PFAS 2018:

Understanding PFAS Analysis and Reporting

When you think PFAS, think…

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When you think PFAS, think…

SCOTCHGARD™ PROTECTOR 3M

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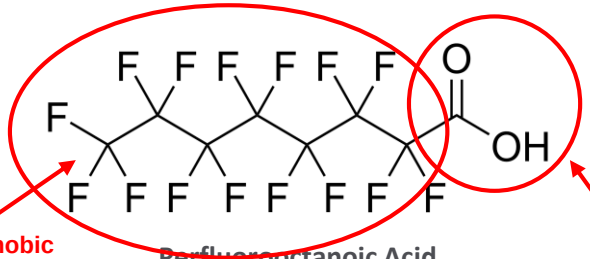
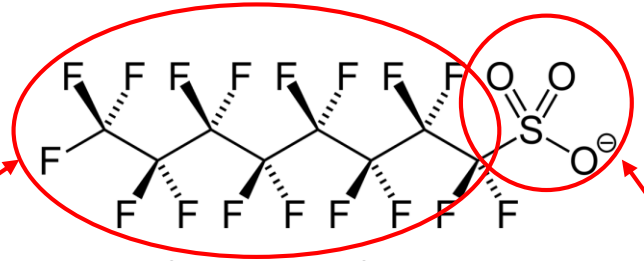
PFAS – Target Compounds



Hydrophobic

Hydrophilic

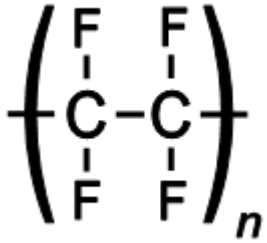
Perfluorooctanoic Acid
(PFOA)
"Teflon®"

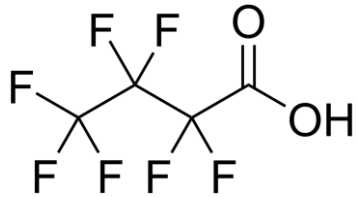


Hydrophobic

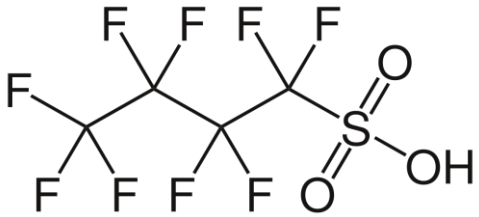
Hydrophilic

Perfluorooctanesulfonic Acid
(PFOS)
"Scotchguard®"

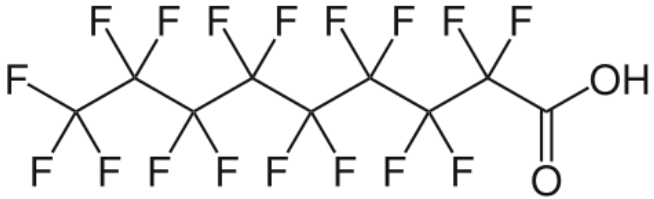




Perfluorobutanoic Acid
(PFBA)



Perfluorobutanesulfonic Acid
(PFBS)



Perfluorononanoic Acid
(PFNA)

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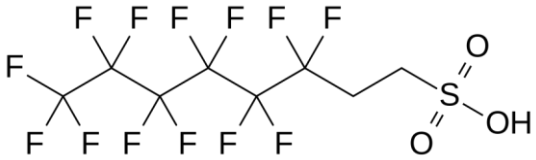
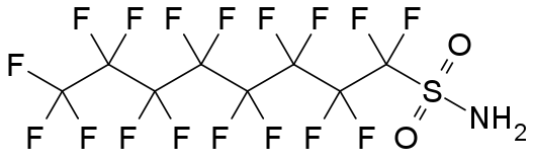
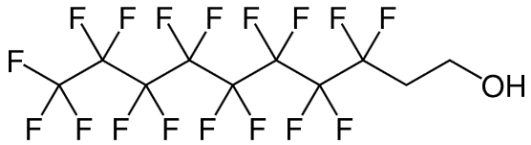
PFAS – Precursor Compounds



