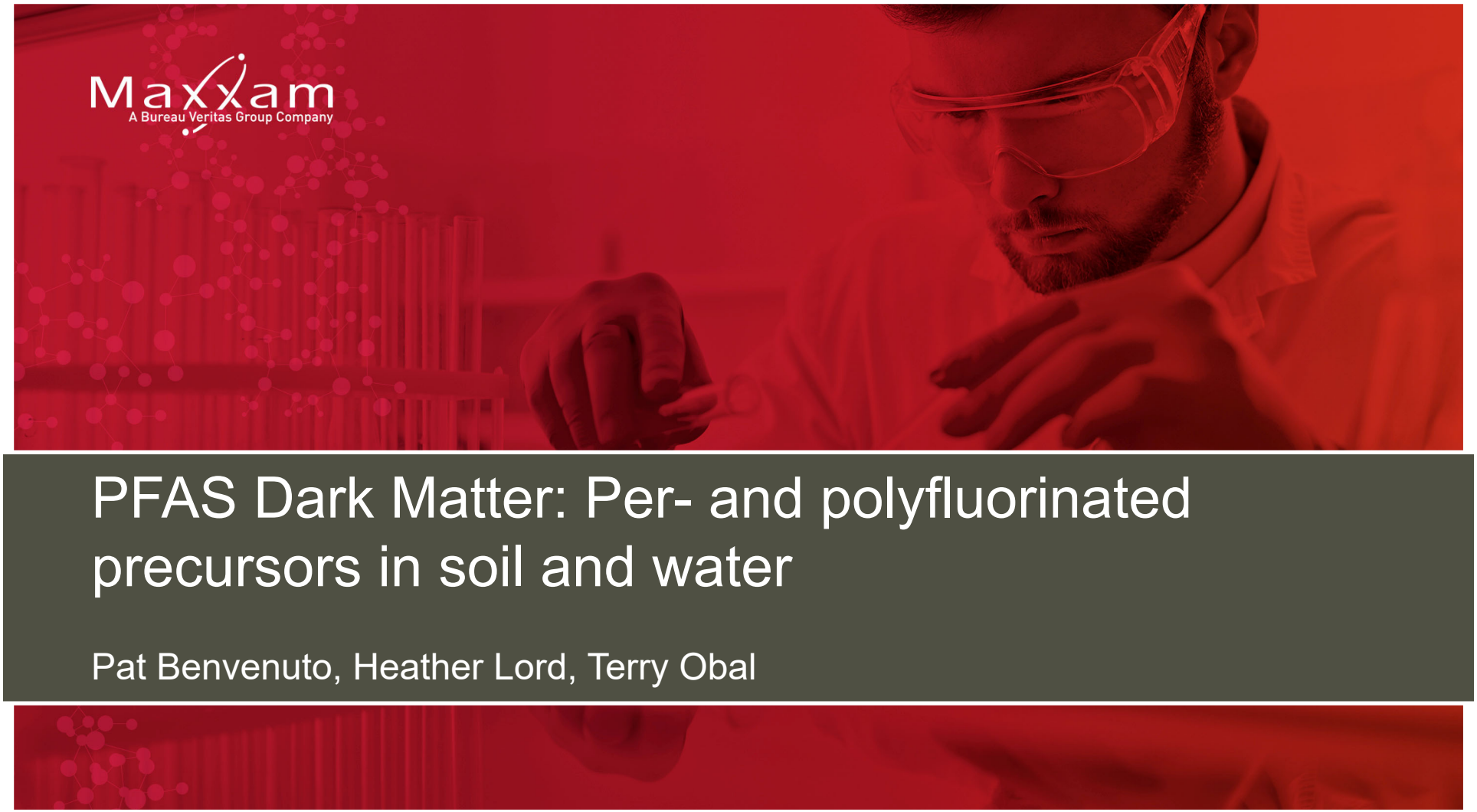


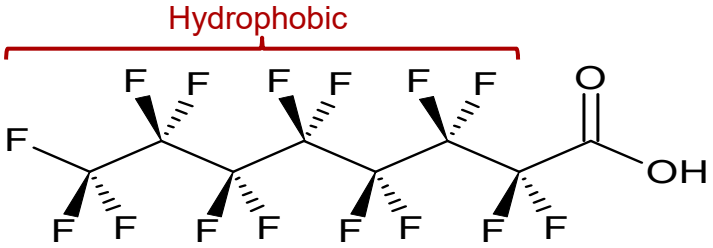
PFAS Dark Matter: Per- and polyfluorinated precursors in soil and water

Pat Benvenuto, Heather Lord, Terry Obal

PFASs

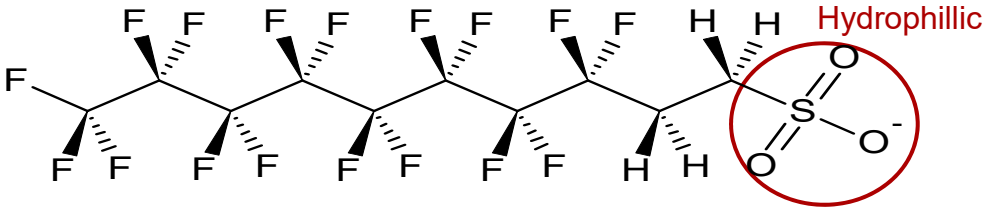
What are PFASs?

