2	1.9

- Guidelines for PFOS in soil and groundwater for the Protection of Environmental and Human Health are currently being developed by the CCME
- Expected to be published in 2021

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



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).

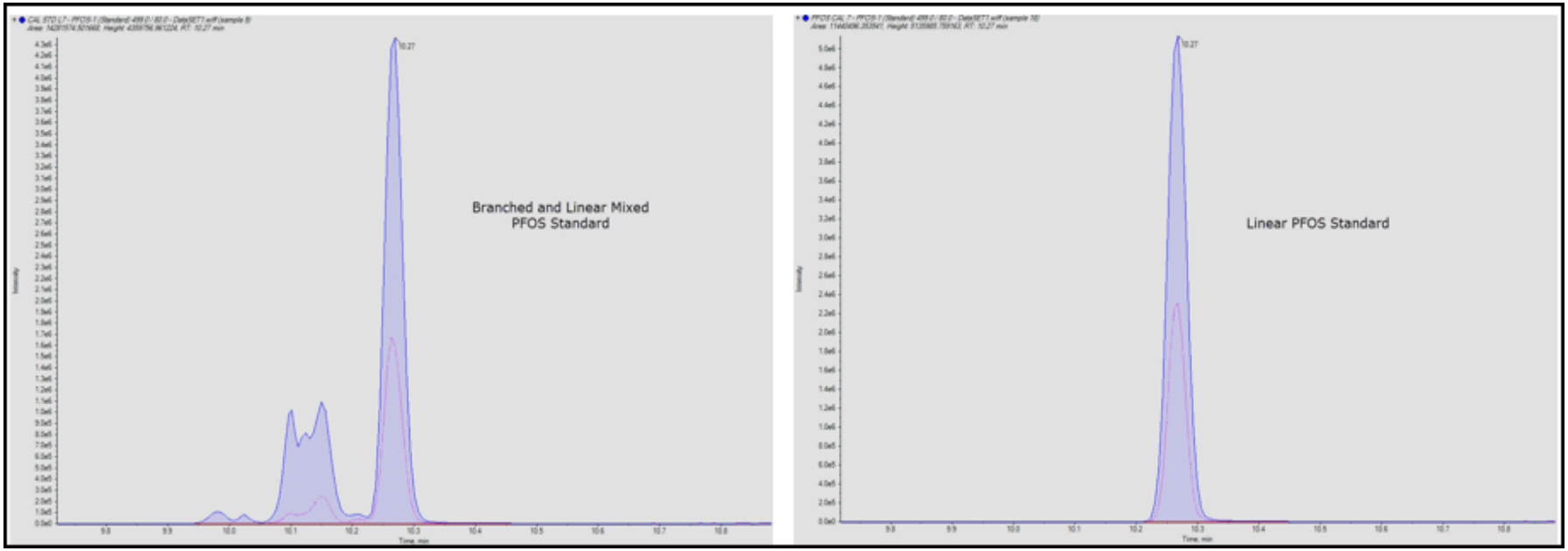
- **Soil (low level)**

  – 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 done for Serum and Tissue Samples**

Branched vs Linear Isomers

- PFOS in the environment is usually a mixture of branched and linear isomers
- Quantitation using a mixed linear/branched standard will be more representative of environmental contamination and therefore more accurate.
- Mixed standards used for PFOS, PFHxS, NMeFOSAA and NEtFOSAA



Use of Linear vs branched/linear standards for perfluorooctane sulfonate (PFOS)