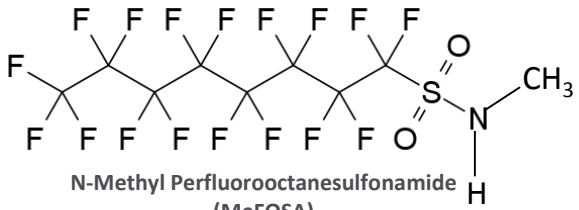
6:2 Fluorotelomersulfonic Acid
(6:2 FTS)



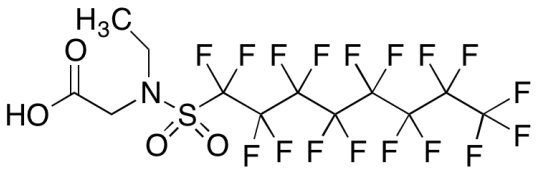
Perfluorooctanesulfonamide
(PFOSA)



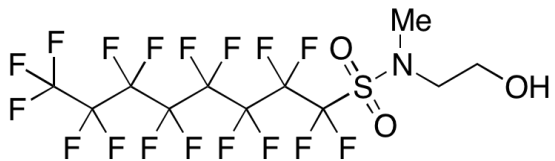
8:2 Fluorotelomer Alcohol
(8:2 FTOH)



N-Methyl Perfluorooctanesulfonamide
(MeFOSA)



N-Ethylperfluorooctanesulfonamidoacetic Acid
(EtFOSAA)



N-Methylperfluorooctanesulfonamidoethanol
(MeFOSE)

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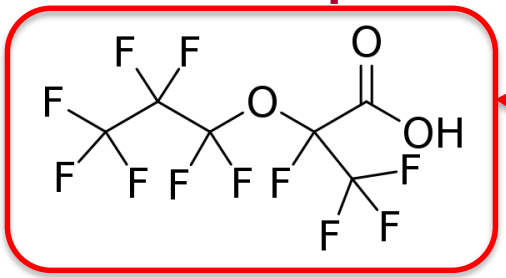
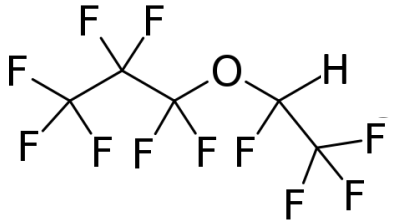
PFAS – Replacement Compounds



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

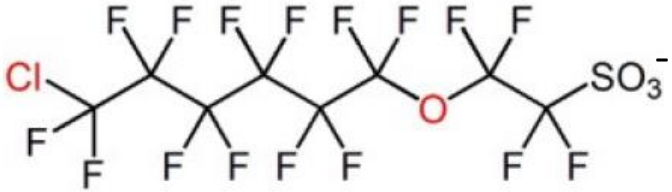
(FRD-902)

GenX



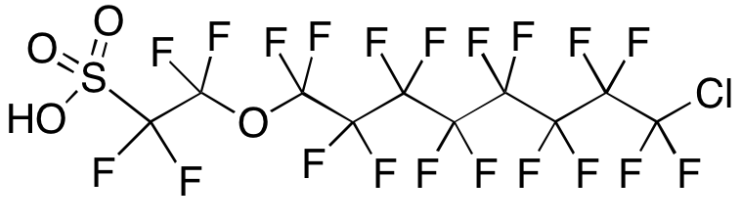
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether

(E1)



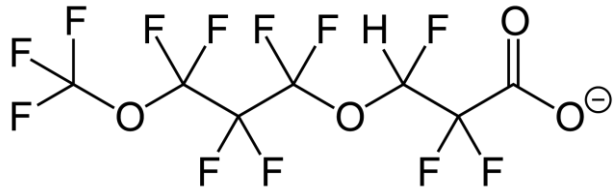
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate

(F53B major)



11-Chlororeicosafluoro-3-oxaundecane-1-sulfonic Acid

(F53B minor)



Dodecafluoro-3H-4,8-dioxanoate

(ADONA)

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Why do we care?