- PFASs are **P**er- and **P**oly**F**luorinated **A**lkyl **S**ubstances. Exclusively anthropogenic.
- Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophillic 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

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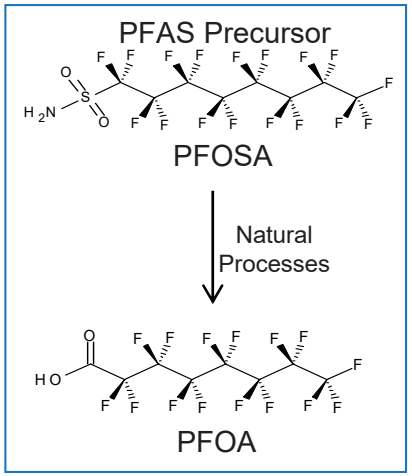
PFAS Precursor Pool

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

- **Problem:** Evidence suggests precursors can be transformed, through biological and environmental processes, to target PFASs of interest such as PFOA
- Overlooking precursor pool may lead to underestimates of target PFASs 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

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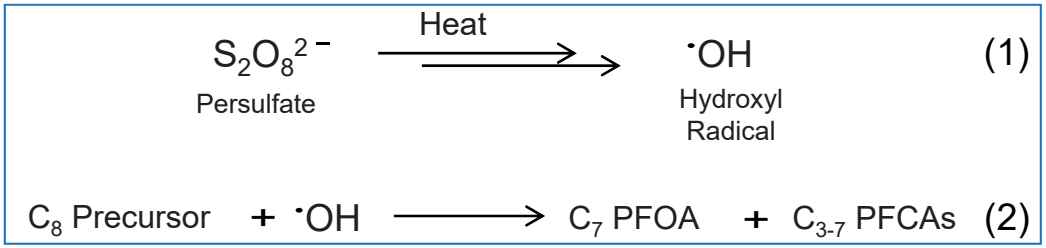
Total Oxidizable Precursor (TOP) Assay

Background

- Chemical oxidation method developed by Houtz and Sedlak[1]
- Transforms PFAS precursors to perfluorocarboxylic acid (PFCA) end products without affecting target PFASs
- 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



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

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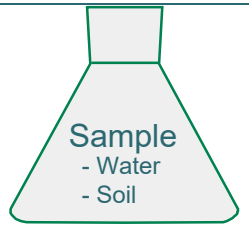
TOP Assay Example Workflow

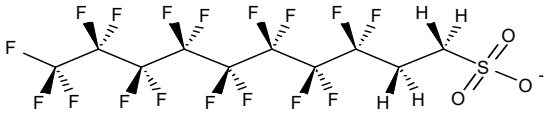
Before TOP Assay



Quantify targets and precursors

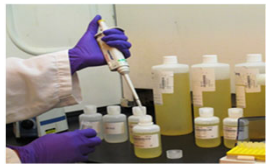
LC/MS/MS Analysis

PFAS Precursor

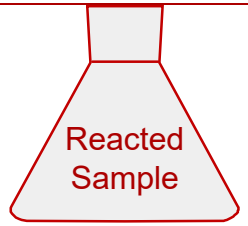


8:2 Fluorotelomer sulfonate
(C_{10} total, C_8 containing F)

Oxidation
($^{\bullet}OH$)

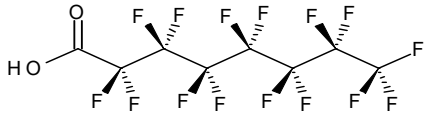


After TOP Assay

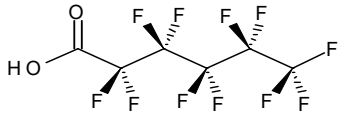


Quantify targets and precursors

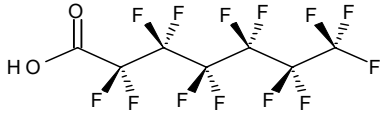
LC/MS/MS Analysis



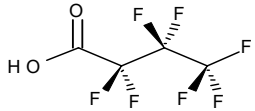
Perfluorooctanoic acid (C_8)



Perfluorohexanoic acid (C_6)



Perfluoroheptanoic acid (C_7)



Perfluorobutanoic acid (C_4)

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PFAS Target List

Target PFASs and Precursors

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

Target PFASs (16 total)

- Perfluorocarboxylic Acids: C4 to C14
- Perfluorosulfonates: C4, C6, C7, C8 and C10

Precursors:

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

Note:

- Four precursors are too volatile to make it through the oxidation!

