



PFAS Dark Matter: Per- and polyfluorinated precursors in soil and water

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Do You Know How Much PFAS Is On Your Site?

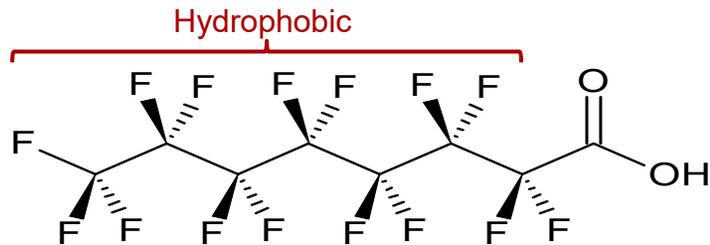
Presentation Outline

1. PFAS Background
2. Chemical and Physical Properties
3. Problem of PFAS Precursor Transformation
4. TOP Assay
5. Experimental Water and Soil Data
6. Method Considerations

PFASs

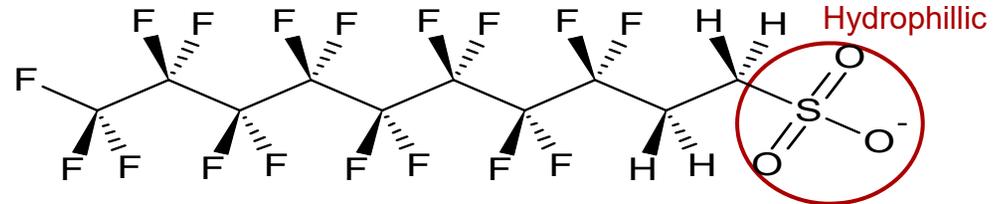
What are PFASs?

- PFASs are Per- and PolyFluorinated AlkyL Substances. Exclusively anthropogenic.
- Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophilic end group
- Include a diverse range of compounds with a variety of chain lengths and end groups



Perfluorooctanoic acid

- PFOA
- Teflon®



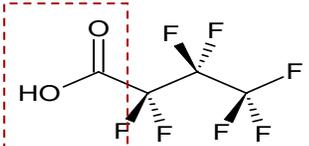
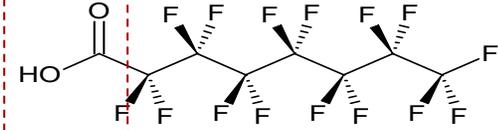
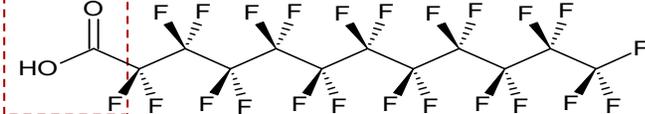
8:2 Fluorotelomer sulfonate

- 8:2 FTS

Perfluorocarboxylic acids

PFAS crash course:

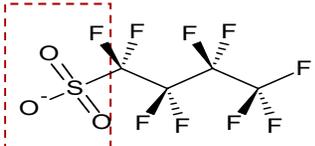
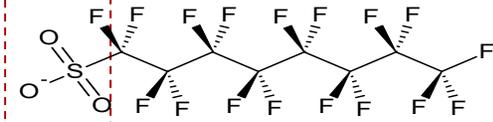
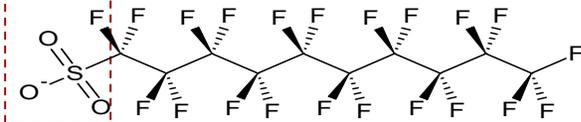
- Within PFAS, compounds are further organized into classes
- PFOA is part of the perfluorocarboxylic acids (PFCA) class

	Structure	# of Carbons	Name
PFCAs		4	Perfluorobutanoic acid (PFBA)
		8	<u>Perfluorooctanoic acid (PFOA)</u>
		12	Perfluorododecanoic acid (PFDoA)

Perfluorosulfonates

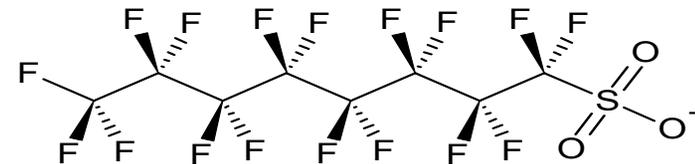
PFAS crash course continued...