PFOA, PFOS D
Composting Fa
County

By Jorja Roman
Updated Monday, March 13, 2017 at 08

WAMC NORTHEAST PUBLIC RADIO (/)

WAMC
BBC World Service

Midday Magazine (/programs/midday-magazine-wamc)

NYS DOH Discusses PFOS Blood Test Results In Newburgh

By ALLISON DUNNE • MAR 31, 2017

recordonline.com

Donate (https://goo.gl/vJCEQ2)

TIMES HERALD-RECORD

aims vs. Newburgh over toxic
water

Newburgh
To Sue The City Over PFOS

By ALLISON DUNNE • MAR 30, 2017

According to *The Philadelphia Inquirer*, tests have shown "levels 20 to thousands of times higher in some

lion to settle
awsuit

Agreement with state of Minnesota comes just as trial was to start

By Marc S. Reisch

[+]Enlarge

3M has agreed to pay $850 million to the state of Minnesota to resolve a $5 billion lawsuit over drinking water contaminated with fluorochemicals such as perfluorooctanoic acid (PFOA). 3M resolved the case on Feb. 20, just as it was about to go to trial in state court.

The settlement comes in the form of what 3M

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Toxicity

Animals:

Int. J. Hyg. Env. Health. 2017, 220, 766-775.

Minireview

Recent experimental results of effects of perfluoroalkyl substances in laboratory animals – Relation to current regulations and guidance values

Hellmuth Lilienthal[a,*], Hermann H. Dieter[b], Jürgen Hölzer[a], Michael Wilhelm[a]

The range of guideline limits established is related to:

- interspecies differences in the available studies.
- difference in half-lives between animals and humans.

Humans have higher internal exposures than animals.

Humans:

Environmental Health Perspectives 2014, 122, 1028-1039

The Navigation Guide—Evidence-Based Medicine Meets Environmental Health: Systematic Review of Human Evidence for PFOA Effects on Fetal Growth

Paula I. Johnson,[1] Patrice Sutton,[1] Dylan S. Atchley,[1] Erica Koustas,[2] Juleen Lam,[2] Saunak Sen,[3] Karen A. Robinson,[4,5,6] Daniel A. Axelrad,[7] and Tracey J. Woodruff[1]

Associations between low dose exposures and:

- development and immune responses in children.
- fat metabolism in adults.

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Analytical Methods and Reporting

Method Summary:

- Water methods based on USEPA 537
  - SPE weak anion exchange extraction
  - LC/MS/MS
- Soil methods based on ASTM D7968-14
  - pH adjusted aqueous leach/SPE weak anion exchange extraction
  - LC/MS/MS
- Industry accepted best practices:
  - LC/MS/MS
  - Minimum 2 MRM transitions where possible
  - Isotope Dilution required for quantitation
  - No Blank correction

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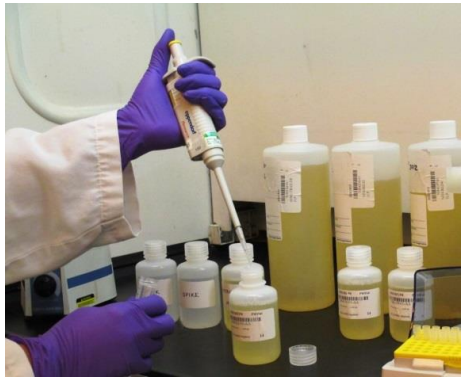
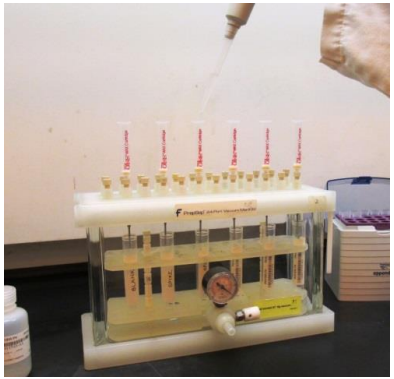
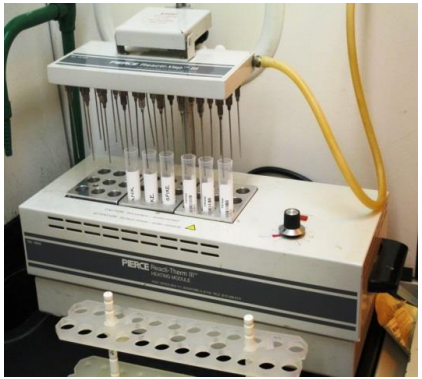
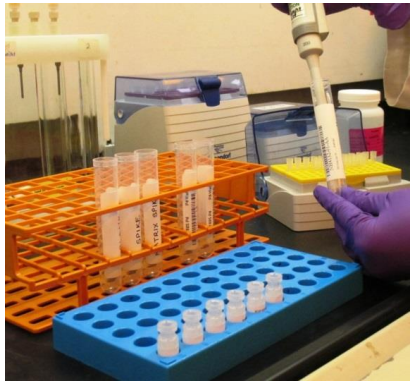
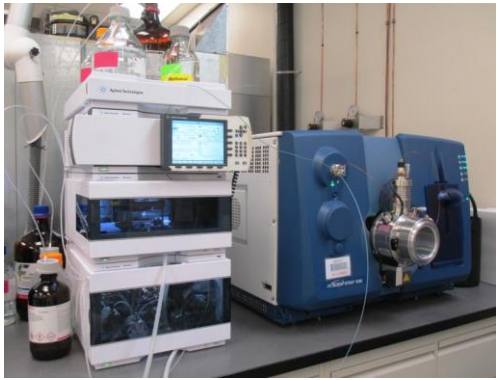
Analytical Methods











