BUREAU VERITAS

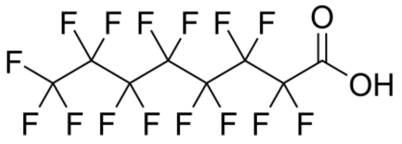
TOTAL ORGANIC FLUORINE (TOF) BY COMBUSTION ION CHROMATOGRAPHY

A New Tool for Monitoring PFAS Impacts

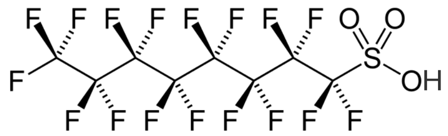
Terry Obal, Lusine Khachatryan, Alicia Wilson and Heather Lord

ENVIRONMENTAL INTEREST IN PFAS

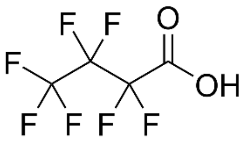
Where it began…



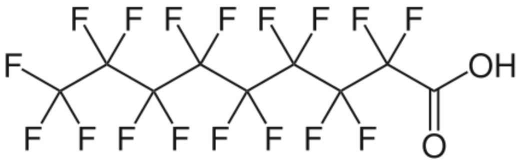
Perfluorooctanoic Acid
(PFOA)
≈ "Teflon®"



Perfluorooctanesulfonic Acid
(PFOS)
≈ "Scotchguard®"

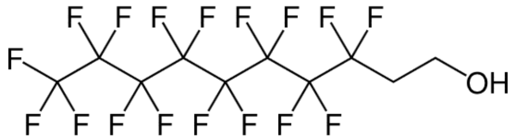


Perfluorobutanoic Acid
(PFBA)

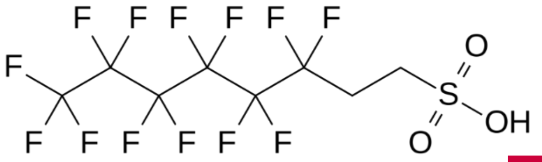


Perfluorononanoic Acid
(PFNA)

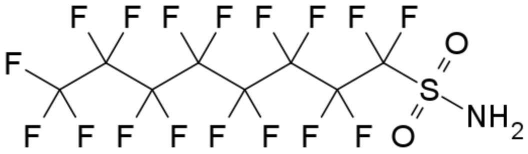
Precursors



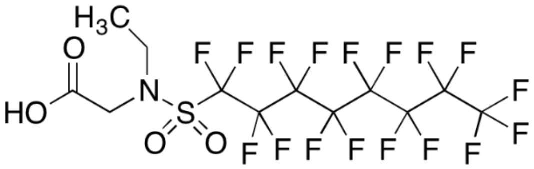
8:2 Fluorotelomer Alcohol
(8:2 FTOH)



6:2 Fluorotelomersulfonic Acid
(6:2 FTS)

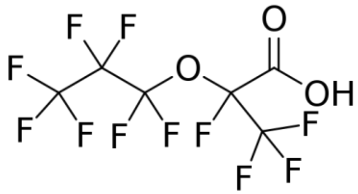


Perfluorooctanesulfonamide
(PFOSA)

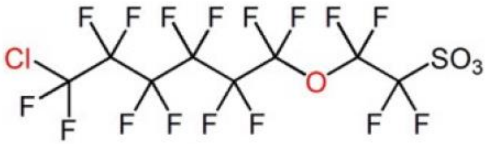


N-Ethylperfluorooctanesulfonamidoacetic Acid
(EtFOSAA)

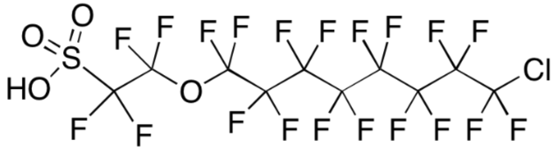
Replacements



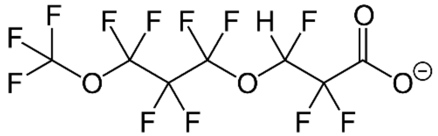
2,3,3,3-Tetrafluoro-2-
(heptafluoropropoxy)propanoic acid
(GenX)