- Perfluorosulfonates is another important class
- PFOS belongs to this class

	Structure	# of Carbons	Name
Perfluoro-sulfonates		4	Perfluorobutane sulfonate (PFBS)
		8	<u>Perfluorooctane sulfonate (PFOS)</u>
		10	Perfluorodecane sulfonate (PFDS)

Chemical and physical properties

- CF bonds are very strong
 - End groups may be reactive and transformed
- Good stability under heat and chemical stress
- Low volatility
- Soluble in water
- Good surfactants
- Sorb to a variety of materials



Perfluorooctane sulfonate

- PFOS
- Scotchguard®

Where do they come from?

Industrial Uses

- PFAS are used in a variety of applications because of their chemical and physical properties. These include:
 - Industrial polymers (Teflon® - PFOA)
 - Stain repellants (Scotch Guard® - PFOS)
 - Aqueous film forming foams (AFFF) – fire fighting applications

Sources

- Can be found anywhere at differing (generally lower) concentrations,
- Areas of elevated concentration and concern are:
 - Airports
 - Run-off from incidents of fire
 - Landfill leachate
 - WWTP effluent

Toxicology

- Commercial PFAS detected in humans - possible sources of exposure include drinking water, food and dust/ambient air
- Persistent
- Bioaccumulate
- Toxicity of certain PFASs such as PFOA and PFOS has been observed in some rodent studies
- Potential for deleterious effects in humans is suspected and is under further study
- PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POP) in May 2009

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 From the journal:
Environmental Science: Processes & Impacts

Emerging investigator series: a 14-year depositional ice record of perfluoroalkyl substances in the High Arctic

[John J. MacInnis](#)^a [Katherine French](#)^b [Derek C. G. Muir](#)^b [Christine Spencer](#)^b [Alison Criscitiello](#)^c [Amila O. De Silva](#)^{*b} and [Cora J. Young](#)^{*a}

Regulatory status

In Canada:

- Risk management strategies seek to have environmental PFOS concentrations as low as possible, prevent re-introduction to market, and address remaining uses (restrictions, exemptions, BMP etc.)
- On and after May 29, 2013, manufacture, use, sale, import of PFOS and PFOS-containing products is prohibited in Canada

Limit Guidelines:

Jurisdiction	PFAS	Drinking Water	Soil Concentration (µg/g)		
		Concentration (µg/L)	Residential	Commercial	Industrial
Canada - Health Canada	PFOA	0.2	0.85	1.28	12.1
	PFOS	0.6	2.1	3.2	30.5
U.S.A - EPA	PFOA	0.07	-	-	-
	PFOS	0.07	-	-	-
U.S.A - EPA Region IV	PFOA	-	16	-	-
	PFOS	-	6	-	-

*When both PFOA and PFOS are present, their combined ratio of measured to screening value should not exceed 1

** 0.07 µg/L combined when both PFOA and PFOS are present in drinking water

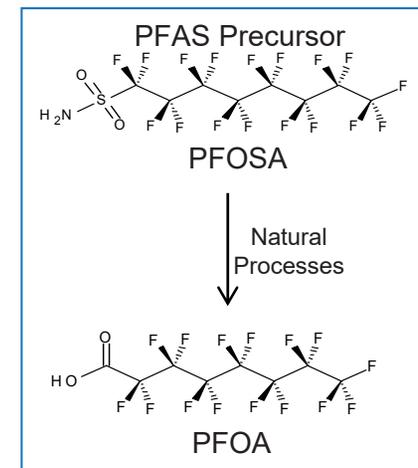
PFAS Precursor Pool

Much larger PFAS compounds – “Precursors” - are often released along with those typically monitored. PFAS precursors are themselves PFAS.

