PFAS and Precursor Analysis in Biosolids: Current Knowledge and Ongoing Challenges

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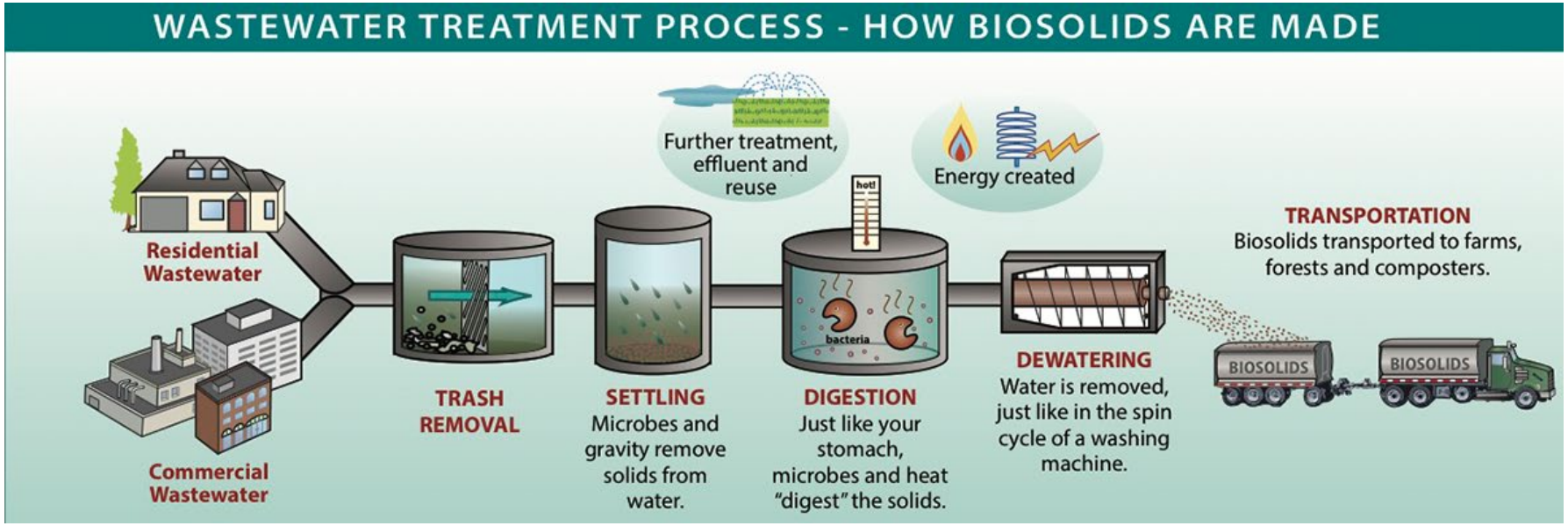
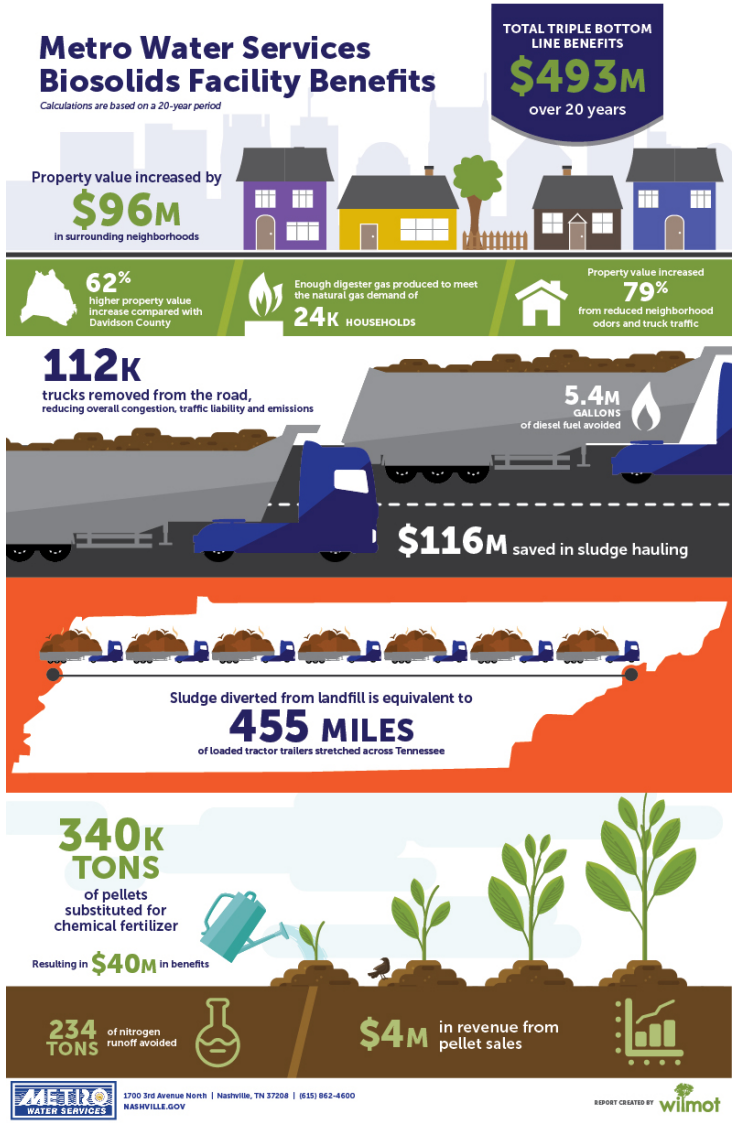
Chemical
Biochemical and
Environmental
Engineering

UMBC

Biosolids generated from the sludge processing train at wastewater treatment plants are valuable soil amendments…





Top: https://nwbiosolids.org/what-are-biosolids/
Bottom: https://www.synagro.com/dillo-dirt/
Right: https://wilmotinc.com/new-blog/2019/5/22/biosolids

…but biosolids also represent a key component of the PFAS cycle, especially because application can introduce PFAS into *unimpacted* areas

Major sources:

