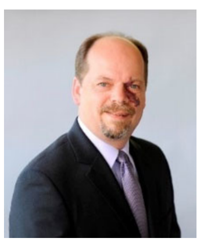
PFAS, Total Oxidizable Precursors (TOPs) and Total Organic Fluorine (TOF)



Taras (Terry) Obal
Bureau Veritas

Virtual SMART Remediation Seminar Series 2021
February 11, 2021

SMART is Powered by: VERTEX Environmental Inc.

www.vertexenvironmental.ca

PFAS, TOTAL OXIDIZABLE PRECURSORS (TOPs) AND TOTAL ORGANIC FLUORINE (TOF)

What's the difference and when to use one over the other

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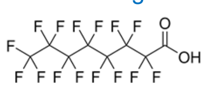
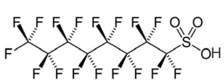
ENVIRONMENTAL INTEREST IN PFAS

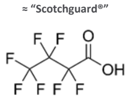
Where it began…



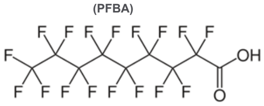
Perfluorooctanoic Acid
(PFOA)
≈ "Teflon®"



Perfluorooctanesulfonic Acid
(PFOS)
≈ "Scotchguard®"

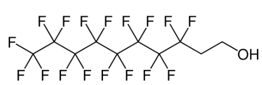


Perfluorobutanoic Acid
(PFBA)



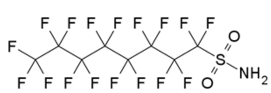
Perfluorononanoic Acid
(PFNA)

Precursors

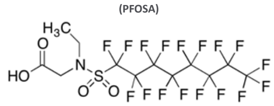


8:2 Fluorotelomer Alcohol
(8:2 FTOH)

6:2 Fluorotelomersulfonic Acid
(6:2 FTS)

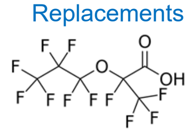


Perfluorooctanesulfonamide
(PFOSA)

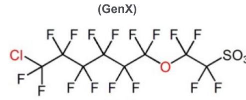


N-Ethylperfluorooctanesulfonamidoacetic Acid
(EtFOSAA)

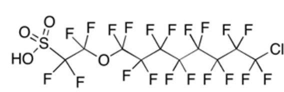
Replacements



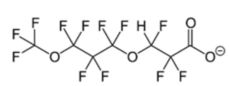
2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid
(GenX)



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



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



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

5000+ Compounds

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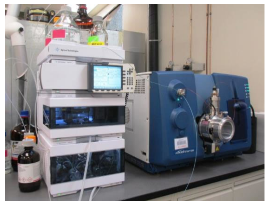
THE EVOLUTION OF THE PFAS "TOOLKIT"

PFAS by LC/MS/MS

PFAS (individual)

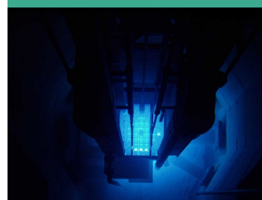


PFAS by LC/MS/MS
(as received)

+

PFAS by LC/MS/MS
(oxidized)

Total Oxidizable Precursors (TOPs) Assay



Particle Induced Gamma Ray Emission (PIGE)

Neutron Activation Analysis (NAA)

Combustion Ion Chromatography (CIC)

Total Organic Fluorine (TOF)

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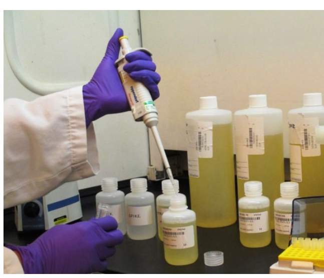
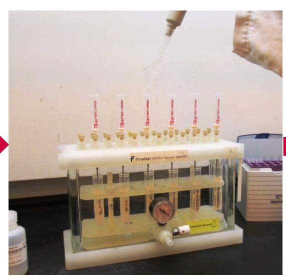
PFAS BY LC/MS/MS

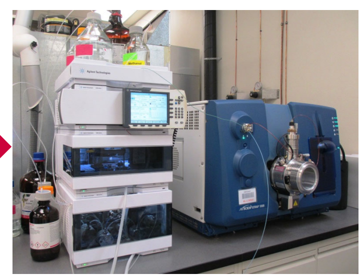
Industry Best Practice:



Isotope Dilution



SPE



LC/MS/MS

Reporting Limits (soil) = 1 – 2 ppb
- *Detection Limits = 0.1 – 0.5 ppb*

Reporting Limits (water) = 2 - 4 ppt
- *Detection Limits = 0.1 – 0.5 ppt*

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APPLICATION: REGULATORY REQUIREMENTS