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



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



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

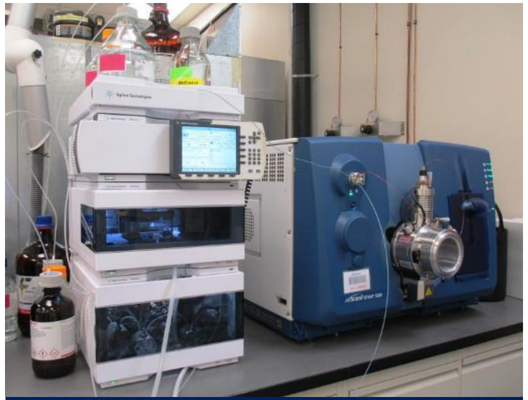
5000+
Compounds

Environmental
Transformation

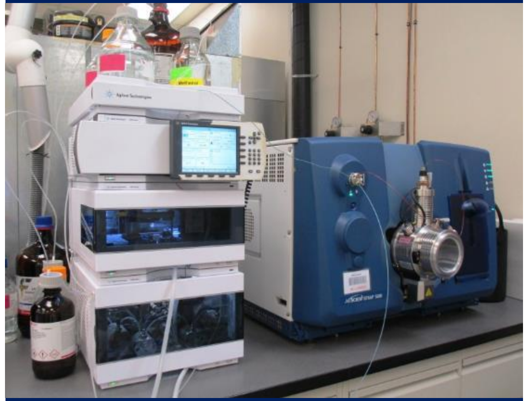
THE EVOLUTION OF THE PFAS “TOOLKIT”

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)

PFAS BY LC/MS/MS (TARGET COMPOUNDS): REGULATORY COMPLIANCE

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
Atlantic RBCA EQS	Human Health	**0.2**	**0.6**	**30**	**15**	**0.6**	**0.2**	**0.2**	**0.2**	**0.02**	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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TARGET PFAS AND PRECURSORS BY LC/MS/MS (TOPS ASSAY): REGULATORY COMPLIANCE + INDICATION OF OTHER PFAS

Maxxam Job [redacted]		RESULTS							
Maxxam ID		[redacted]							
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

PFAS "DARK MATTER"