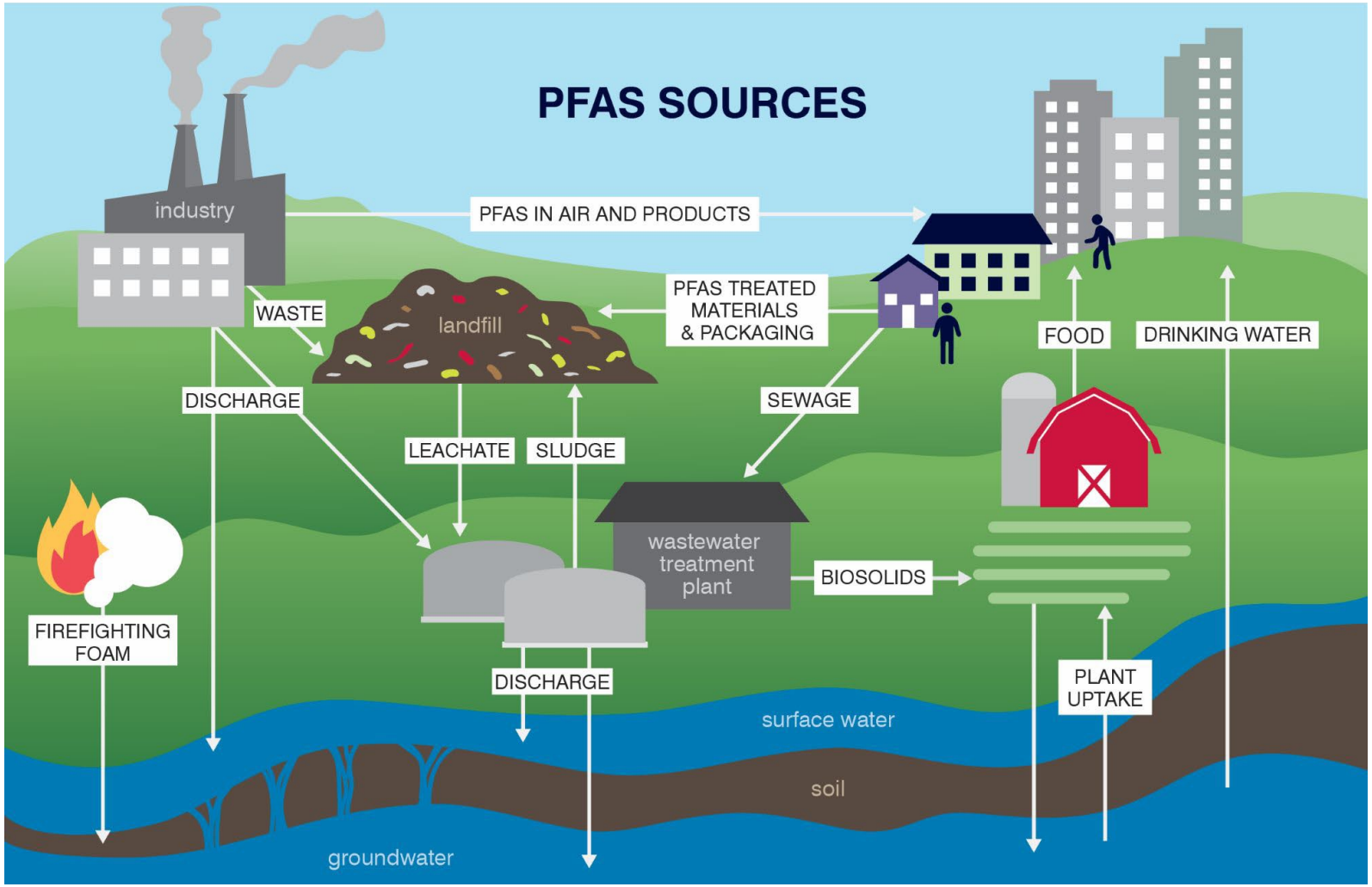
- Fire-training areas (AFFF)
- Industrial wastewater
- Landfill leachate
- Wastewater effluent

Biosolids application can introduce PFAS to …

- Unimpacted areas
- Drinking water supplies
- Food crops
- Aquatic and terrestrial animals

Challenges

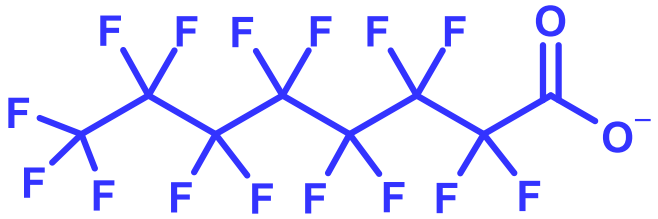
- High organic matter content
- Precursor presence



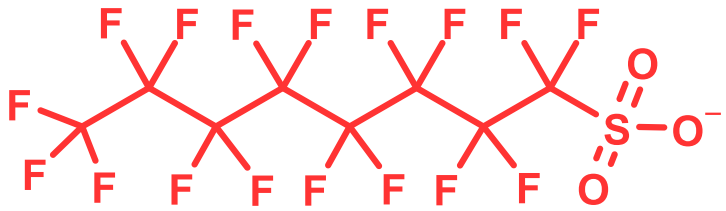
https://www.westonandsampson.com/services/environmental-consulting/pfas-emerging-contaminants/

Representative PFAS from major classes of concern and key structural components that control interactions with solids

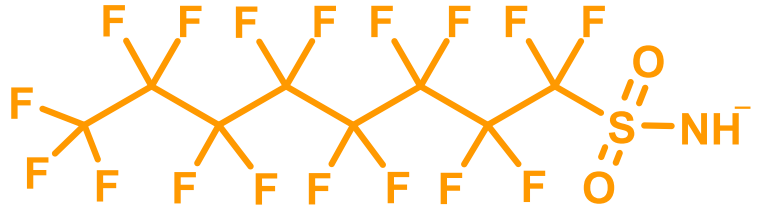
Perfluorooctane carboxylate (PFOA)



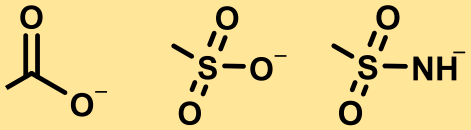
Perfluorooctane sulfonate (PFOS)