- **Problem:** Evidence suggests precursors can be transformed, through biological and environmental processes, to target PFAS of interest such as PFOA
- Overlooking precursor pool may lead to underestimates of target PFAS of interest
- Pool of potential precursors is large and generally unknown – PFAS “Dark Matter”

What is Needed:

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



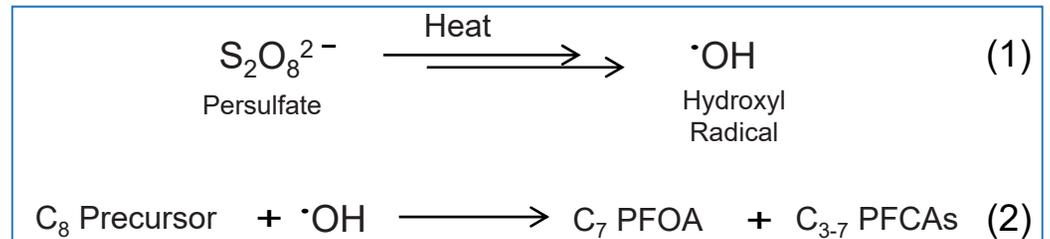
Total Oxidizable Precursor (TOP) Assay

Background

- Chemical oxidation method developed by Houtz and Sedlak¹
- Transforms PFAS precursors to perfluorocarboxylic acid (PFCA) end products without affecting target PFAS
- Accelerated “mimic” of the natural transformation of PFAS precursors

How it works

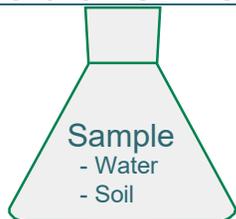
- Heat and persulfate generate hydroxyl radicals
- Hydroxyl radicals react with PFAS precursors and break them down to compounds such as PFOA and other carboxylic acid end products
 - Based on laboratory spiking experiments



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

TOP Assay Example Workflow

Before TOP Assay

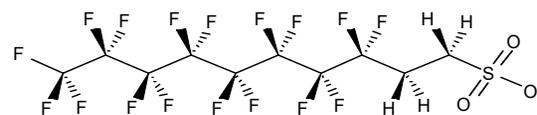


Quantify targets and precursors



LC/MS/MS Analysis

PFAS Precursor

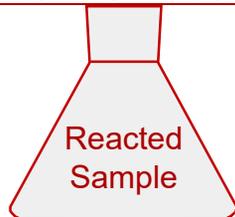


8:2 Fluorotelomer sulfonate
(C₁₀ total, C₈ containing F)

Oxidation
(OH)



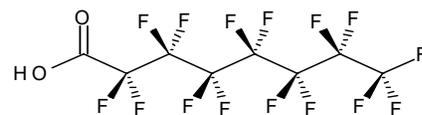
After TOP Assay



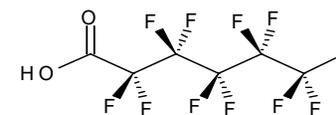
Quantify targets and precursors



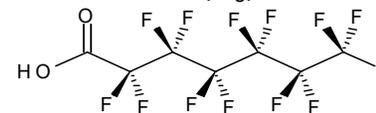
LC/MS/MS Analysis



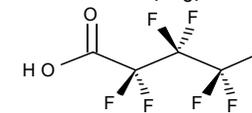
Perfluorooctanoic acid (C₈)



Perfluorohexanoic acid (C₆)



Perfluoroheptanoic acid (C₇)



Perfluorobutanoic acid (C₄)

PFAS Target List

Target PFAS and Precursors

Pool of PFAS targets and precursors is large. Maxxam monitors 16 target PFAS and 9 precursors

Target PFAS (16 total)

- Perfluorocarboxylic Acids: C4 to C14
- Perfluorosulfonates: C4, C6-C8 and C10

Precursors:

- Perfluorooctane sulfonamide (PFOSA)
- N-methylperfluorooctane sulfonamide (MeFOSA)
- N-ethylperfluorooctane sulfonamide (EtFOSA)
- N-methylperfluorooctane sulfonamidoethanol (MeFOSE)
- N-ethylperfluorooctane sulfonamidoethanol (EtFOSE)
- N-methylperfluorooctane sulfonamidoacetic acid (MeFOSAA)
- N-ethylperfluorooctane sulfonamidoacetic acid (EtFOSAA)
- 6:2 Fluorotelomer sulfonate (6:2FTS)
- 8:2 Fluorotelomer sulfonate (8:2 FTS)