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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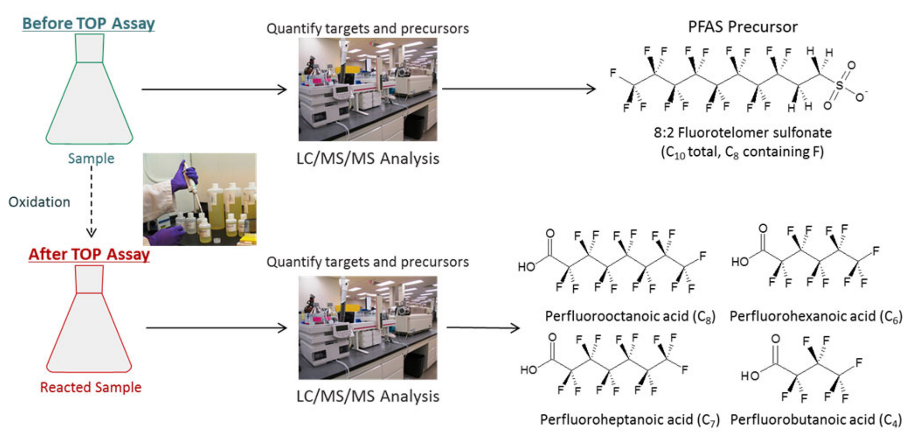
TOTAL OXIDIZABLE PRECURSORS (TOPs) ASSAY



- Chemical oxidation method (Houtz and Sedlak (2012). *Environ. Sci. Technol.*, 46, 9342-9349)
- Transforms PFAS precursors to perfluorocarboxylic acid (PFCA) end products without affecting target PFASs
- The change in PFAS concentration is representative of higher molecular weight PFAS ("precursors") that may, over time, convert to the lower molecular weight dead end PFAS
- Accelerated approach to predicting *in situ* precursor behavior

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Maxxam Job [redacted]

Maxxam ID		[redacted]							
		RESULTS							
Sampling Date		2019/08/02							
Client Sample ID		[redacted]							
Parameter	**Units**	**Pre Oxidation Concentration**	**RDL**	**QC Batch**	**Post Oxidation Concentration**	**RDL**	**QC Batch**	**Difference in Pre and Post Oxidation Concentration**	**QC Batch**
Perfluorobutanoic acid	µg/L	4.3	0.80	6282486	1100	100	6309573	1100	6274728
Perfluoropentanoic Acid (PFPeA)	µg/L	3.2	0.80	6282486	1400	100	6309573	1400	6274728
Perfluorohexanoic Acid (PFHxA)	µg/L	9.7	0.80	6282486	1200	100	6309573	1200	6274728
Perfluoroheptanoic Acid (PFHpA)	µg/L	4.2	0.80	6282486	1100	100	6309573	1100	6274728
Perfluorooctanoic Acid (PFOA)	µg/L	6.4	0.80	6282486	650	100	6309573	640	6274728
Perfluorononanoic Acid (PFNA)	µg/L	ND	0.80	6282486	310	10	6309573	310	6274728
Perfluorodecanoic Acid (PFDA)	µg/L	1.2	0.80	6282486	170	10	6309573	170	6274728
Perfluoroundecanoic Acid (PFUnA)	µg/L	ND	0.80	6282486	97	10	6309573	97	6274728
Perfluorododecanoic Acid (PFDoA)	µg/L	ND	0.80	6282486	54	10	6309573	54	6274728
Perfluorotridecanoic Acid	µg/L	ND	0.80	6282486	30	10	6309573	30	6274728
Perfluorotetradecanoic Acid	µg/L	ND	0.80	6282486	19	10	6309573	19	6274728
Perfluorobutanesulfonic Acid (PFBS)	µg/L	2.2	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
Perfluorohexanesulfonic Acid (PFHxS)	µg/L	8.9	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
Perfluoroheptanesulfonic Acid	µg/L	0.99	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
Perfluorooctanesulfonic Acid (PFOS)	µg/L	58	8.0	6282486	51	10	6309573	-7	6274728
Perfluorodecanesulfonic Acid	µg/L	ND	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
Perfluorooctane Sulfonamide (PFOSA)	µg/L	ND	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
EtFOSA	µg/L	ND	0.80	6282486	NR	10	6309573	NR	6274728
MeFOSA	µg/L	ND	0.80	6282486	NR	10	6309573	NR	6274728
EtFOSE	µg/L	ND	0.80	6282486	NR	10	6309573	NR	6274728
MeFOSE	µg/L	ND	0.80	6282486	NR	10	6309573	NR	6274728
EtFOSAA	µg/L	ND	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
MeFOSAA	µg/L	ND	0.80	6282486	ND	10	6309573	<RDL (post-oxidation)	6274728
6:2 Fluorotelomer sulfonic Acid	µg/L	210	8.0	6282486	ND	10	6309573	-210	6274728
8:2 Fluorotelomer sulfonic Acid	µg/L	380	8.0	6282486	ND	10	6309573	-380	6274728

RDL = Reportable Detection Limit
QC Batch = Quality Control Batch

Results relate only to the items tested.