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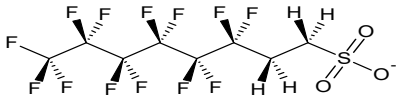
TOP Assay Results

Individual precursor oxidation

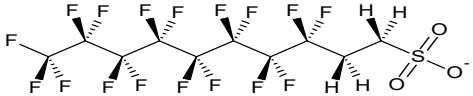
- Known amount of an individual precursor was spiked in water and taken through the TOP assay
- Detected breakdown products were expressed as a molar percentage relative to the spiked amount

6:2 Fluorotelomer sulfonate (6:2 FTS)



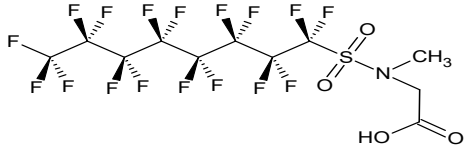
6:2 FTS Precursor	
Breakdown Product(s)	**Product Conversion (%)**
Perfluorobutanoic acid (C_4)	25
Perfluoropentanoic acid (C_5)	29
Perfluorohexanoic acid (C_6)	20
Perfluoroheptanoic acid (C_7)	2
6:2 FtS	1
Sum	77

8:2 Fluorotelomer sulfonate (8:2 FTS)



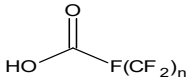
8:2 FTS Precursor	
Breakdown Product(s)	**Product Conversion (%)**
Perfluorobutanoic acid (C_4)	12
Perfluoropentanoic acid (C_5)	17
Perfluorohexanoic acid (C_6)	20
Perfluoroheptanoic acid (C_7)	22
Perfluorooctanoic acid (C_8)	17
Perfluorononanoic acid (C_9)	2
8:2 FtS	1
sum	91

N-methylperfluorooctane sulfonamidoacetic acid (MeFOSAA)



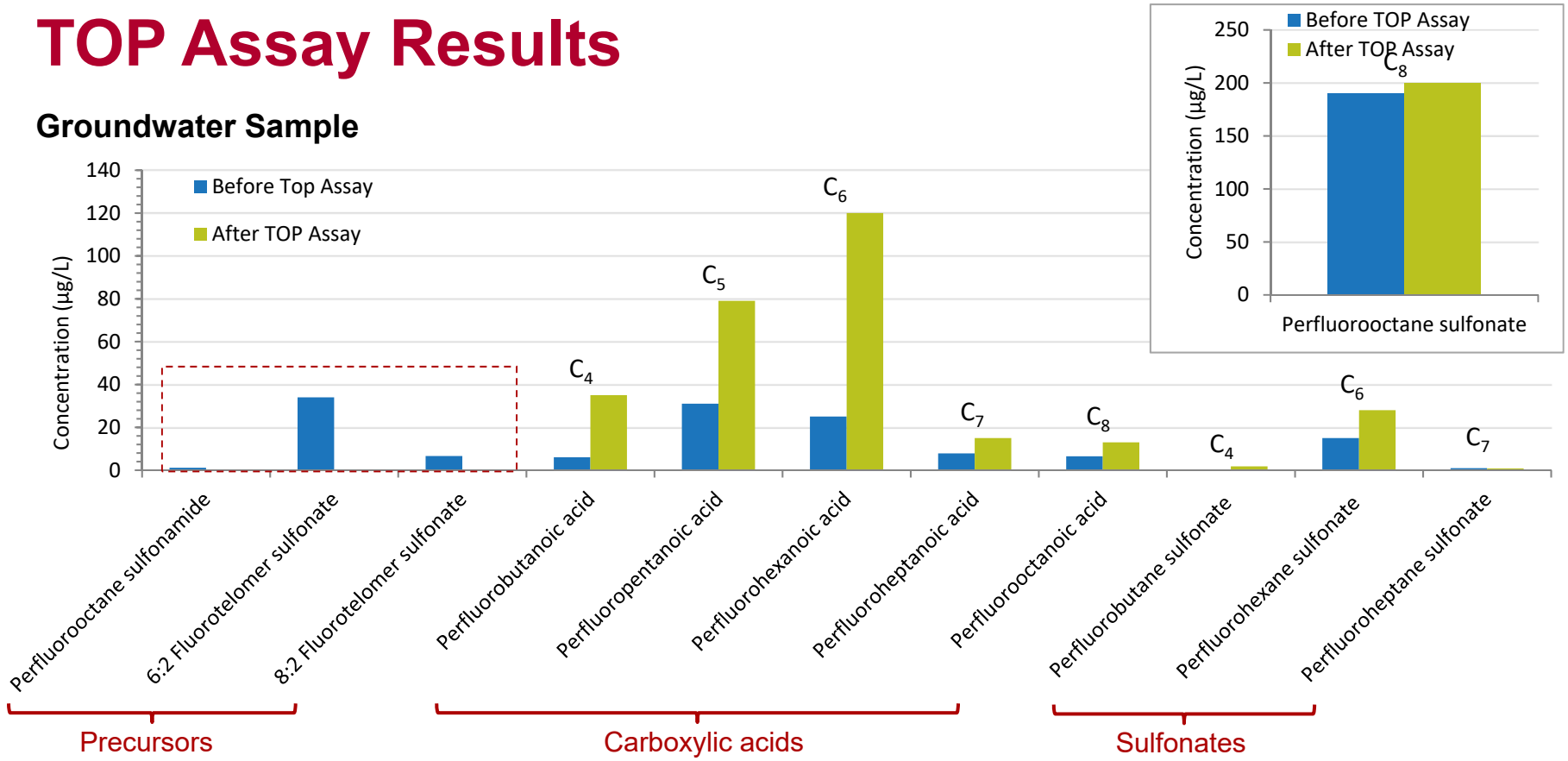
MeFOSAA Precursor	
Breakdown Product(s)	**Product Conversion (%)**
Perfluorooctanoic acid (C_8)	92
Sum	92