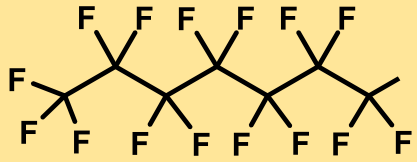
Perfluorooctane sulfonamide (PFOSA)



Head:

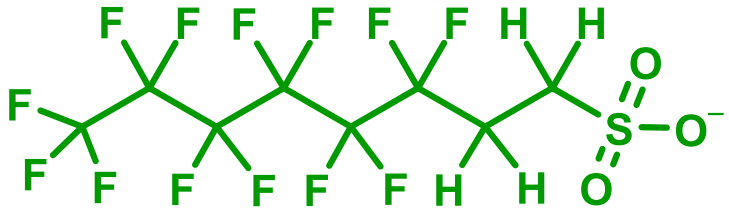


Tail:

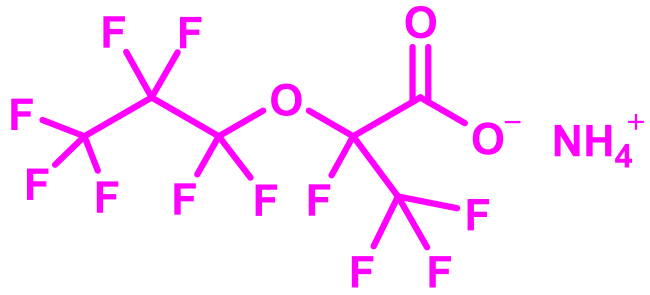


Chain-length: C4-C14 (*e.g.*, PFCAs)

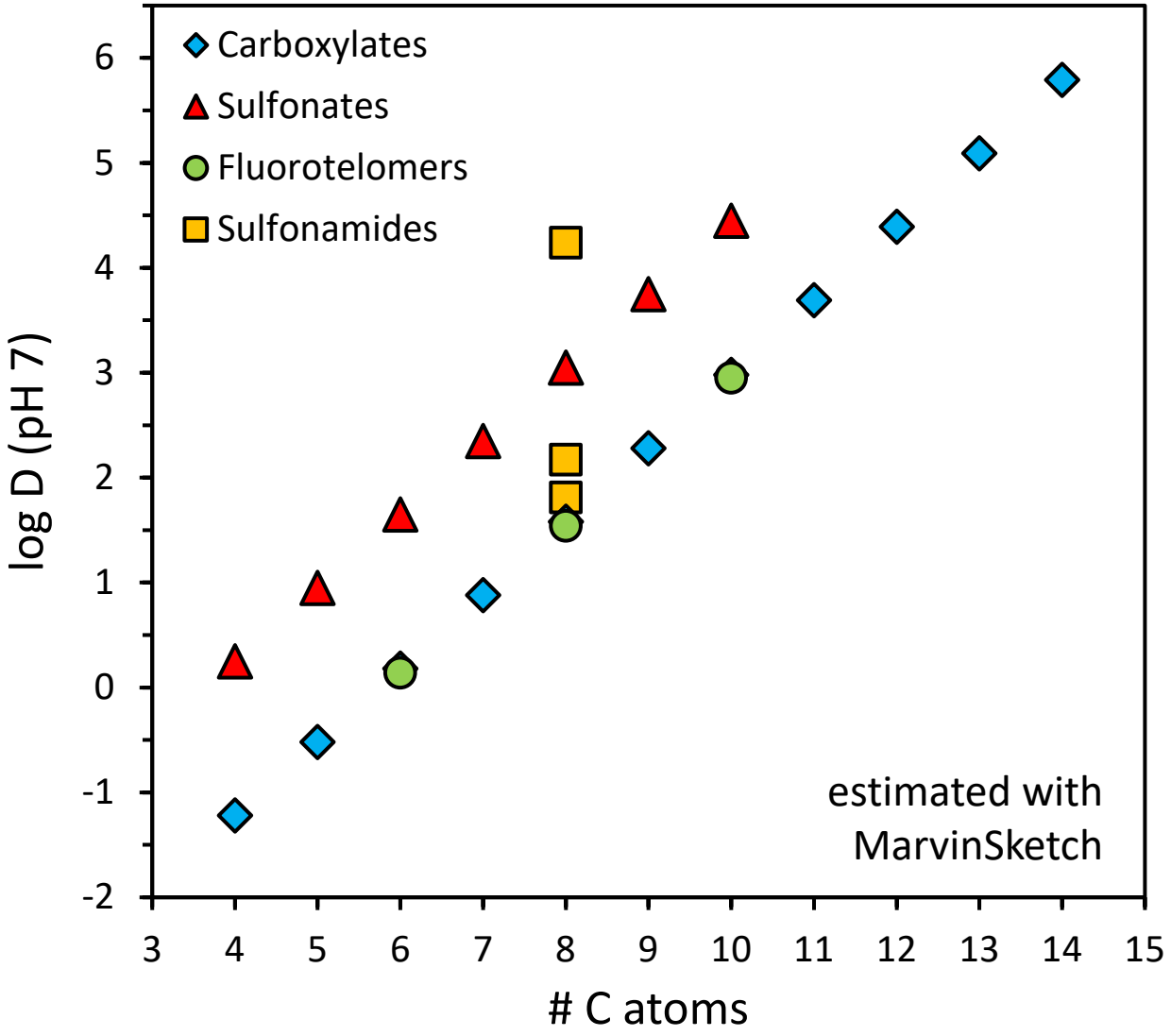
6:2 fluorotelomer sulfonate (PFOS)



GenX



PFAS partitioning into biosolids is mostly* a function of hydrophobicity



The hydrophobicity of targeted PFAS can be estimated with the log D parameter:

$$\log D = \log\left(\frac{[\text{H- PFAS}]_{\text{octanol}}}{[\text{H- PFAS}]_{\text{water}} + [\text{PFAS}^{-}]_{\text{water}}}\right)$$

Using prior conventions, PFAS with log D > 2.0 are more likely to partition into biosolids at high concentrations. Due to uncertainty in the log D estimates, this threshold can be lowered to log D > 1.5 …