Notes: The change in PFAS concentration was calculated by subtracting the pre oxidation concentration from the post oxidation concentration.
A negative change indicates a decrease in the PFAS concentration after oxidation.
If the concentration of a parameter was <RDL either prior to or post oxidation, the concentration was treated as "zero" for the difference calculation.
Difference calculation performed using raw data. The rounding of final results may result in an apparent difference.
Not reported (NR) due to high volatility under the conditions used for oxidation.
Approximately 20% of PFOSA is known to be lost due to volatility under the conditions used for oxidation.
Oxidation was performed adhering to the protocol as described by Houtz, E.F. and Sedlak, D.L. (2012). *Environ. Sci. Technol.*, 46, 9342-9349.
Due to high concentrations of target analytes, the sample required dilution prior to oxidation.
PFOS: The pre and post oxidation concentrations are within the acceptable laboratory tolerance limits for reproducibility

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PFAS "DARK MATTER"

- Typical PFAS analyses report 20-50 PFAS
- It is well understood that there are thousands of PFAS compounds present in the environment, most are unknown or uncharacterized:

  "Dark Matter"

- PFAS Dark Matter can:
  - Break down or transform into PFAS that are measured
  - Contribute toxicity risk beyond that identified by the currently reported PFAS
- How do you accurately assess site risk or required remedial effort with this unknown?
- The Total Oxidizable Precursors (TOPs) assay gave us a glimpse of the Dark Matter but most now agree it is not a full solution.
  - Not fully quantitative
  - High sample variability.
  - Does not necessarily capture all of the Dark Matter

The answer… Total Organic Fluorine (TOF)

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FIRST COMMERCIALLY VIABLE CIC-TOF METHOD


Science of the Total Environment 673 (2019) 384–391

Contents lists available at ScienceDirect

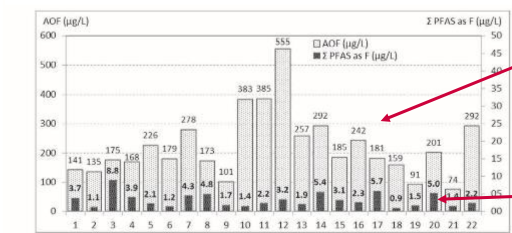
Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

ELSEVIER

Determination of adsorbable organically bound fluorine (AOF) and adsorbable organically bound halogens as sum parameters in aqueous environmental samples using combustion ion chromatography (CIC)

Total Organofluorine vs Σ PFAS in Wastewater



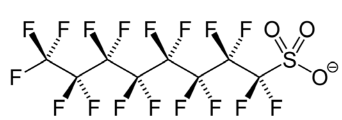
- Semi-automated SPE
  - Isolate organofluorine from inorganic fluorine
- Automated combustion
  - Organofluorine converted to HF and trapped in water.
- Automated transfer to ion chromatograph.
- Total organofluorine in wastewater typically 100x higher than sum of PFAS suggests.

Reference: von Abercron *et.al.*: *Sci. Tot. Environ.*, 2019, 673, 384-391

WHAT DO TOF RESULTS MEAN?

Remember…

TOF by CIC is measuring the fluorine contribution from all of the fluorine-containing compounds in the sample



PFOS
($C_8F_{17}SO_3^-$)

Mol. Wt. = [8 x C(12.011)] + [17 x F(18.998)] + [1 x S(32.065)] + [3 x O(15.999)]

= 96.088 + 322.966 + 32.065 + 47.997

= 499.116

Fluorine Contribution = 322.966 ÷ 499.116

= 64.7 %

Measured amounts…

PFOS (by LC/MS/MS) = **250 ng/L PFOS**

F_{total} (by CIC) = 0.647 x 250 ng/L

= **162 ng/L F**

"REAL WORLD" SAMPLES – LC/MS/MS vs. TOF-CIC

Sample #	6:2 FTS (µg/L)	PFOS (µg/L)	PFHxS (µg/L)	Σ PFAS by LC/MS/MS (µg/L)	Calculated Organic Fluorine[1] (µg/L)	TOF by CIC (µg/L)	Increase
PC-11	13	12	0.7	25.7	10	23	2.3 x
MW-12	<0.3	3.5	1.1	4.6	4	50	12.5 x
Petroseal 3%	53,000	<RDL	<RDL	53,000	30,500	>>2,400,000	> 80 x