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



TOP Assay Results

Groundwater Sample



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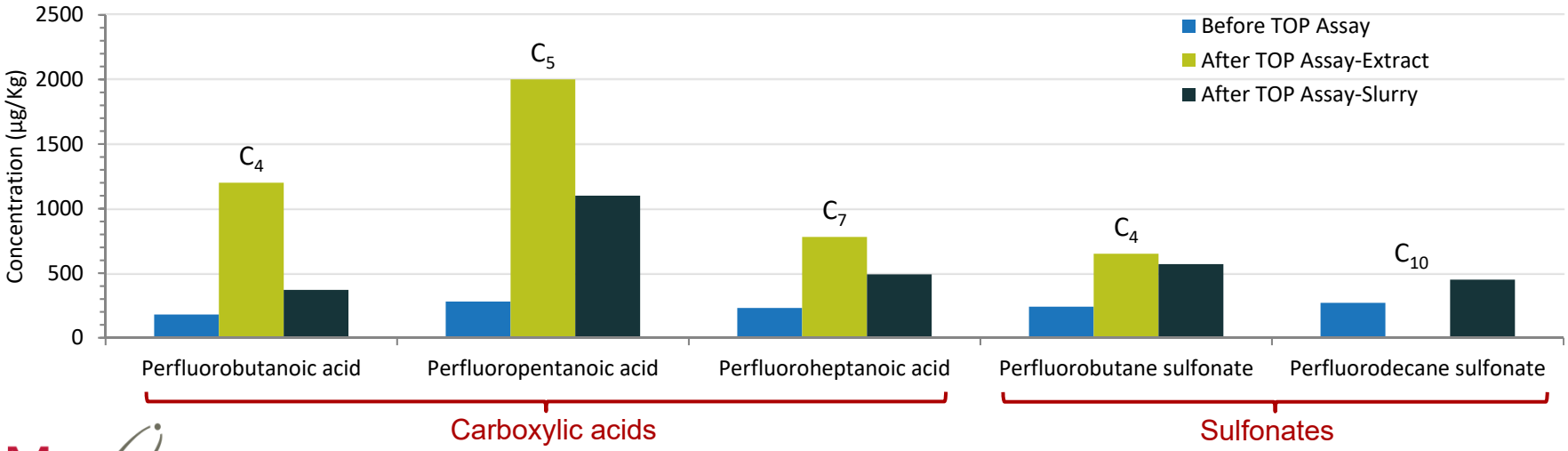
TOP Assay Results

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



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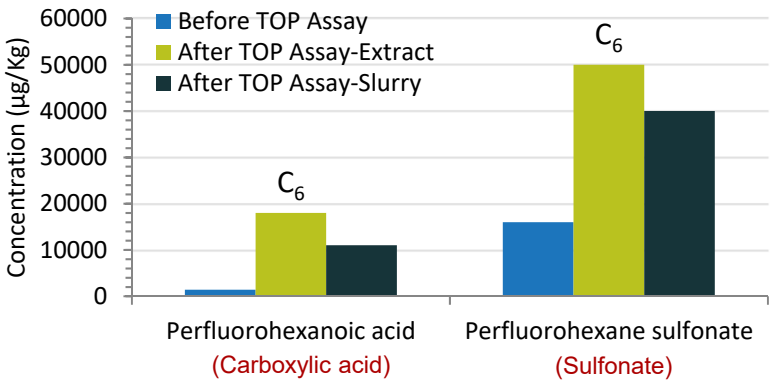
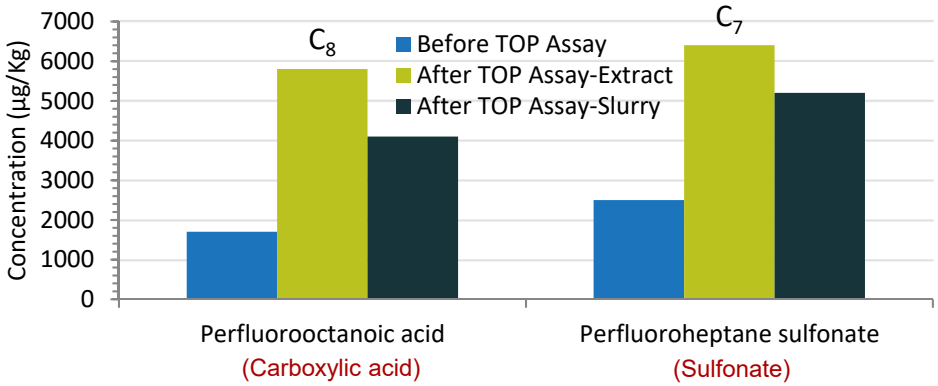
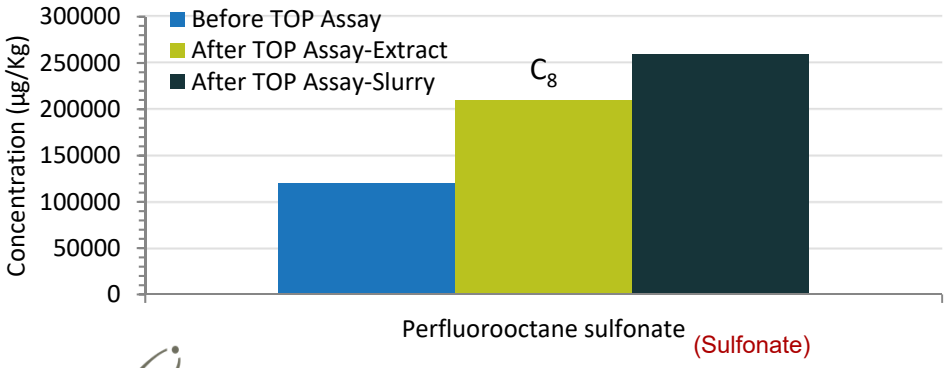
TOP Assay Results