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Turbidity or samples containing sediment

- Do NOT filter. Absorption to filters.
- Centrifuge, or allow sample to settle, prior to sampling supernatant.
- For low levels, where whole bottle is extracted, becomes a non-issue (may introduce a high bias).

PFAS	Filtered (ng/L)	Centrifuged (ng/L)
PFOS	29.3	96.6

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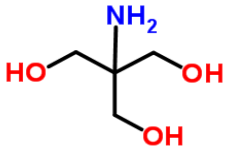
Trizma Preservative



TRIS: tris(hydroxymethyl)aminomethane
TRIZMA: 2-Amino-2-(hydroxymethyl)-1,3-propanediol

Purpose:
To buffer the samples (pH ≈ 7), remove free chlorine in chlorinated finished waters and prevent microbial degradation. [According to reference method EPA 537]

- PFAS are considered chemically, thermally and biologically stable, and resist typical environmental degradation processes. Microbes can degrade precursor molecules, making more PFOS / PFOA
- Preservative added: 5g/L
- Should it only apply to chlorinated water supplies? **YES**

Alternative Preservation:
An alternative to Trizma (if the clients do not receive bottles from Maxxam) is *Sodium Thiosulfate* which is also a chlorine neutralizer.

Shoemaker, et. al.: "Development of a U.S. EPA Drinking Water Method for the Analysis of Selected Perfluoroalkyl Acids by Solid-Phase Extraction and LC-MS-MS". *J. Chrom. Sci.*, Vol. 47, pp. 3-11 (2009)

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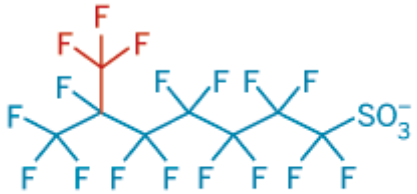
Important Considerations:

Branched vs. Linear Isomers

- When interpreting PFOS data, it is important to understand if it is being quantified as the linear or branched chain isomers
- Technical PFOS is a mixture of linear and branched chain PFOS isomers; Linear PFOS is typically pure

PFOS Linear Isomer



PFOS Branched Isomer (P6MHpS)

Isomer	Wellington[1]	Sigma-Aldrich/ Fluka[2]
Normal (linear)	68.9	82.2
Monomethyl	17.9	9.8
Isopropyl	10.8	10.0
Alpha	1.9	1.2
T-Butyl	0.2	0.4
Dimethyl	0.3	0.5
Total Branched	31.1	21.4

[1] Lot #TPFOS0405: Wellington Laboratories, Guelph, ON, Canada
[2] Batch #312421000: Sigma-Aldrich/Fluka, Buchs, Switzerland

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Measurement Uncertainty and the Value of Isotope Dilution

Measurement Uncertainty Definition

- A parameter associated with the result of the measurement, that characterizes the dispersion of the values that could be reasonably attributed to the measurand.*

* ISO *Guide to the Expression of Uncertainty in Measurement*

- A value that gives an idea of variability within a set of measurements that is specific to a sample or group of samples.