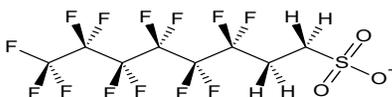
TOP Assay: Application and Results

TOP Assay Results

Individual precursor oxidation

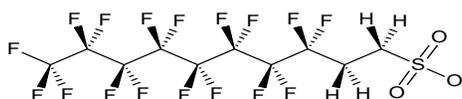
- Known amount of an individual precursor was spiked in water and taken through the TOP assay
- Detected breakdown products were expressed as a molar percentage relative to the spiked amount

6:2 Fluorotelomer sulfonate (6:2 FTS)



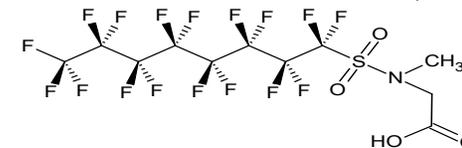
6:2 FTS Precursor	
Breakdown Product(s)	Product Conversion (%)
Perfluorobutanoic acid (C ₄)	25
Perfluoropentanoic acid (C ₅)	29
Perfluorohexanoic acid (C ₆)	20
Perfluoroheptanoic acid (C ₇)	2
6:2 FtS	1
Sum	77

8:2 Fluorotelomer sulfonate (8:2 FTS)



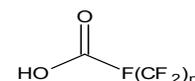
8:2 FTS Precursor	
Breakdown Product(s)	Product Conversion (%)
Perfluorobutanoic acid (C ₄)	12
Perfluoropentanoic acid (C ₅)	17
Perfluorohexanoic acid (C ₆)	20
Perfluoroheptanoic acid (C ₇)	22
Perfluorooctanoic acid (C ₈)	17
Perfluorononanoic acid (C ₉)	2
8:2 FtS	1
sum	91

N-methylperfluorooctane sulfonamidoacetic acid (MeFOSAA)



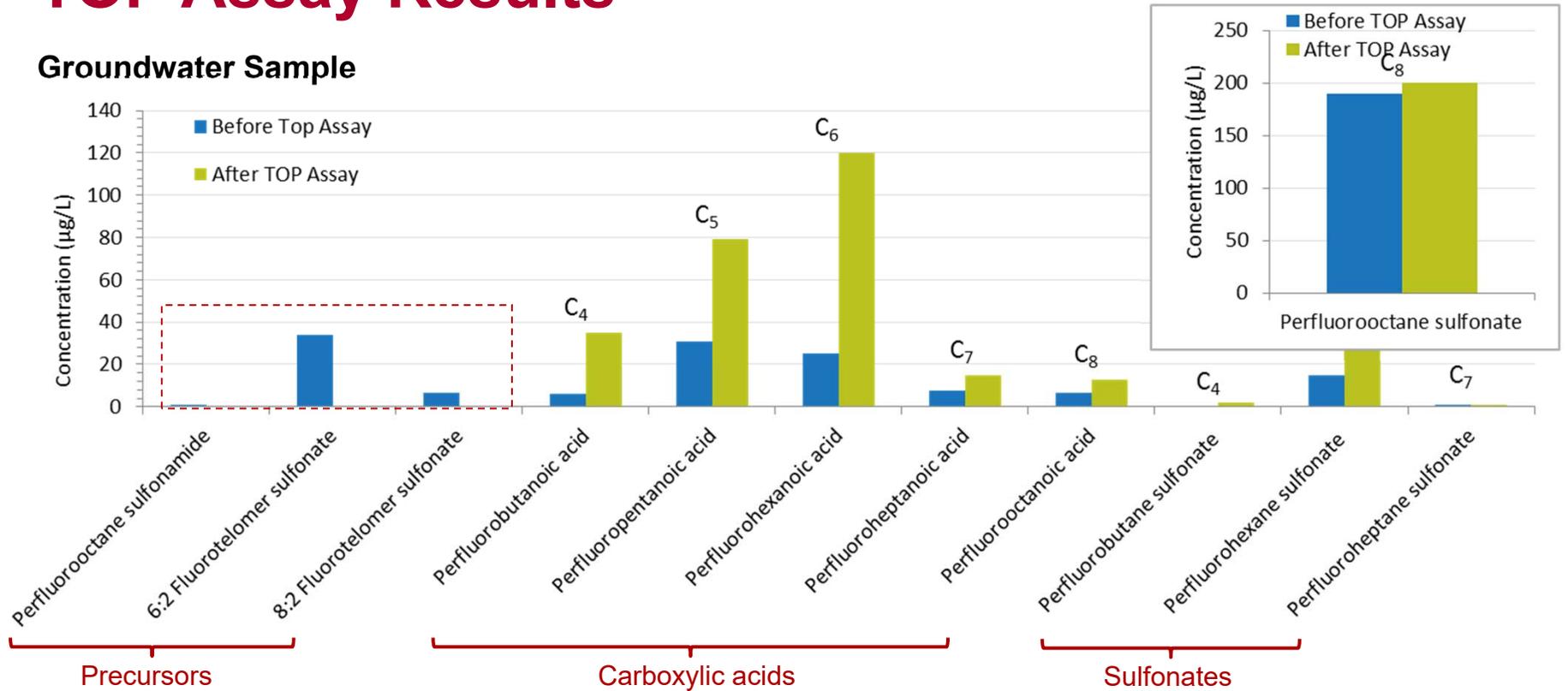
MeFOSAA Precursor	
Breakdown Product(s)	Product Conversion (%)
Perfluorooctanoic acid (C ₈)	92
Sum	92