Soil Sample continued…







Observations:

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

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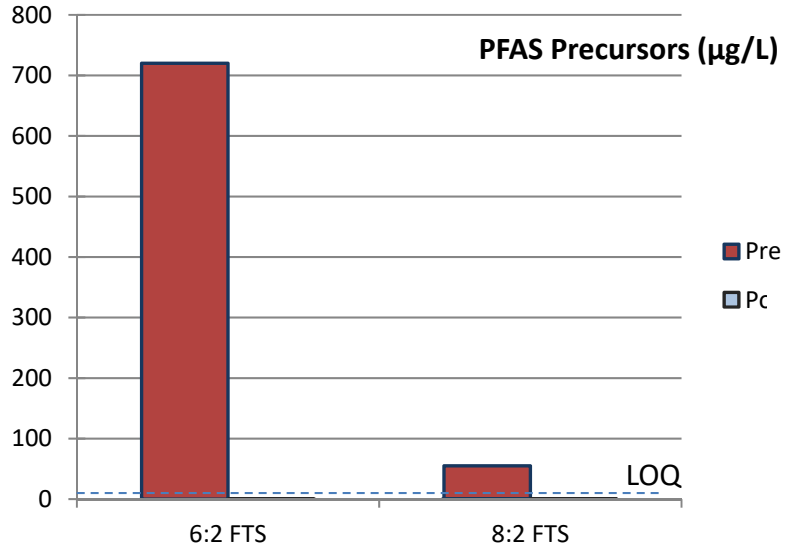
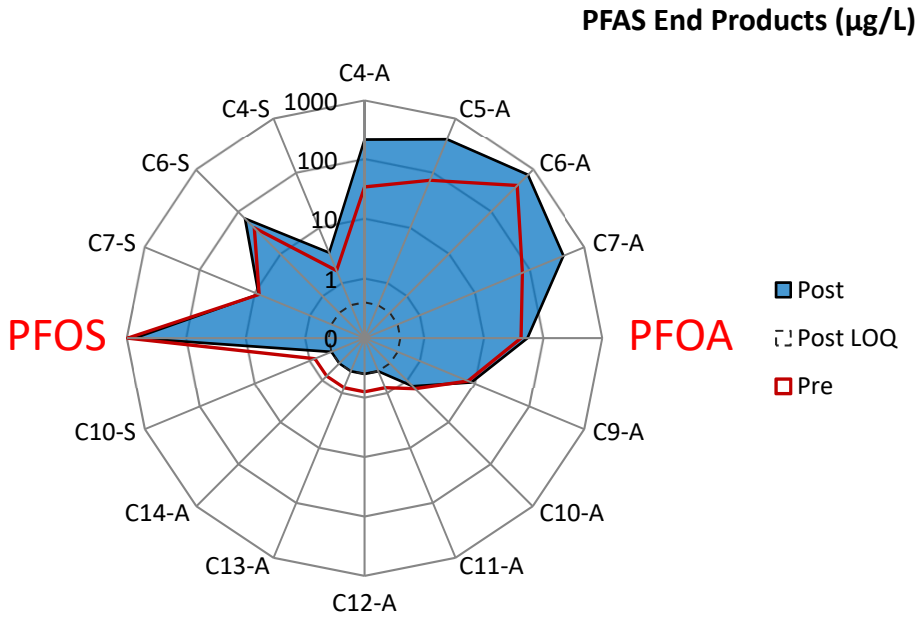
Water Results