- **Carboxylates:** PFOA and longer
- **Sulfonates:** PFHxS and longer
- **Fluorotelomers:** 6:2 FtS and longer
- **Sulfonamides:** PFOSA, N-MeFOSAA, N-EtFOSAA

These fundamental expectations align with biosolids composition data from WWTPs in Michigan

Total conc. ($ng\ g^{-1}$):

Composition (%):

Maximum conc.:

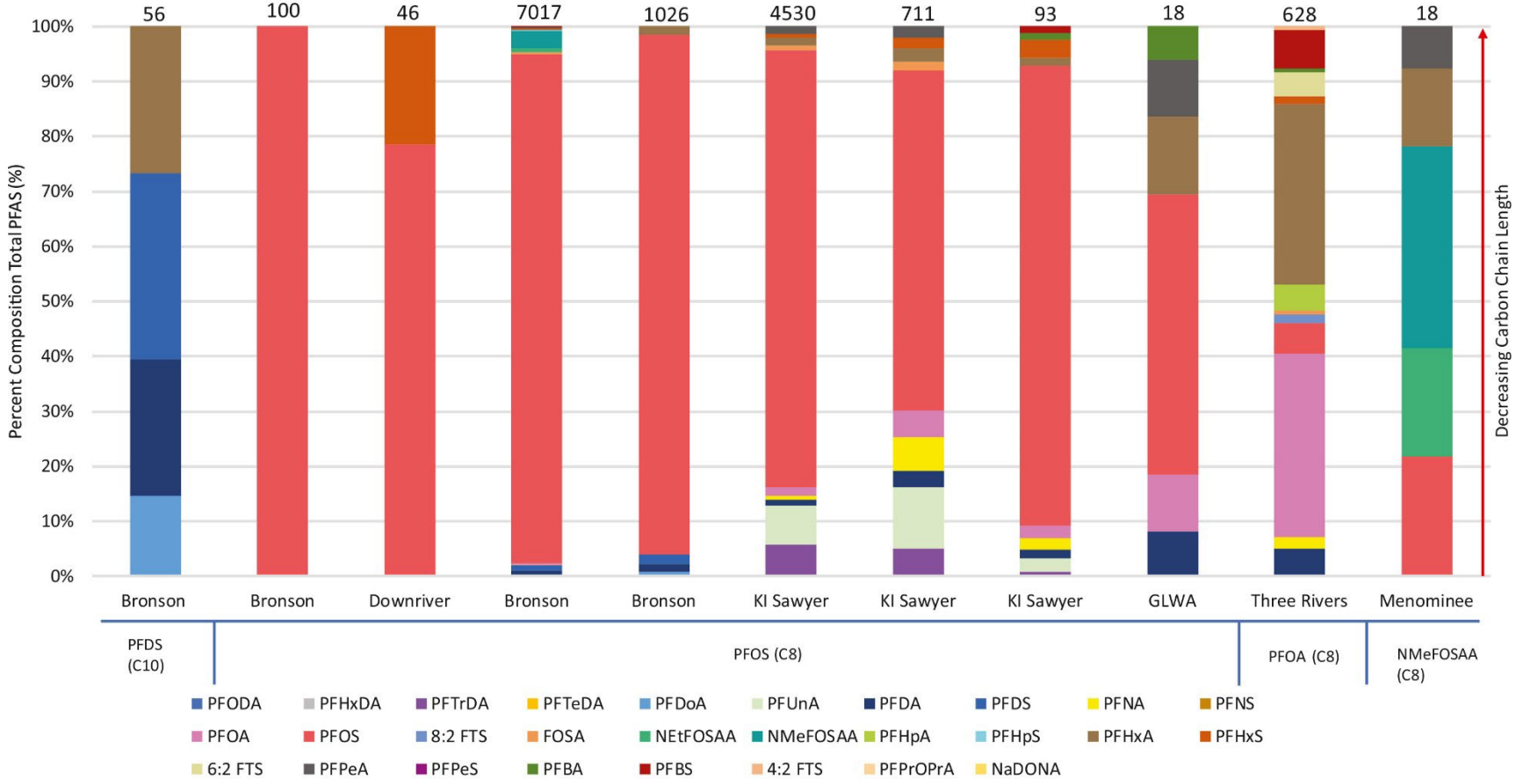
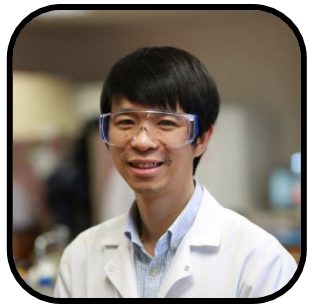


Fig. 8. Percent composition of biosolids from 6 Michigan WWTPs. Total PFAS concentration in ng/g is located at the top of each column.

Helmer *et al.*, *Water Res.*, 2022

Measuring targeted PFAS in biosolids – EPA draft Method 1633



Dr. Ke He

4th Draft Method 1633*

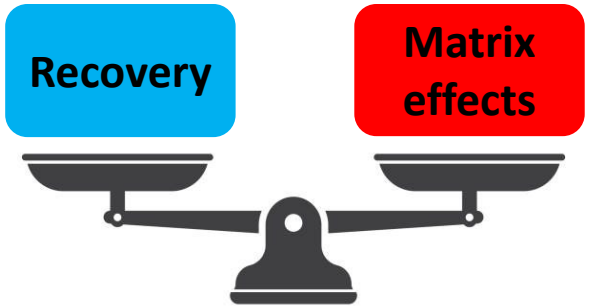
Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