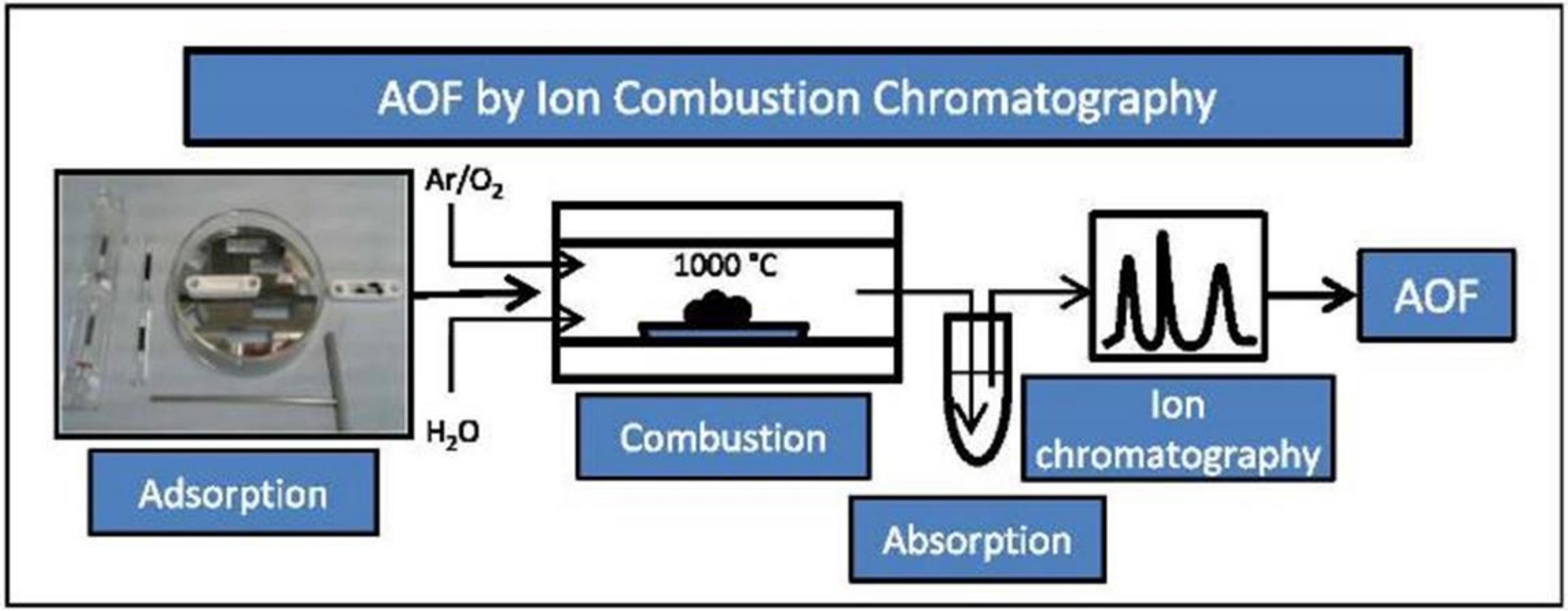
- Typical PFAS analyses report 20-50 PFAS
- It is well understood that there are thousands of PFAS compounds present in the environment, most are unknown or uncharacterized:

  "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)

COMBUSTION ION CHROMATOGRAPHY (CIC)



- Adsorption
- Combustion
- Absorption
- Ion Chromatography (F^-)

FIRST COMMERCIALLY VIABLE CIC-TOF METHOD

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

Contents lists available at ScienceDirect

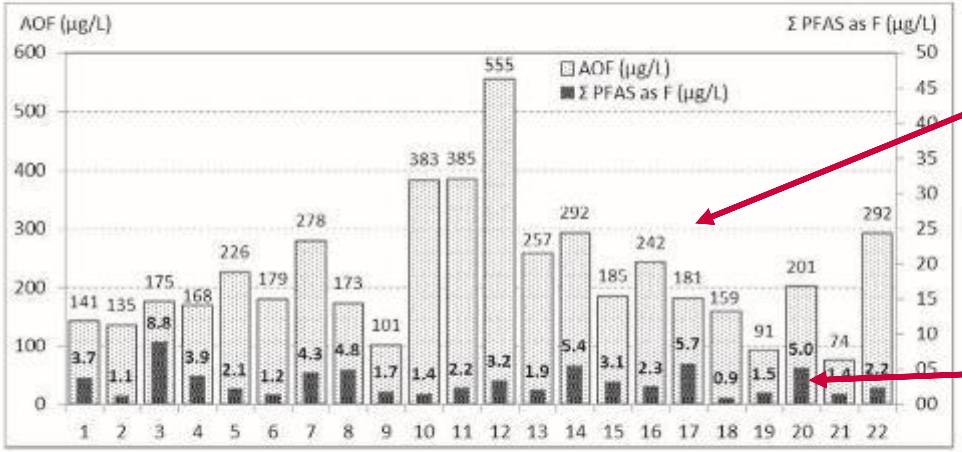
Science of the Total Environment

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



Organofluorine

Σ PFAS (as F)

- 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

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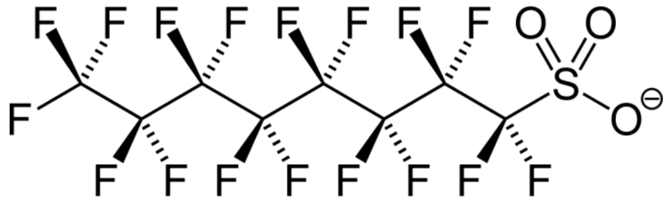
WHAT DO TOF RESULTS MEAN?