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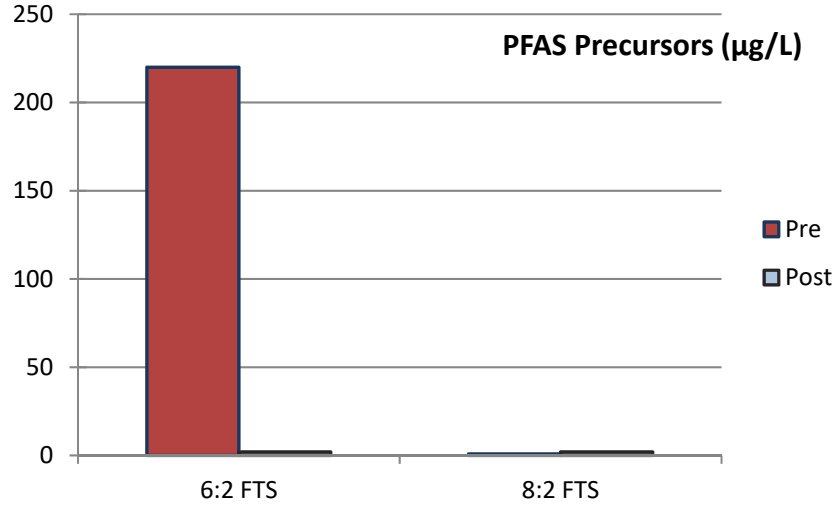
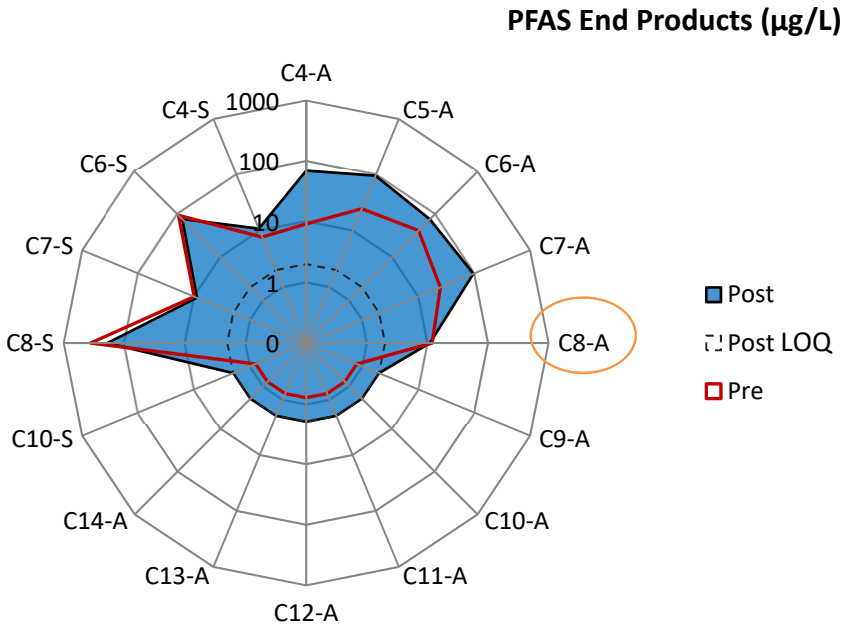
Thanks go to Stefano Marconetto of Golder Associates for demonstrating the use of Excel spider charts to visualize TOP Assay data.

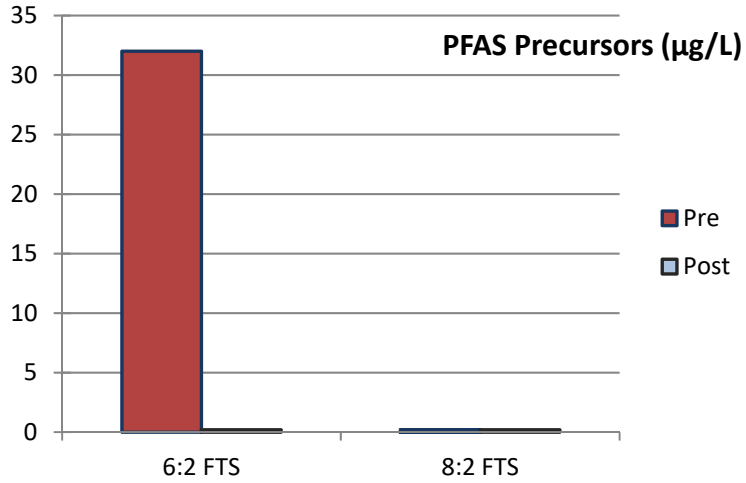
Water Results

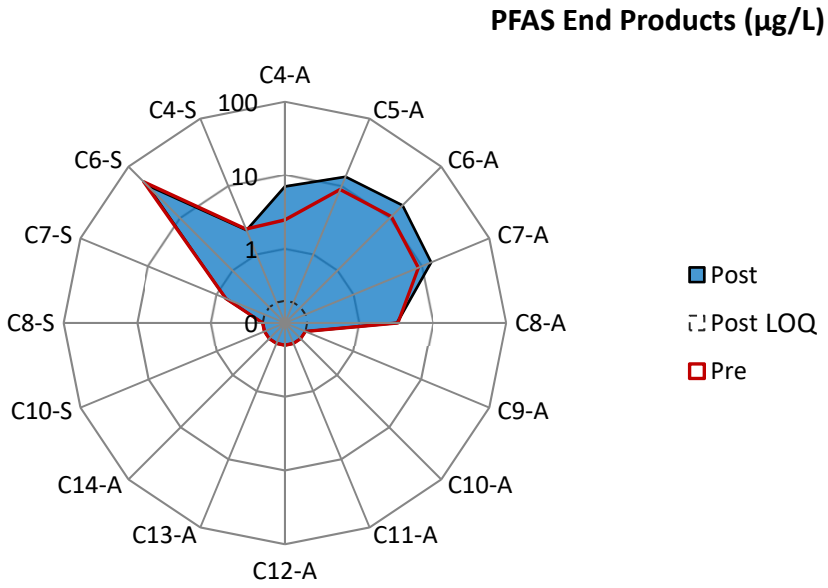




No 8:2 FTS in this sample, TOP pattern is similar to the previous example.
Note there is no PFOA in these water samples.