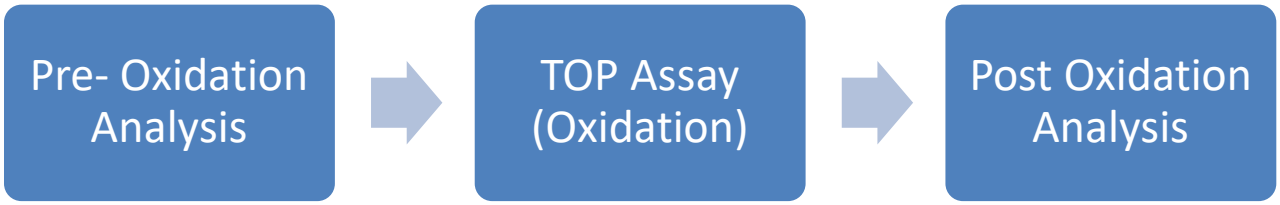
PFAS Testing – Compound Lists

PFAS Sulfonic Acids	PFAS Carboxylic Acids	Perfluoroalkyl Sulfonamides & Sulfonamido Ethanols (Precursors)	Fluorotelomers (Precursors)	PFAS Replacement Compounds	Other
PFBS	PFBA	PFOSA	4:2 FTS	ADONA	**PFMPA**
PFPeS	PFPeA	MeFOSA	6:2 FTS	9Cl-PF3ONS F-53B	**PFMBA**
PFHxS	PFHxA	EtFOSA	8:2 FTS	11Cl-PF3OUdS F-35B	**NFDHA**
PFHpS	PFHpA	MeFOSA	10:2 FTS	**HFPO-DA "Gen-X"**	**PFECHS**
PFOS	PFOA	MeFOSE	**(3:3 FTCA) FPrPA**		**FHUEA**
PFNS	PFNA	NMeFOSAA	**(5:3 FTCA) FPePA**		**FouEA**
PFDS	PFDA	N-EtFOSAA	**7:3 FTCA) FHpPA**		
PFDoS	PFUnDA		**6:2 FTCA**		
PFTrDS	PFDoDA		**8:2 FTCA**		
PFUnDS	PFTrDA				
PFEESA	PFTeDA				
	PFOcDA				
	PFHxDA				

New compounds are in support of new EPA method being developed based on list of 40 compounds – expected in 2021

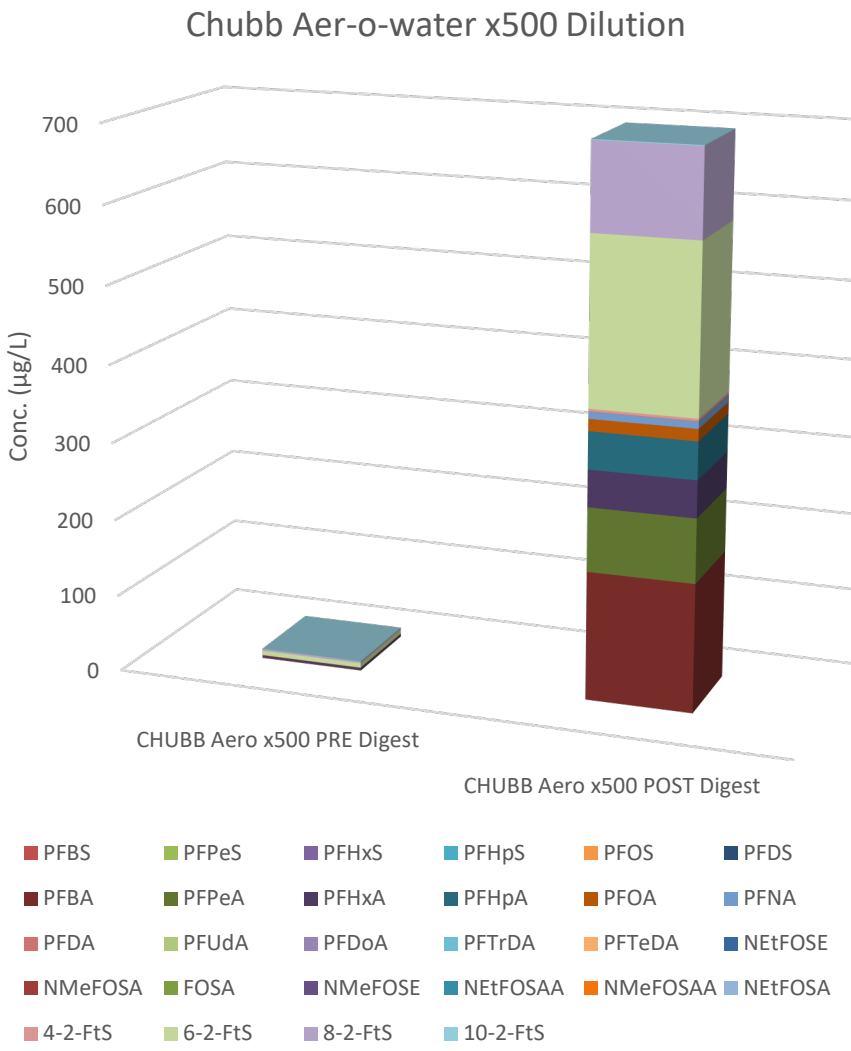
Option 2:Total Oxidisable Precursor Assay (TOP Assay)