±value specific to the result

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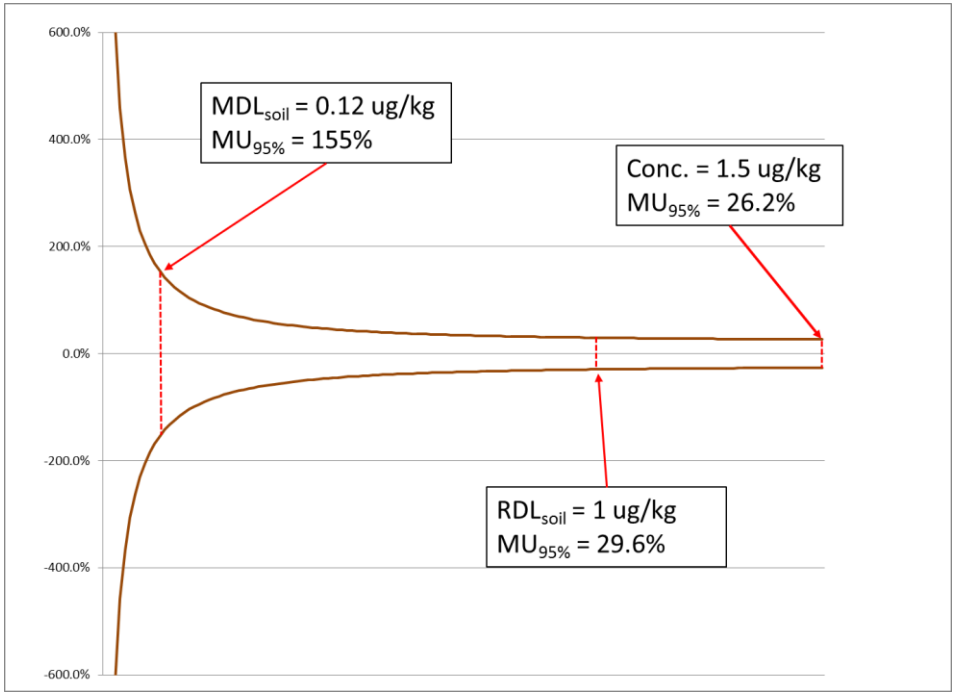
Interpretation of Low Level Data

PFOS in Soil by LC/MS/MS



- Variability in analytical results increases as concentrations approach the limits of detection or the upper end of the system's linear range.

MDL (LOD) ~ 3 x S.D.

RDL (LOQ) ~ 3 x LOD or ~ 10 x S.D

What this means is that the level of confidence in the value reported at or above the RDL (LOQ) is much higher than the level of confidence reported at the MDL (LOD)

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PFOS – Laboratory MU

		MDL	RL	Low	Medium	High
Water	Concentration (ug/L)	0.0033	0.02	0.10	5.0	50
	MU (%)	129%	31%	23%	23%	23%
	Range (ug/L)	**"0.000" - 0.007**	**0.01 - 0.03**	**0.08 - 0.12**	**3.9 - 6.1**	**39 - 61**
Soil	Concentration (ug/kg)	0.12	1	2.0	10	20
	MU (%)	154%	30%	25%	23%	23%
	Range (ug/g)	**"0.00" - 0.31**	**0.7 - 1.3**	**1.5 - 3.5**	**7.7 - 12**	**15 - 25**

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Isotope Dilution LC/MS/MS

- IDMS provides greater accuracy than other calibration methods because it compensates for any matrix effects that may suppress recovery of the parameters being measured.
- Simply put…

  …the recovery of the labeled compound, which is not naturally present in the sample, is an exact representation of the recovery of the native compound which is present in the sample