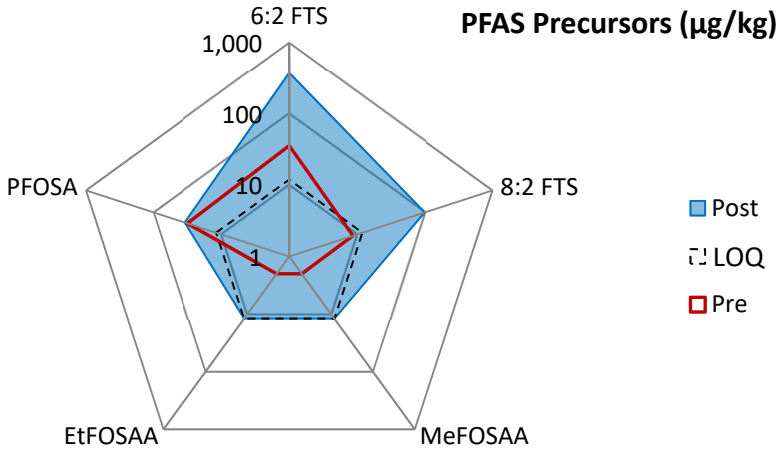
Water Results

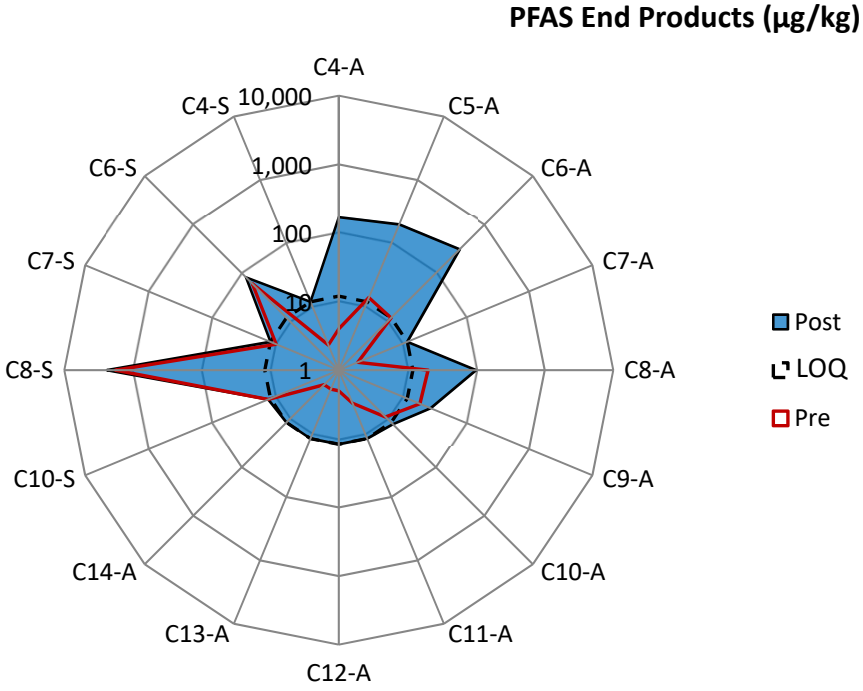




Precursor pattern similar to the previous example, TOP pattern does not have PFOS, acid products are similar to the previous example.

Soil Results





Other precursors seen more often in soil samples.
Precursors can increase as well as decrease!
TOP profile: C4, C5, C6 and C8 acids (i.e. PFOA) increase but no C7.