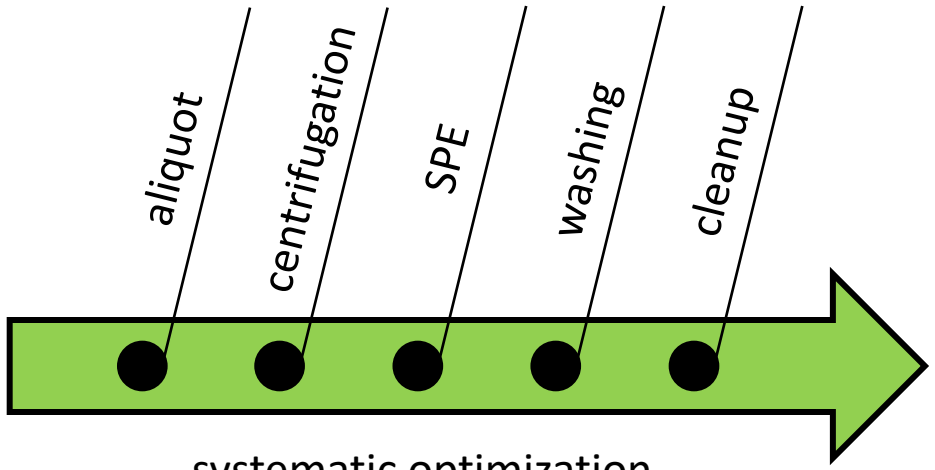
**Finalized for the Aqueous Matrices: Wastewater, Surface Water, and Groundwater*

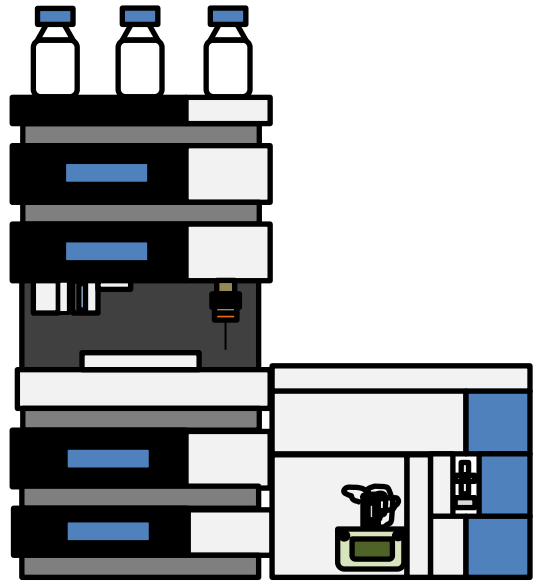
Some key points:

- Max. sample weight is 0.5 g dw biosolids
- Biosolids samples may be held for up to 90 d if stored in the dark at < 6 °C (preferably, –20 °C)
- Add biosolids to centrifuge tube, spike extracted internal standards (recovery surrogates)
- Extract into 0.3% methanolic ammonium hydroxide, add carbon (matrix effects cleanup), dilute (optional, matrix effects cleanup)
- SPE, cleanup, add non-extracted internal standards, analyze by LC-MS/MS

The biggest issue with biosolids analysis is the strong matrix, which can result in a “milky” extract that is not suitable for injection

