Ultra Short PFAS Analysis and its Impacts on the Environment

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SAFER GREENER SMARTER

Agenda

- Background
- Ultra Short Chain PFAS
- Measurement and Occurrence of Ultra Short Chain PFAS
- Analytical Methods for Ultra Short Chain PFAS
- Summary

Background

Background

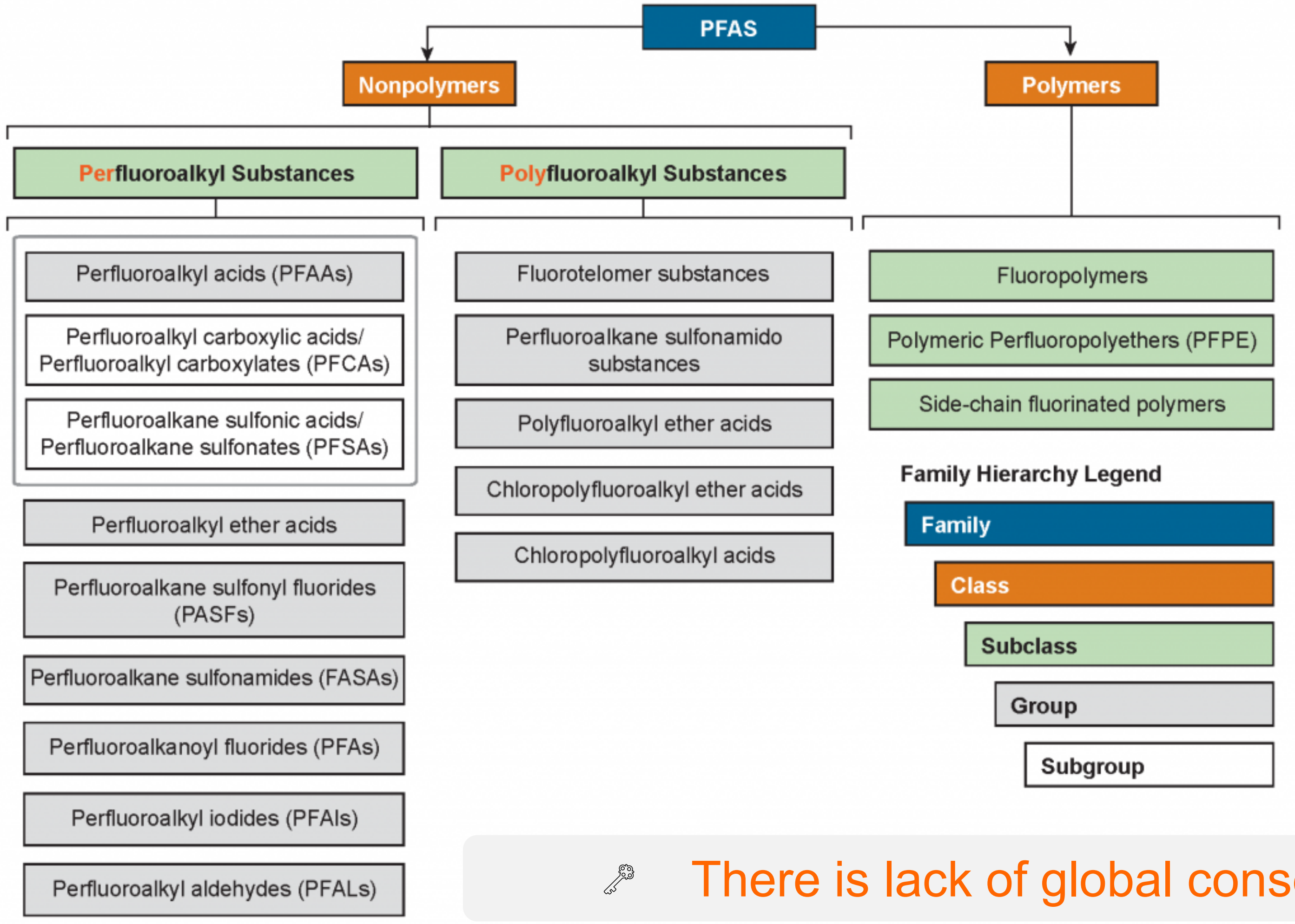
- Regular PFAS 3000 – 7000 isomers
- No Standard Method for measuring Ultrashort PFAS (C1-C3)
- SGS Axys developed an Ultrashort PFAS method
- Definition of Ultrashort PFAS
- >7 Million isomers due to definition of Ultrashort PFAS
- Current EPA Method 1633 measures Short and Long Chain PFAS (C4 – C14)

Background

- Moissan reported on perfluorocarbon synthesis in 1890
- The first perfluoroalkyl acid, trifluoracetic acid (TFA) first synthesized in 1922 by Belgian chemist Frederic Swarts at the University of Ghent (chromic acid oxidation of n-trifluoromethyl aniline)
- Trifluoroacetic acid was the strongest organic acid known at that time and described as being resistant to chemical attack
- Industrial scale synthesis of PFAS >100 tons p.a. during 1930's as azo dyes used in military applications.
- >250,000 synthetic organofluorine compounds reported in 1983
- Evidence for PFAS biological recalcitrance since before 1950

Ref: *Ultrashort PFAS – the long and the short of it!, Ian Ross, CDM Smith, August 2024.*

Background - PFAS terminology and family tree



- EPA: At least two continuous carbons containing fluorine where one carbon is fully fluorinated and the other is at least partially fluorinated. **Also, case by case (August 2023)!**
- OECD: Atleast one fully fluorinated CF3 or CF2