- Ideal is to have as many isotopically labelled analogues as possible

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Total Oxidizable Precursors

PFAS Precursors

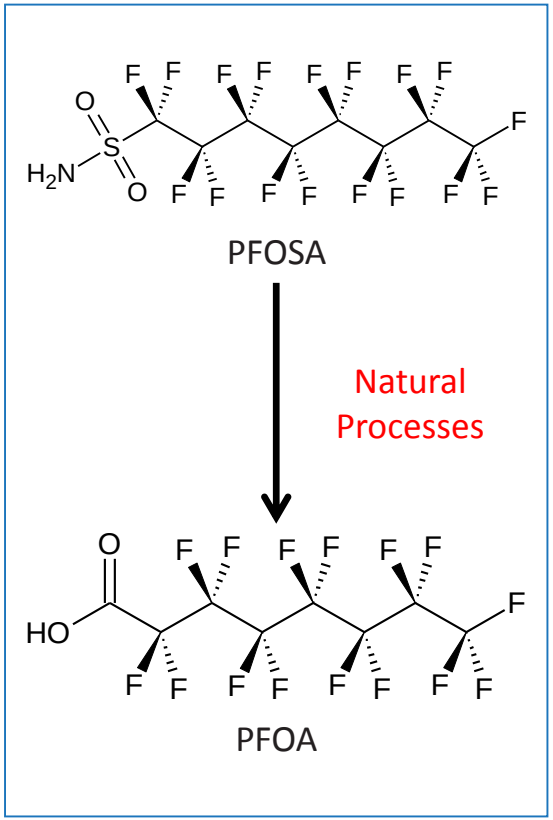
- PFAS such as PFOA and PFOS are directly released into the environment
- PFAS precursor compounds are also released along with PFOS and PFOA. The precursors are themselves PFAS.
- Target PFAS and selected precursors are monitored in the environment for remedial action

Problem Statement

- Pool of potential precursors is large and generally unknown – PFAS "Dark Matter"
- Precursors can be transformed, through biological and environmental processes, to target PFAS of interest such as PFOS/PFOA
- Overlooking precursor pool may lead to underestimates of target PFAS of interest

Requirement

- A method to estimate the potential magnitude of the precursor pool



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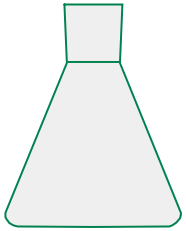
TOPs Assay[1]

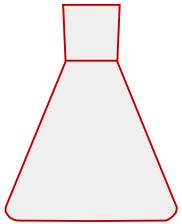
Before TOP Assay



Sample

Oxidation

After TOP Assay



Reacted Sample

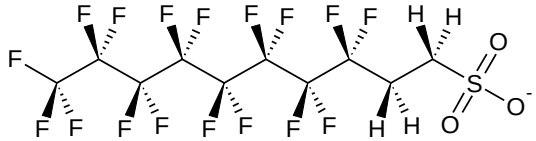
Quantify targets and precursors

LC/MS/MS Analysis

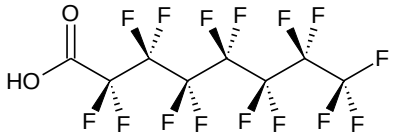
Quantify targets and precursors

LC/MS/MS Analysis

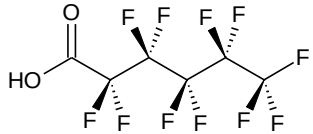
PFAS Precursor



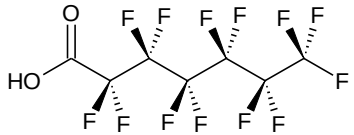
8:2 Fluorotelomer sulfonate
(C_{10} total, C_8 containing F)



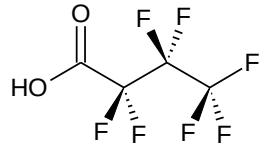
Perfluorooctanoic acid (C_8)



Perfluorohexanoic acid (C_6)



Perfluoroheptanoic acid (C_7)



Perfluorobutanoic acid (C_4)