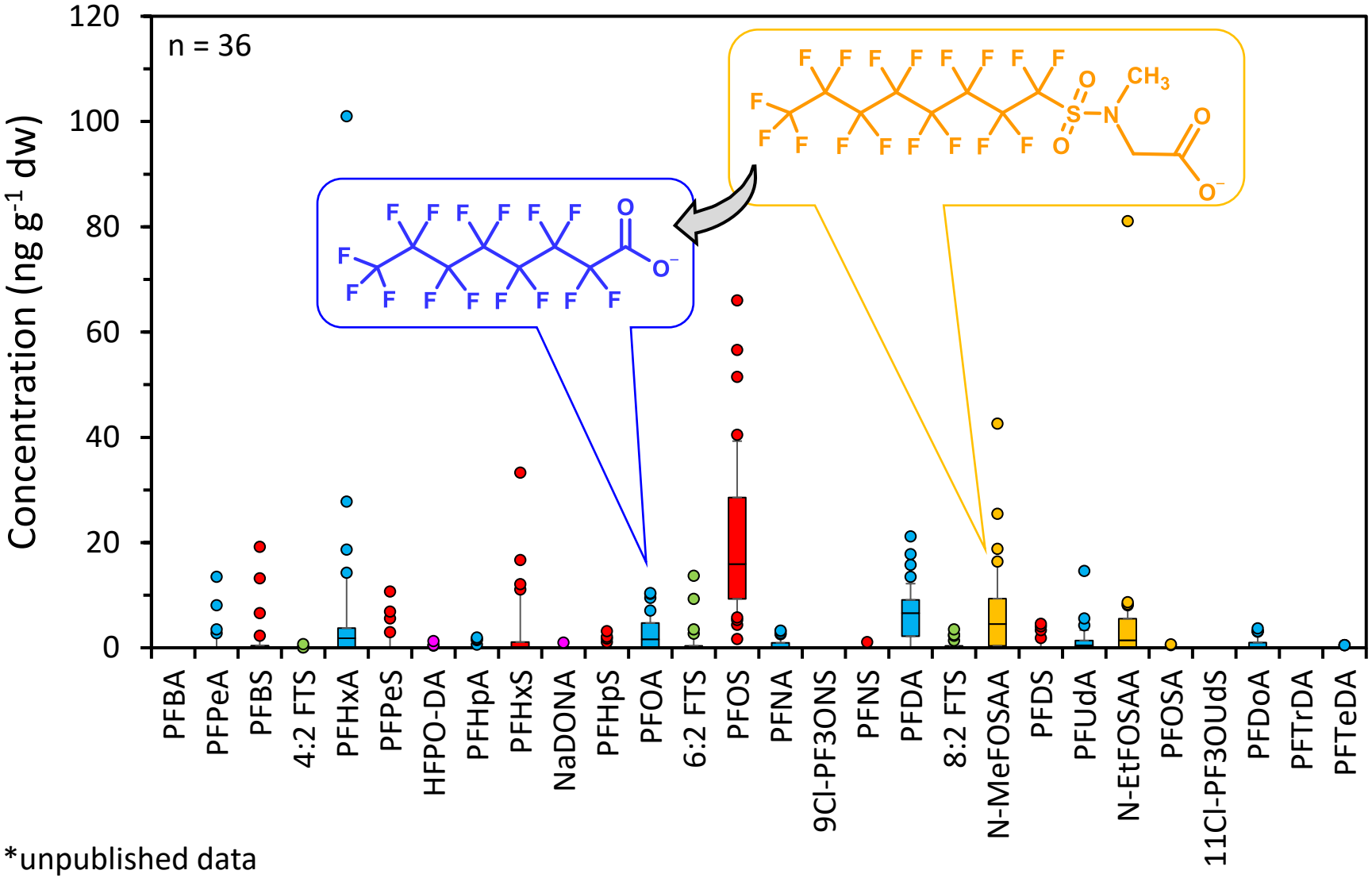


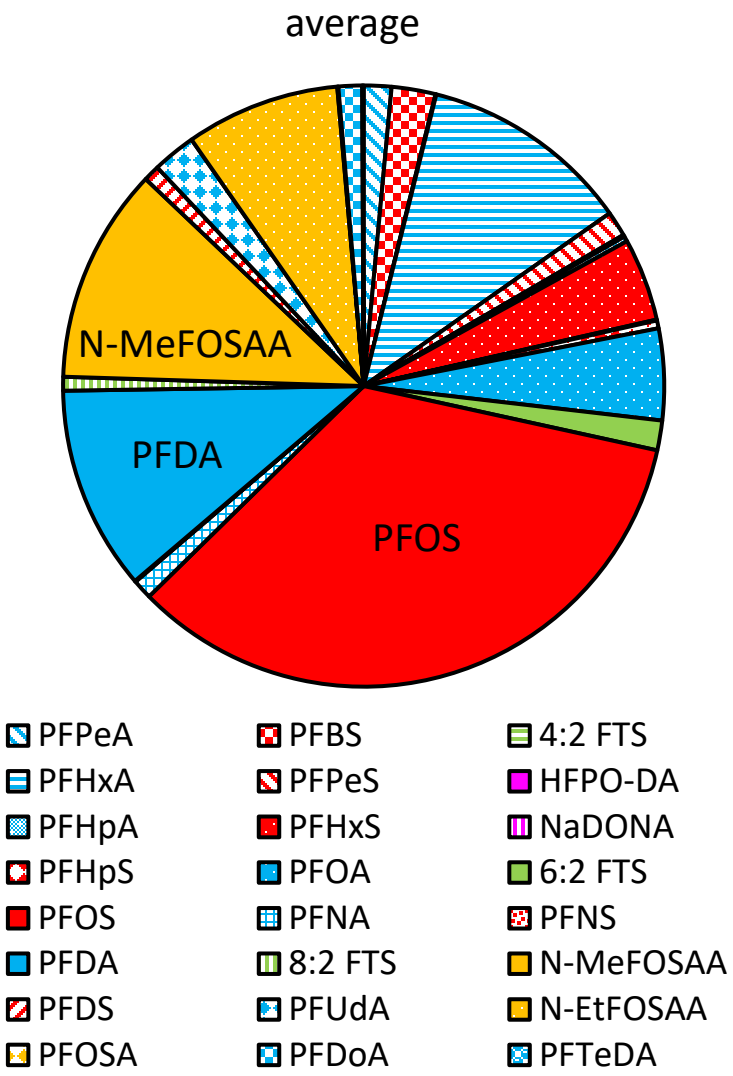




Margaret Siao

Typical levels of targeted PFAS in biosolids produced at WWTPs in the Chesapeake Bay watershed





*unpublished data

A quick introduction to three options for precursor analysis

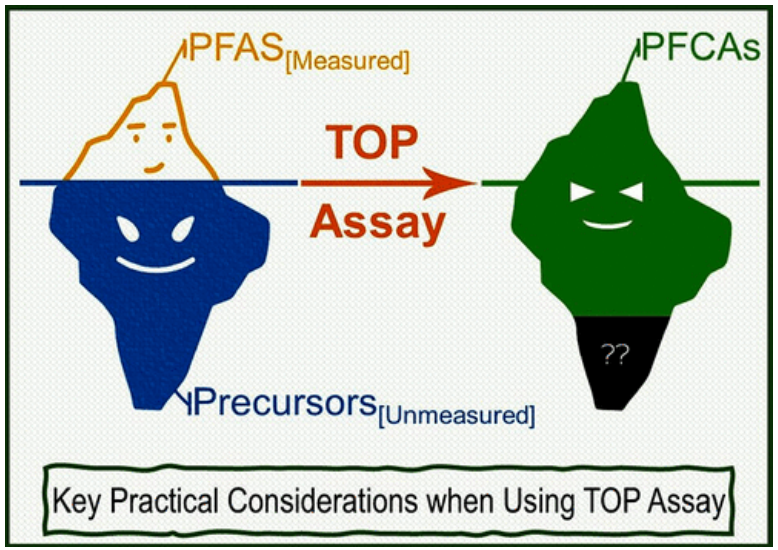
High-resolution mass spectrometry (HRMS)

https://ms.fiu.edu/instruments/bruker-solarix-70t/

Combustion ion chromatography (CIC)

https://www.thermofisher.com/order/catalog/product/IQLAAAGADHFAMJMBIQ

Total oxidizable precursor (TOP) assay



https://doi.org/10.1021/acs.estlett.3c00061

Nontargeted analysis of PFAS precursors – a powerful tool for fingerprinting and source allocation (requires expert user & specialized equipment)

Mass-to-charge ratios are measured and converted into chemical formulae that correspond to PFAS (or background dissolved organic matter). Structure can sometimes be ineferred but not confirmed without standards.