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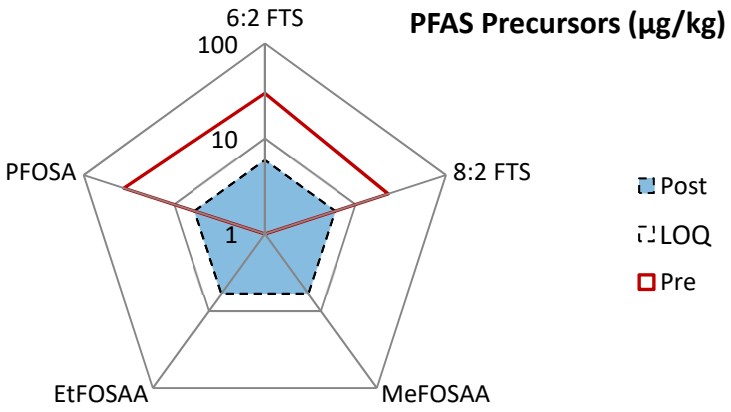
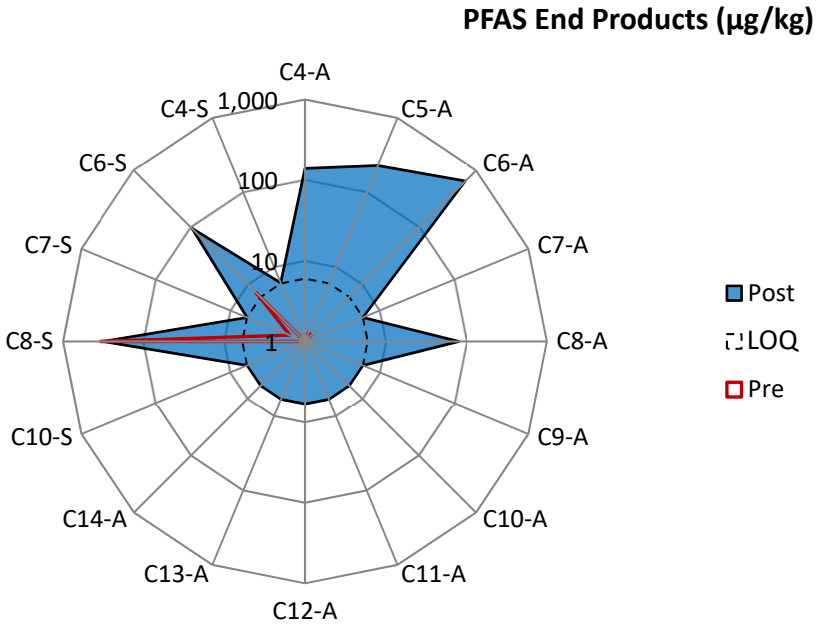
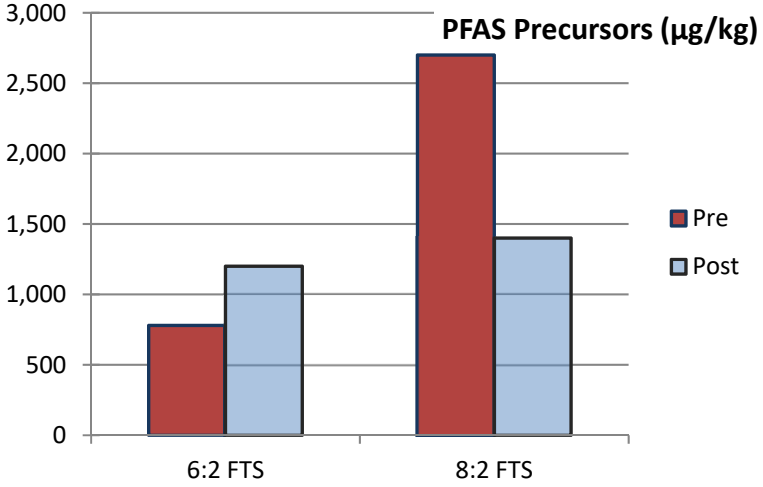
Soil Results

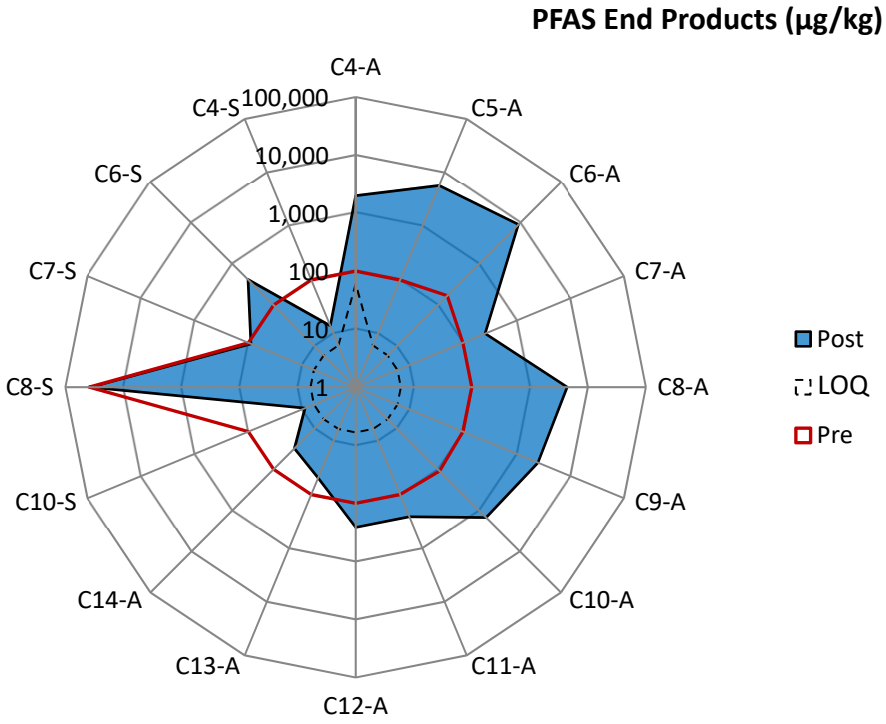




Sample has minimal levels of precursors; PFOS is the only significant product.
Significant levels of C4, C5, C6 acids and PFOA produced.

Soil Results





This high concentration sample had significant production of C8 to C12 acids. Still minimal C7 acid seen.

Considerations

Items to note

- Method is limited only 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 PFASs 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 PFASs 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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Conclusions

What the TOP Assay offers

- Quick and simple method of oxidation that can be performed on soil and water
- Provides 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
- Assay report provides concentrations of 25 PFASs before and after oxidation as well as the magnitude of the change.

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ACKNOWLEDGEMENTS

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