Remember…

TOF by CIC is measuring the fluorine contribution from all of the fluorine-containing organic 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	15.7	23	1.5 x
MW-12	<0.3	3.5	1.1	4.6	2.9	50	17 x
Petroseal 3%[2]	53,000	<RDL	<RDL	53,000	30,500	>>2,400,000	> 80 x

[1] **Calculated based on LC/MS/MS results**

[2] **Supplier Information:** ***“…readily biodegradable and virtually nontoxic to aquatic organisms. It is based on a natural protein foaming agent and contains no harmful synthetic detergent… can be successfully treated in biological wastewater treatment systems.”***

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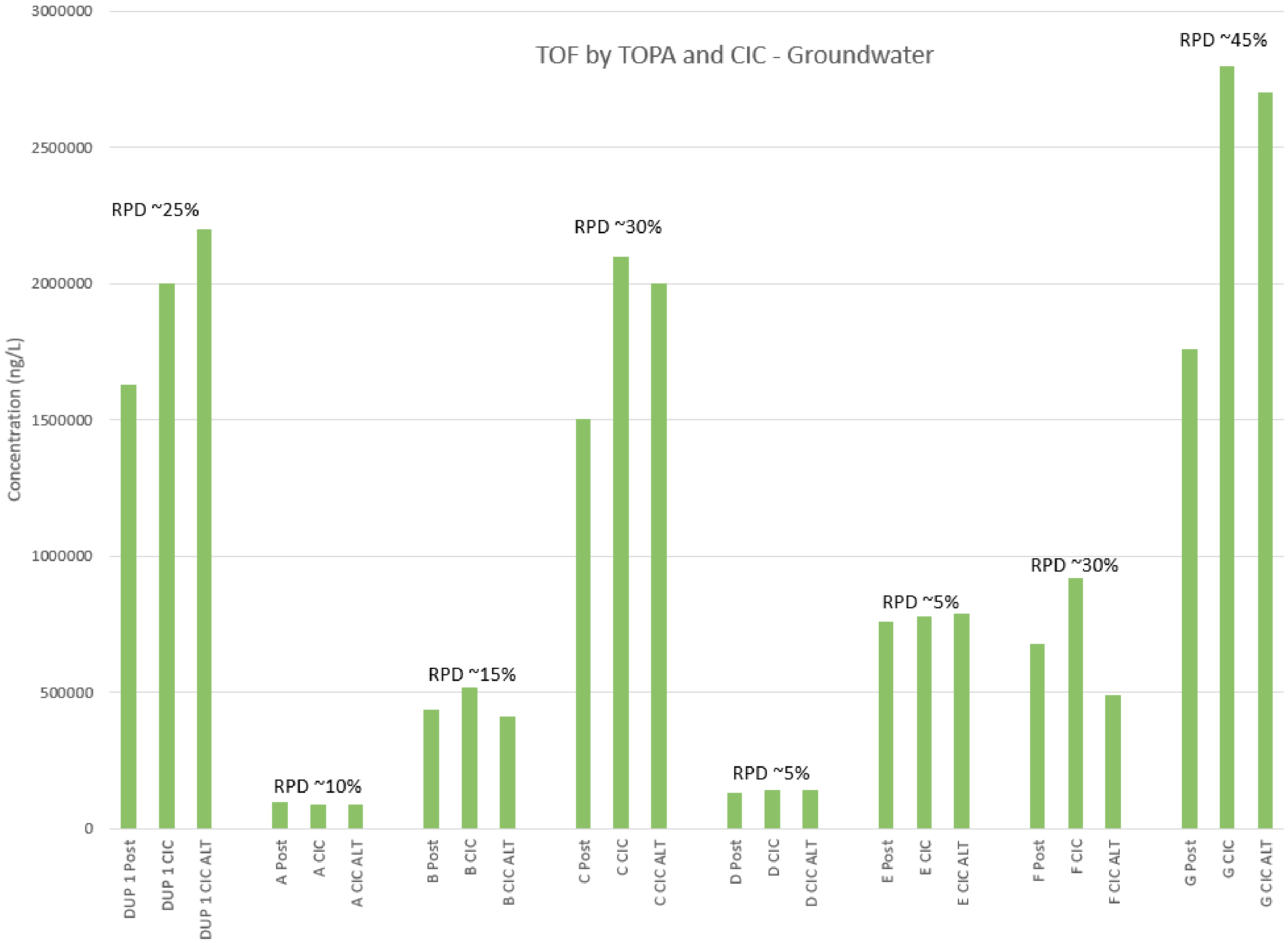
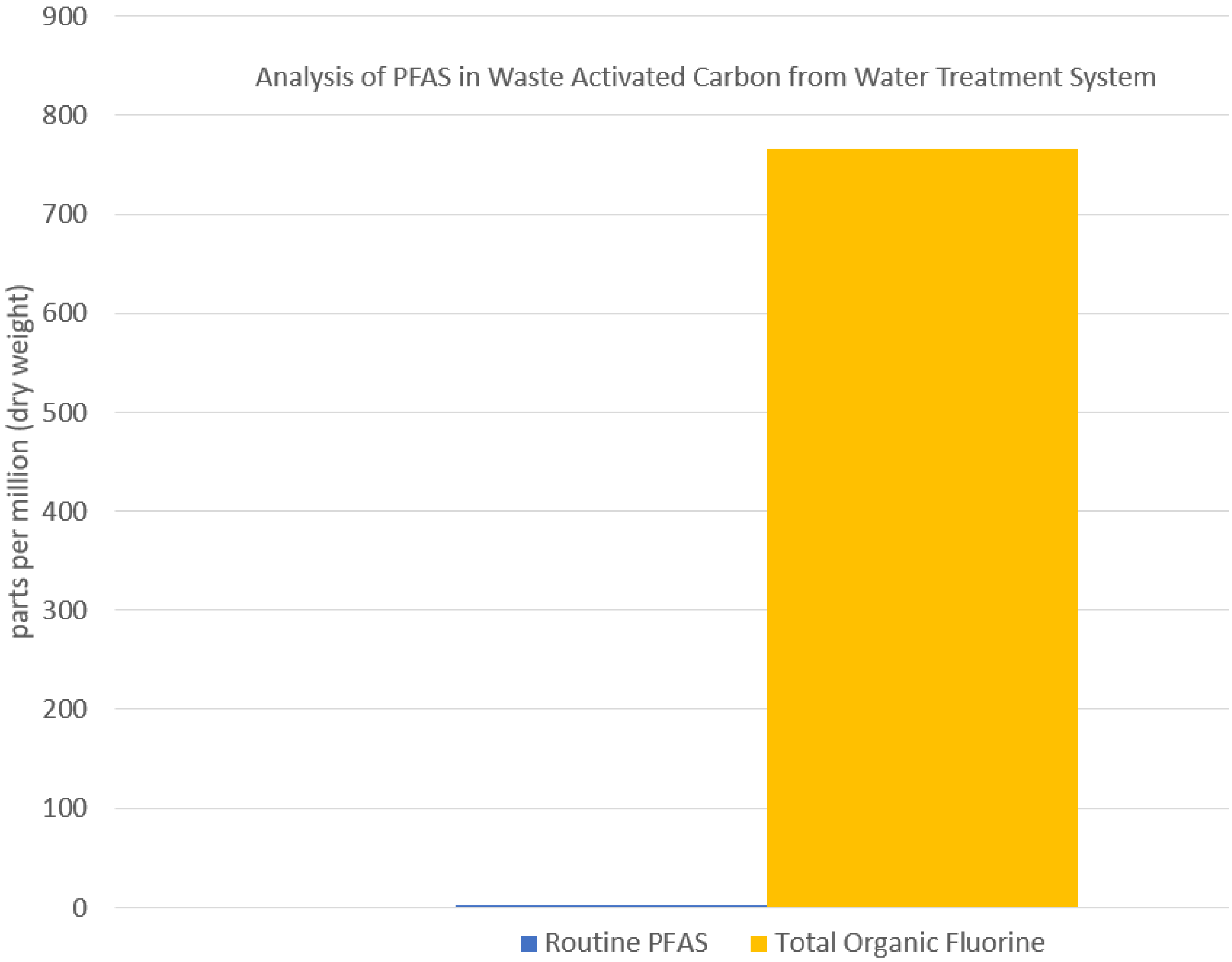
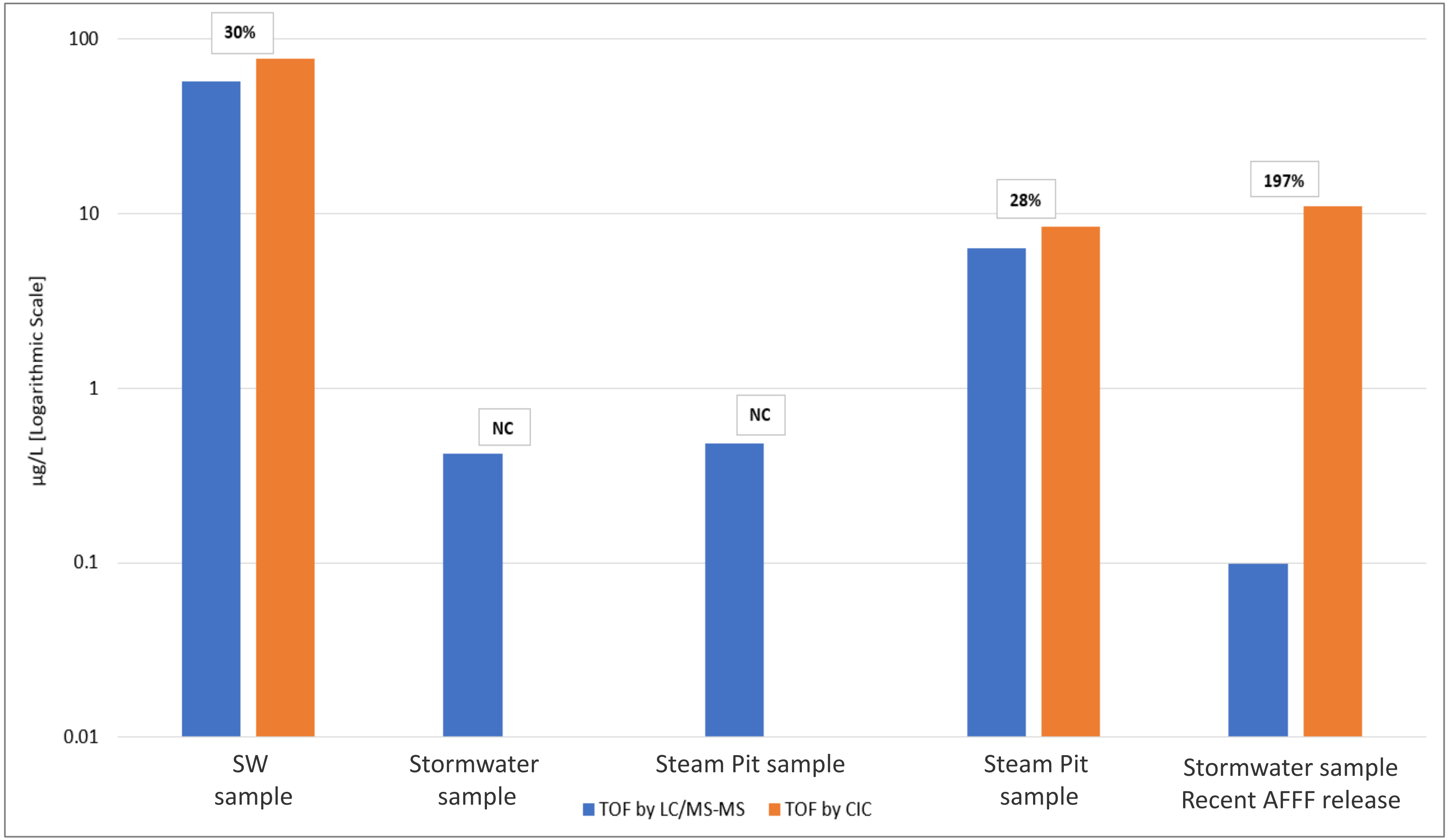
GROUNDWATER
TOPs ASSAY (ΣPFAS) vs. TOF (CIC)