1) **Calculated based on LC/MS/MS results**

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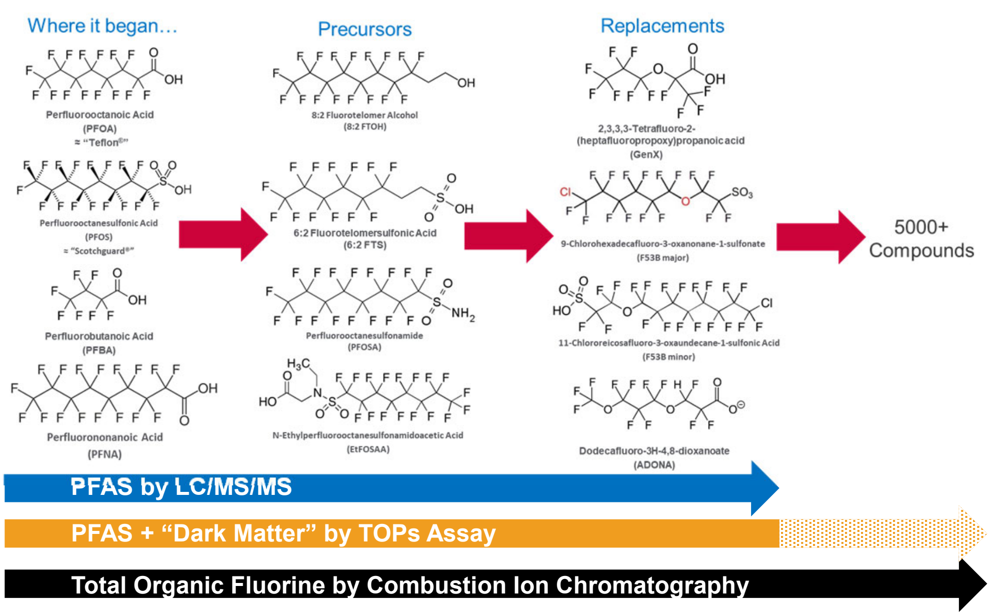
PFAS – ANALYTICAL OPTIONS



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ADVANTAGES AND LIMITATIONS

Test Name	Problem Statement	Advantages	Limitations
PFAS by LC/MS/MS	• Characterization and quantitation of individual PFAS at ultra trace levels • Regulatory compliance • Risk Assessment	• Provides accurate concentrations for individual PFAS • 1-2 ng/L reporting limits meets all current regulatory standards	• Higher cost test • "Targeted" analysis • 30-40 individual compounds …out of a potential 5000+ PFAS
Total Oxidizable Precursors (TOPs) Assay	• Characterization and quantitation of individual PFAS at ultra trace levels • Regulatory compliance • *Indication* of total PFAS	• Provides accurate concentrations for individual PFAS • Indicates the presence of PFAS not measured by LC/MS/MS • ("Dark Matter")	• High cost • Labor intensive assay…longer turnaround times • High sample variability • Not fully quantitative • Does not necessarily provide a "total" PFAS result
Total Organic Fluorine (TOF)	• *Measure* of total PFAS • "Is my sample "PFAS-free?"	• Provides concentration of organic fluorine, which is representative of the presence or absence of PFAS • Less labour intensive • Lower priced analysis	• Reporting limits: - 600 ng/L (total F) in water - 200-700 ng/g (total F) in soil • Non-selective analysis

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WHEN TO USE WHICH TOOLS?

Analytical Need	PFAS by LC/MS/MS	TOPs Assay	TOF by CIC
Regulatory Compliance	✓		
Site Characterization	✓	(✓)	
Contaminant Delineation	✓	✓	(✓)
Completeness of Remedial Action	(✓)	✓	✓
Site Risk (Future Liability)		✓	✓
PFAS-Free AFFF			✓

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BUREAU VERITAS PFAS TOOL KIT

PFAS by LC-MS/MS

- Report specific PFAS chemicals with low reporting limits
- $$
- Compliant with modified EPA Methods 537.1 and 533.1
- Bureau Veritas Accredited in Canada (SCC), many US states (NELAP) and US DoD (QSM Ver. 5.3)

TOPs Assay

- Report specific PFAS chemicals with low reporting limits – BEFORE & AFTER sample oxidation to simulate natural processes
- $$$
- Compliant with modified EPA Methods 537.1 and 533.1
- Bureau Veritas Accredited in Canada (SCC) and many US states (NELAP)

TOF by CIC

- Report total organofluorine from 'all' PFAS in the sample
- $
- No current EPA method; Bureau Veritas method based on ISO 9562:2014 "*Determination of adsorbable organically bound halogens (AOX)*"
- Bureau Veritas Accreditation through Standards Council of Canada (SCC)

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ACKNOWLEDGEMENTS

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Adam Robinson
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Project Management
Lori Dufour, BSc
Stephanie Pollen, BSc

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Shaping a World of Trust

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