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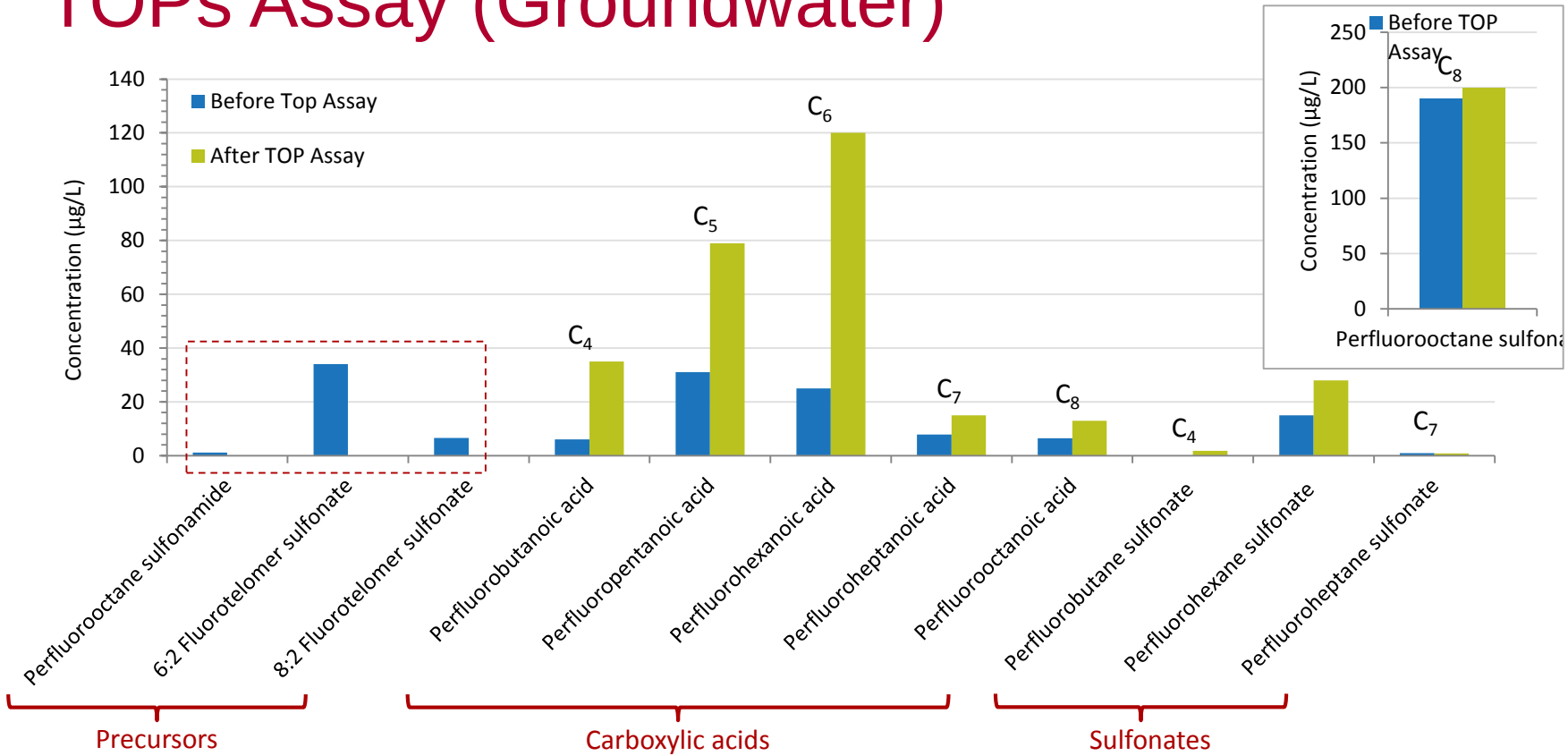
[1]Houtz, E.F. and Sedlak, D.L. (2012). *Environ. Sci. Technol.*, 46, 9342-9349.

TOPs Assay (Groundwater)



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Considerations

- Method limited only to compounds that are oxidizable by the Assay
  - the precursor pool may be underestimated if not all precursors are transformed/oxidized
- Not all of the PFAS that are produced during the TOP assay necessarily originate from only the 9 precursors that are monitored
  - pool of precursors is large
- There could be numerous target PFAS that are produced beyond the 16 that are currently monitored
- It is unknown if all precursors are fully oxidized by the TOP assay
- How representative is the TOP assay of the transformations that would occur naturally? - Timescale

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What the TOPs Assay Offers

- Quick and simple method of oxidation that can be performed on soil and water
- Provides estimate of target PFAS increase that could occur at a contaminated site
- Potential indication of which precursors are being oxidized
- Assay will become more informative as more PFAS targets and precursors of concern are added to the analysis list
- Assay report provides concentrations of 25 PFAS before and after oxidation

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Regulatory Limits and Laboratory Reporting Limits

Regulatory Limits

- What were once guidance limits are being promulgated as regulated standards, particularly in drinking water
- BC only jurisdiction in Canada (to date) to legislate PFAS regulatory limits
  - PFOS, PFOA and PFBS regulated in water
  - PFOS, PFBS regulated in soil
- All other provinces and many US states have Health Advisories or guidelines…but this is changing

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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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Reporting:
RDL vs. MDL