- 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



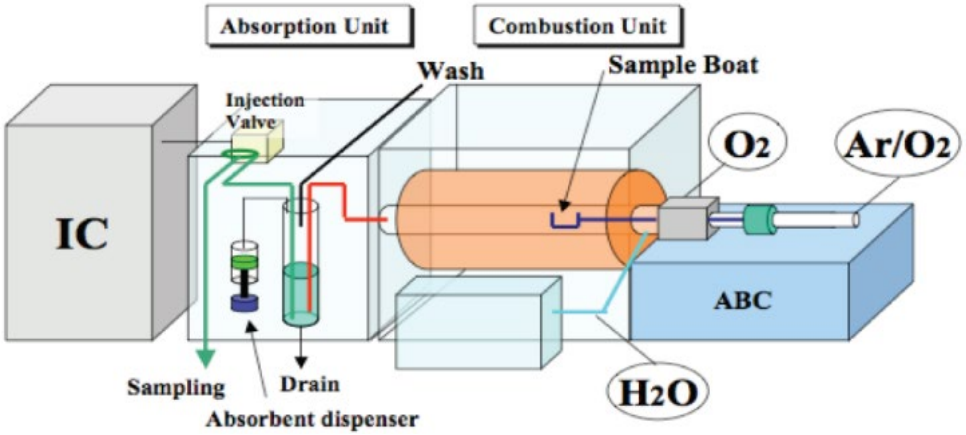
- The difference between these data sets will give an idea of precursor levels found in the sample

TOP Assay Example



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

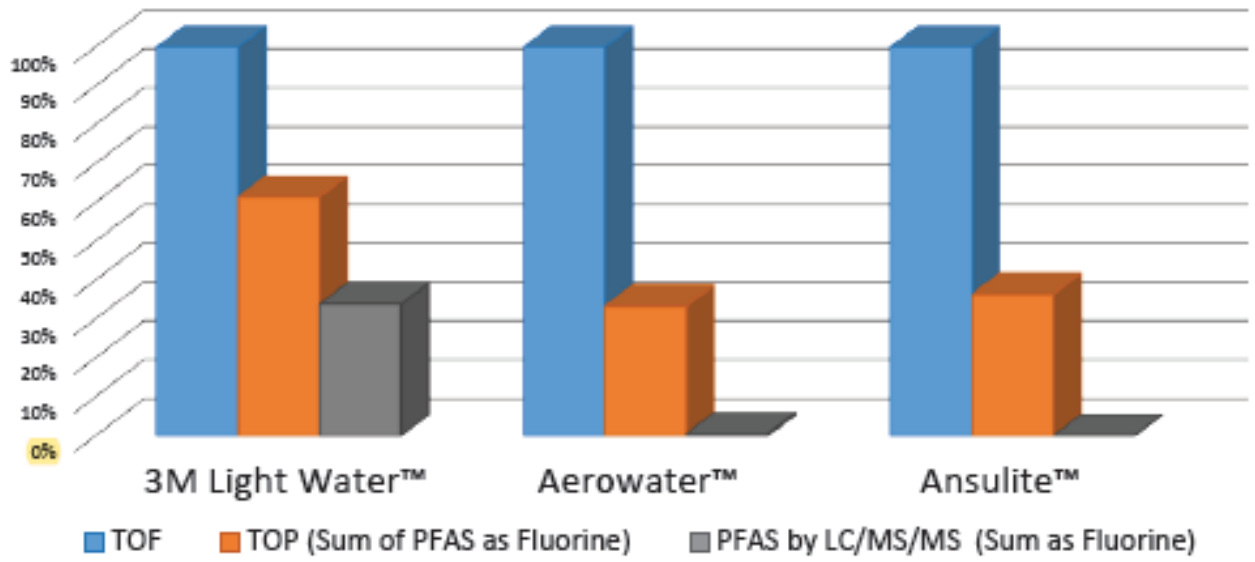


Figure 1. TOF vs TOP vs PFAS (LC/MS/MS) for 3 AFFF Products

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 ** 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)

What's next : PFAS in Air

- PFAS compounds generally have low volatility
- PFAS in air from stationary sources:
    - Hazardous Waste Incinerators
    - Sewage Sludge Incinerators
    - Thermal Oxidizers
    - Thermal Desorbers
    - Chemical Plants and Process Vents

- Concern for long range air dispersion of PFAS attached to fine water droplets
- Recently set up a method for testing PFAS in stack emissions using XAD-2 resin tubes

To Summarize…

- 3 options for analysis that can be combined: LCMS/MS, TOP Assay and TOF
- Standard analysis by LCMS/MS: Targeted analysis quantifying individual compounds (Regulatory compliance)
- TOP Assay: Analysis is not fully quantitative, but gives a better idea of total PFAS and non-targeted PFAS precursors
- TOF: Non-targeted analysis that gives a measure of total PFAS, with no compounds specific information
- A combination of the 3 options might be an appropriate way to get the most complete
- Additional Resources: ALS EnviroMails, Transport Canada Field Sampling Guide, ITRC Factsheets

Interesting watch:

The Devil We know (Netflix Documentary)

Dark Waters (Hollywood Dramatization)

Special Thanks

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