WASTE ACTIVATED CARBON TOF (ΣPFAS) vs. TOF (CIC)



SURFACE WATER:
TOF (ΣPFAS) vs. TOF (CIC)



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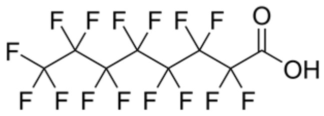
PFAS – ANALYTICAL OPTIONS

Where it began…


Perfluorooctanoic Acid
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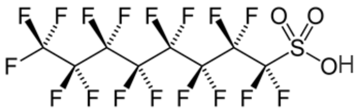
≈ "Teflon®"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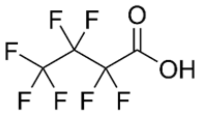
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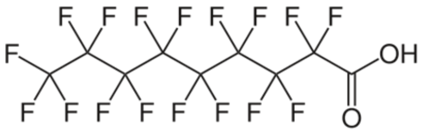
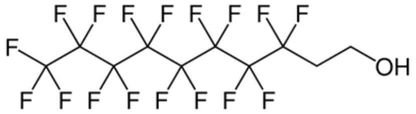

Perfluorononanoic Acid
(PFNA)

Precursors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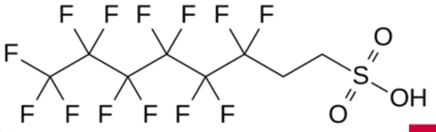
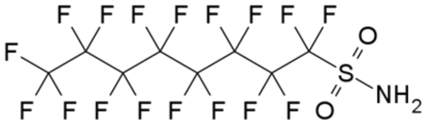

6:2 Fluorotelomersulfonic Acid
(6:2 FTS)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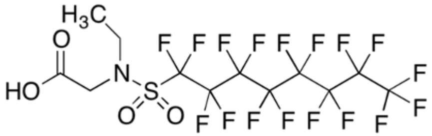
N-Ethylperfluorooctanesulfonamidoacetic Acid
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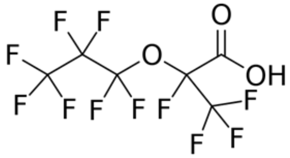
Replacements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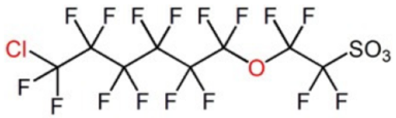
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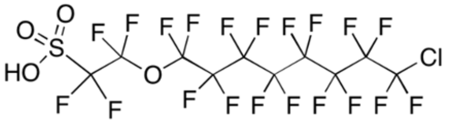
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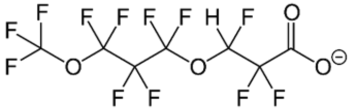
(F53B minor)


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

5000+
Compounds

PFAS by LC/MS/MS

PFAS + "Dark Matter" by TOPs Assay

Total Organic Fluorine by Combustion Ion Chromatography

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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

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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Adam Robinson
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Lori Dufour, BSc
Stephanie Pollen, BSc

Research & Development

Heather Lord, PhD
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