Compound	Water			Soil		Tissue	
	RDL (µg/L)	MDL (µg/L)	*RDL (low) (µg/L)*	RDL (µg/kg)	MDL (µg/kg)	RDL (ng/g)	MDL (ng/g)
Perfluorobutanoic Acid (PFBA)	0.02	0.0066	***0.002***	1.0	0.11	1.0	0.38
Perfluorobutanesulfonic Acid (PFBS)	0.02	0.0019	***0.002***	1.0	0.17	1.0	0.27
Perfluoropentanoic Acid (PFPA)	0.02	0.0036	***0.002***	1.0	0.13	1.0	0.22
Perfluorohexanoic Acid (PFHxA)	0.02	0.0046	***0.002***	1.0	0.11	1.0	0.10
Perfluorohexanesulfonic Acid (PFHxS)	0.02	0.0040	***0.002***	1.0	0.13	1.0	0.18
Perfluoroheptanoic Acid (PFHpA)	0.02	0.0047	***0.002***	1.0	0.14	1.0	0.21
Perfluoroheptanesulfonic Acid (PFHpS)	0.02	0.0036	***0.002***	1.0	0.20	1.0	0.19
Perfluorooctanoic Acid (PFOA)	0.02	0.0053	***0.002***	1.0	0.060	1.0	0.11
Perfluorooctanesulfonic Acid (PFOS)	0.02	0.0033	***0.002***	1.0	0.12	1.0	0.11
Perfluorononanoic Acid (PFNA)	0.02	0.0046	***0.002***	1.0	0.084	1.0	0.16
Perfluorodecanoic Acid (PFDA)	0.02	0.0066	***0.002***	1.0	0.014	1.0	0.14
Perfluorodecanesulfonic Acid (PFDS)	0.02	0.0043	***0.002***	1.0	0.17	1.0	0.18
Perfluoroundecanoic Acid (PFUdA)	0.02	0.0037	***0.002***	1.0	0.13	1.0	0.14
Perfluorododecanoic Acid (PFDoA)	0.02	0.0057	***0.002***	1.0	0.13	1.0	0.15
Perfluorotridecanoic Acid (PFTrDA)	0.02	0.0034	***0.002***	1.0	0.20	1.0	0.10
Perfluorotetradecanoic Acid (PFTeDA)	0.02	0.0052	***0.002***	1.0	0.18	1.0	0.15

Recent References

Interstate Technology & Regulatory Council (ITRC) Fact Sheets:

Printed from: Interstate Technology & Regulatory Council (ITRC). 2018. PFAS Fact Sheets PFAS-1. Washington, D.C.: Interstate Technology & Regulatory Council, PFAS Team. http://pfas-1.itrcweb.org

PFAS Fact Sheets

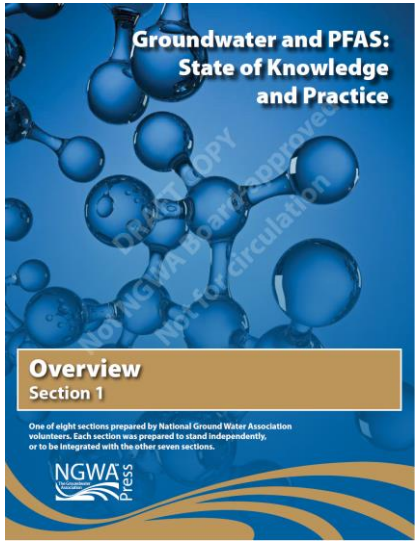
This page includes in the links for the ITRC PFAS fact sheets. The fact sheets are available as PDF files. Several tables of supporting information are published separately so that they can be updated periodically by ITRC. The fact sheet user should visit this page to access the current versions of the files.

An Introductory document (Spanish Version) has been prepared that briefly describes the contents of each of the fact sheets. An Introductory document has been prepared that briefly describes the contents of each of the fact sheets. This web site also includes a combined references list and acronyms list.

- Naming Conventions and Physical and Chemical Properties (updated 3-16-18)
- Regulations, Guidance, and Advisories (updated 1-4-18)
  - Section 4 Tables Excel file – (updated 7-16-18)
    - Table 4-1 presents the available PFAS water values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries)

https://pfas-1.itrcweb.org/fact-sheets/

National Groundwater Association:



http://www.ngwa.org/Media-Center/news/Pages/NGWA-now-accepting-public-comments-on-NGWA%E2%80%99s-Groundwater-and-PFAS-State-of-Knowledge-and-Practice.aspx

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