Recall that perfluorocarboxylic acids have the following structure where n = 3 – 13 for the target PFAS



TOP Assay Results

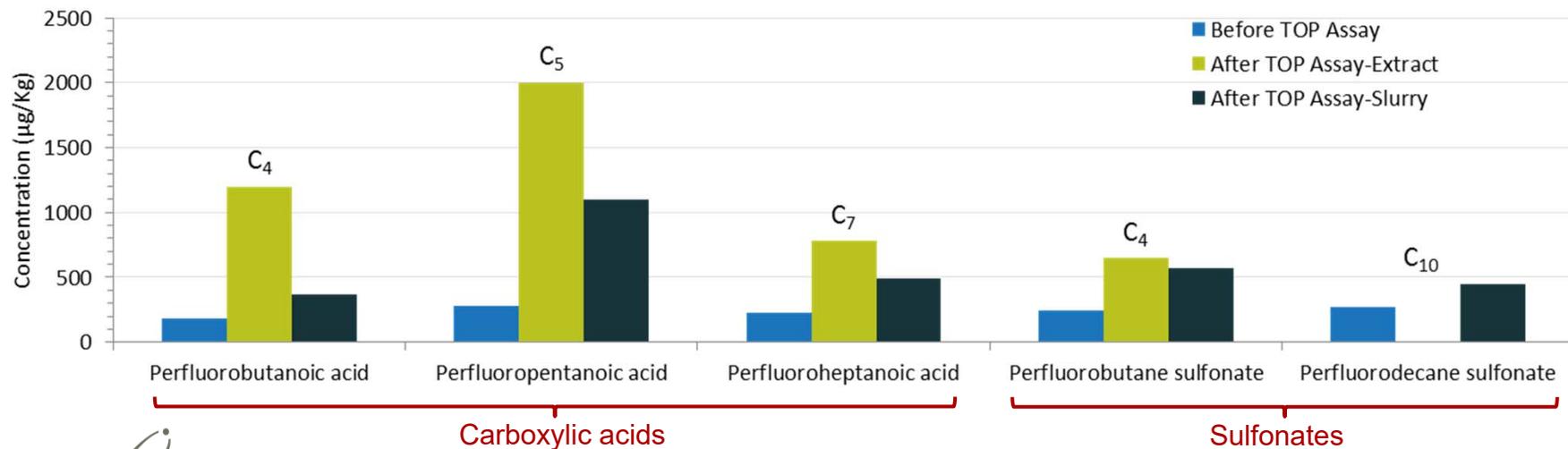
Groundwater Sample



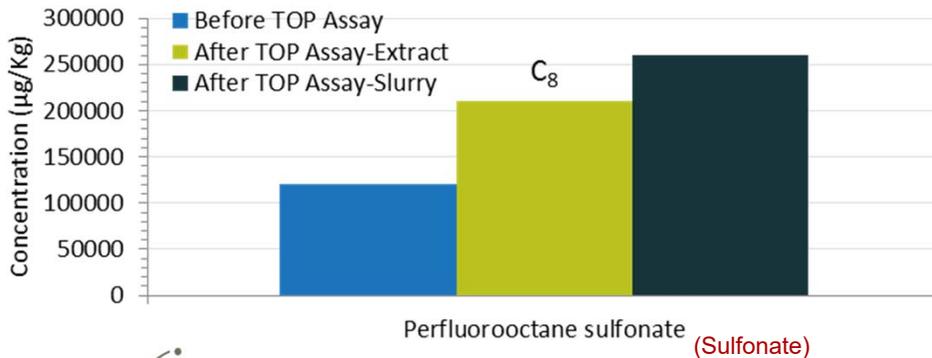
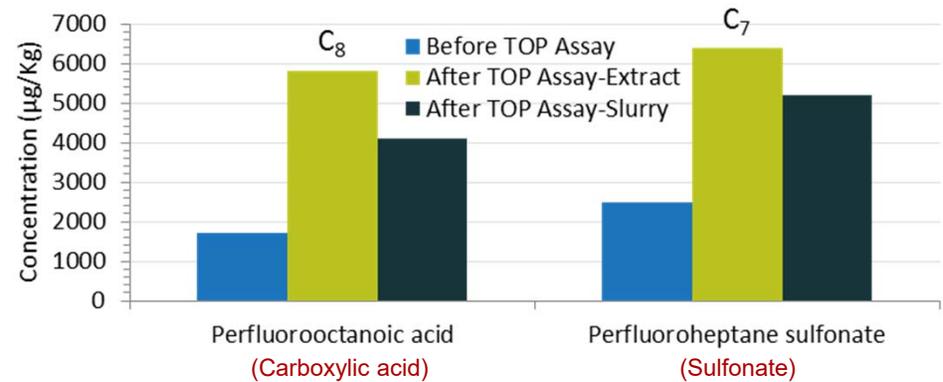
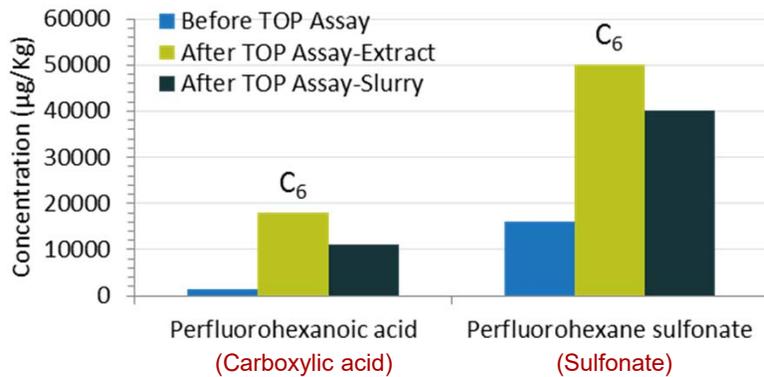
TOP Assay Results

Soil Sample

- No literature precedent for TOP assay on soils. Method had to be developed by Maxxam.
- Two different methods to extract PFASs from soils were evaluated
- Slurry method does not separate soil and solvent whereas extract method does
- TOP assay performed for both extraction methods



TOP Assay Results Soil Sample continued...



Observations:

- No precursors detected – PFAS dark matter
- Slurry and extract results comparable
- Extract method appears to generate slightly more target PFAS on average

Considerations

Items to note

- Method is limited to compounds that are oxidizable by the TOP 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.
- Similarly, 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.
- Not certain how representative the TOP assay is of the transformations that would occur naturally.
 - Variable site conditions, e.g. soil chemistry, oxidation state?
 - Timescale?

Conclusions

What the TOP Assay offers

- Quick and simple method of PFAS oxidation performed on soil and water.
- Report provides concentrations of 25 PFAS before and after oxidation as well as the magnitude of the change.
- **Estimate of magnitude 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.

ACKNOWLEDGEMENTS



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