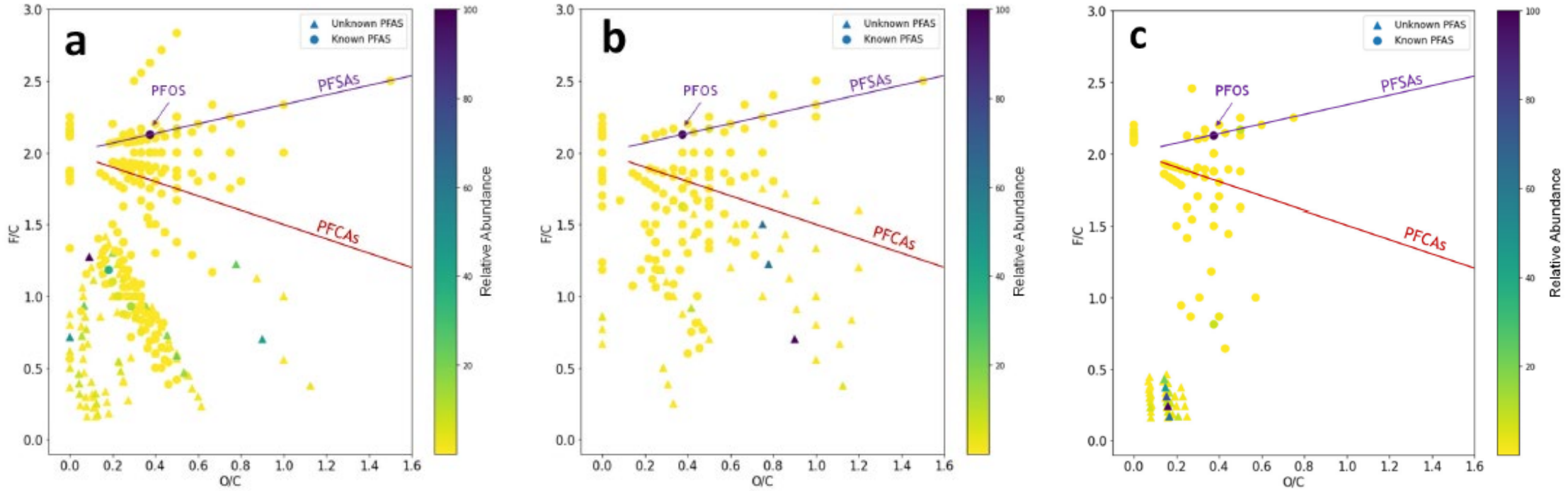


Figure ES 2: Modified van Krevelen diagrams illustrating the PFASs detected at Confidence Levels 1 (Known PFAS) and 2 (Unknown PFAS) in (a) the AFFF sample, (b) the groundwater sample from Site B, and (c) the WWTP effluent sample from Site B. The lines on which PFSAs and PFCAs fall are highlighted.

Blotevogel *et al.*, SERDP Project ER20-1265, 2021

Bulk analysis of unknown PFAS using extractable organofluorine and total fluorine measurements (requires specialized equipment)

Extractable organofluorine (EOF) may only be a small fraction of the **total fluorine** (TF) pool in biosolids (note, log scale of x-axis).

Combustion ion chromatography (CIC) is a new tool to measure TF, but still some optimization needed to prevent interferences and improve quality assurance and quality control between sample types.

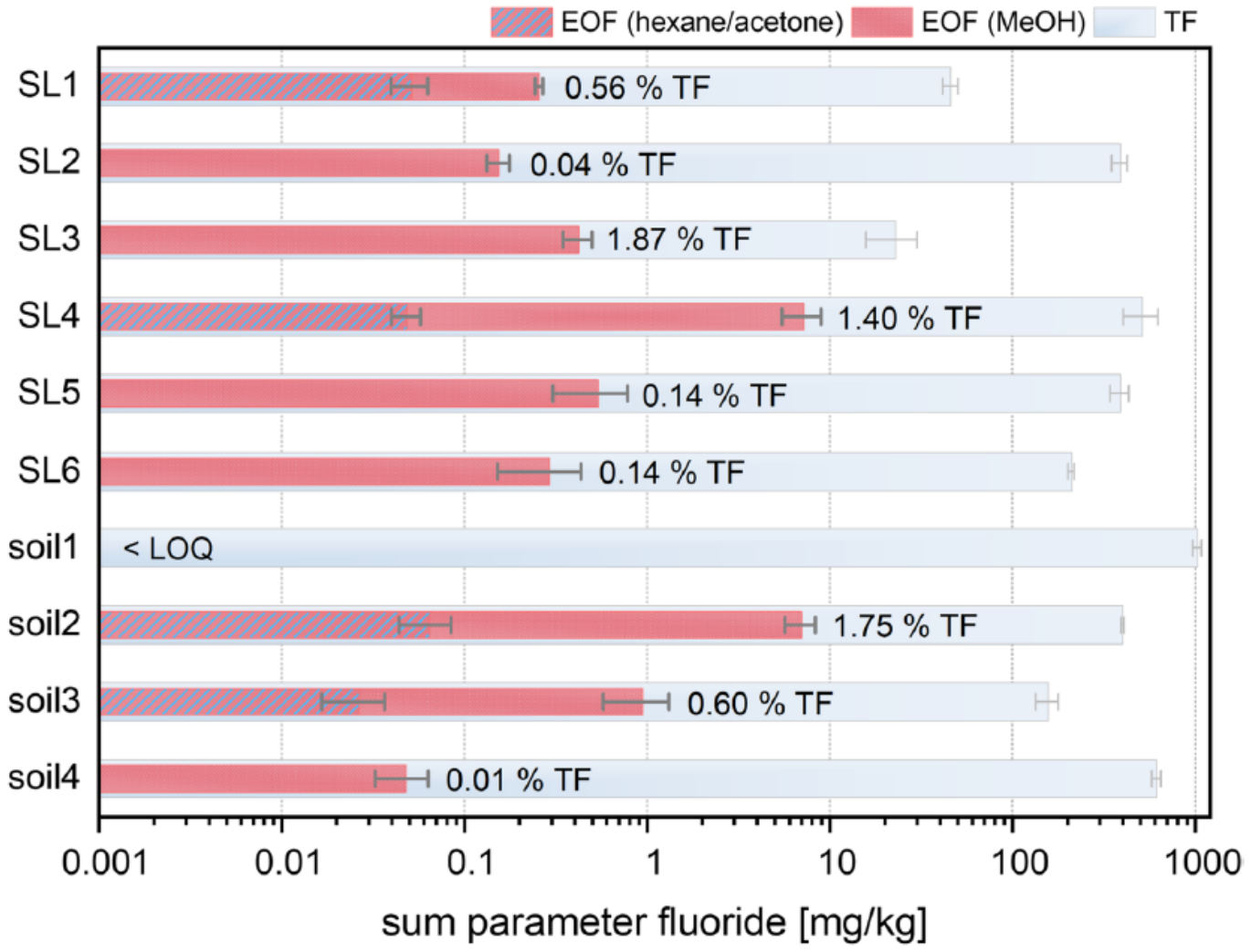


Fig. 6 Cumulated EOF values (combined hexanes/ acetone and MeOH extraction) over TF values (blue) and respective EOF/TF percentages of the investigated sewage sludge and soil samples (note the log scale). The detected EOF value of **soil1** was below the LOQ. All error bars correspond to the respective standard deviations (*n* = 3)

Roesch *et al.*, *Environ. Sci. Pollut. Res.*, 2022

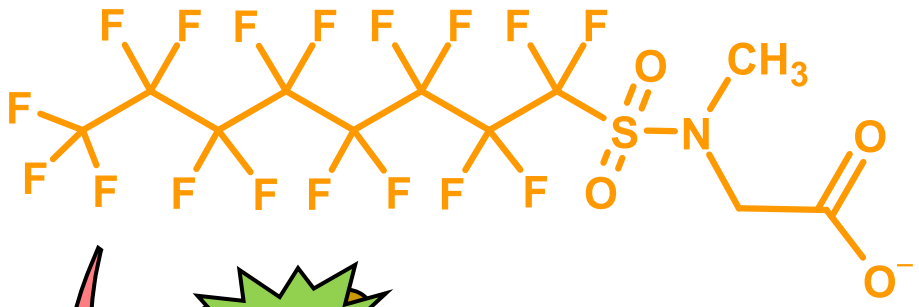
The TOP assay oxidizes precursors into targeted end-products, but organic matter in biosolids scavenges reactive species (available)

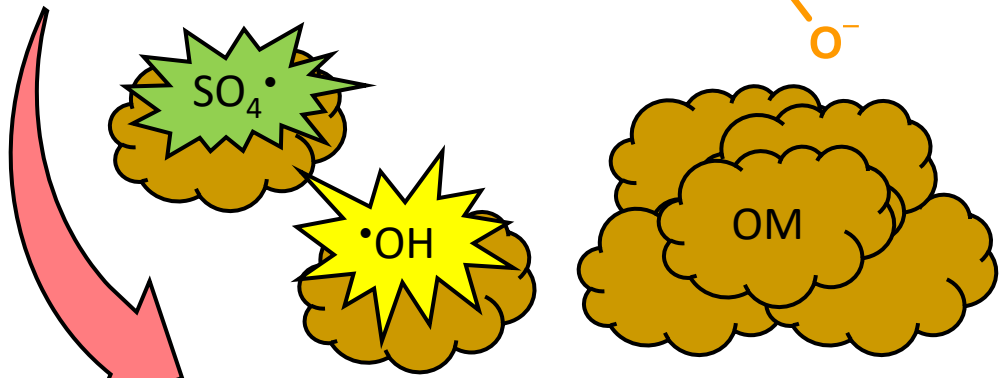
Marriah Ellington

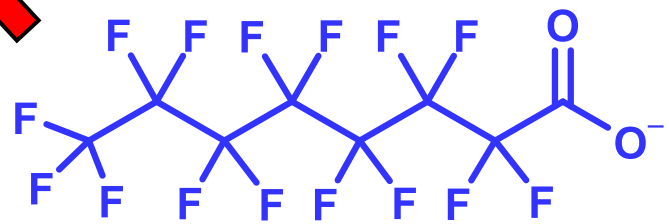
TOP conditions

$K_2(SO_4)_2$
NaOH
85 °C

N-MeFOSAA







PFOA

Modified TOP protocol for biosolids

Our approach

1. **Weigh aliquot, spike surrogates** [a]
2. **Methanol extraction, dilute to 20% MeOH in deionized water**
3. **Conduct solid-phase extraction, elution, N_2 evaporation**
4. **Add TOP reagents** [b]**, sonication, 24-h oxidation**
5. **Check pH, add acetonitrile**
6. **QuEChERS extraction, N_2 evaporation**
7. **Reconstitute extract, add internal standard (IS); LC-MS/MS**

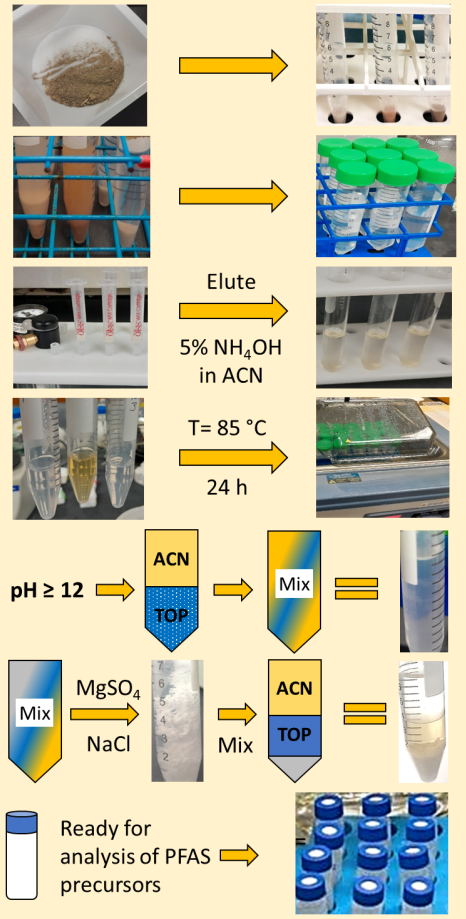


Figure 1. Schematic of the workflow for the modified TOP assay for soil.
[a] Spike: 5 ng g^{-1}; [b] 120 mM potassium persulfate and 300 mM sodium hydroxide

Acknowledgements

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Personal Care Products Council
Strategic Environmental Research and Development Program
UMBC Office of Undergraduate Education
UMBC Office of the Vice President of Research
US-Israel Binational Agricultural Research and Development Fund
US Army Corps of Engineers
USDA Forest Service
USDA National Institute of Food and Agriculture
US Geological Survey

Thanks for your attention

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