There is lack of global consensus on what constitutes a PFAS

PFAS (itrcweb.org)

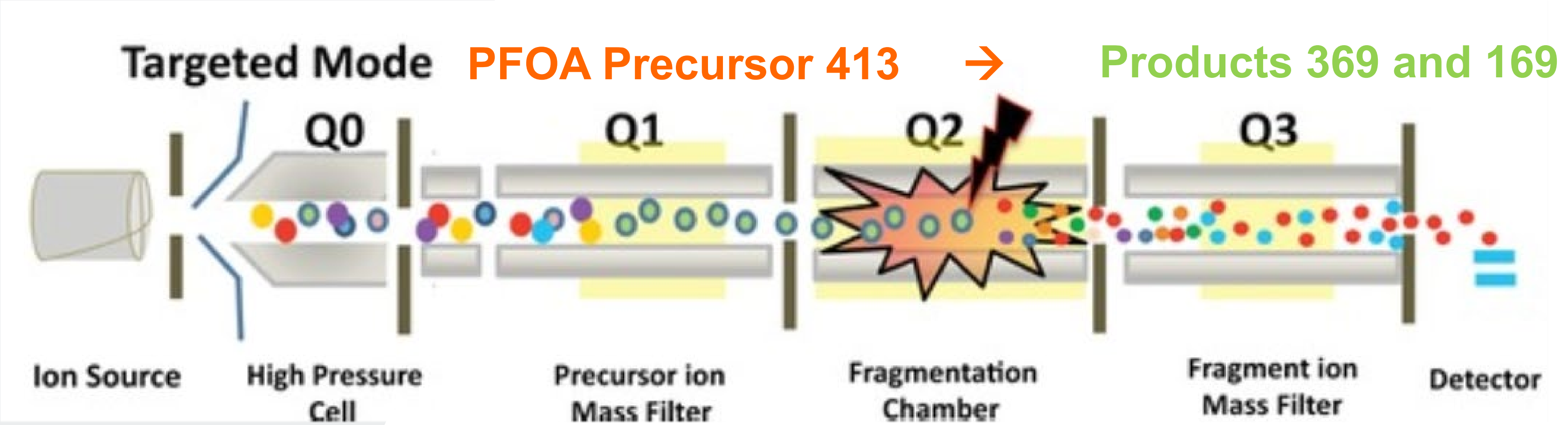
Organisation for **Economic Co-operation and Development** (OECD; French: Organisation de coopération et de développement économiques, OCDE) is an intergovernmental organisation with 38 member countries, founded in 1961 to stimulate economic progress and world trade.

Background: Methods

- Sophisticated Data Acquisition
- Analytical Methods:
  - LC/MS/MS
  - AOF (Combustion IC)
  - TOP Assay (Oxidation)
  - LC qTOF HRMS
  - GC qTOF HRMS
  - Non - Targeted Analysis (NTA)
  - Complex Libraries (CompTox Database – 875,000 Compounds, Instrument Vendor Libraries)
  - Mass Spectral Interpretation

Analytical Methods: LC/MS/MS

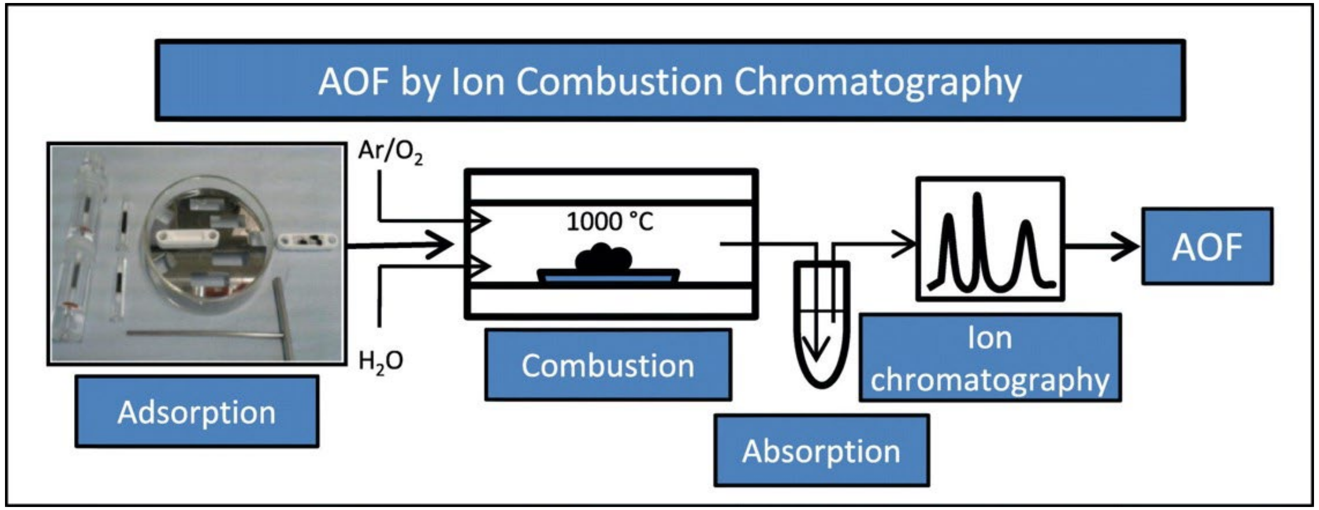
- LC/MS/MS: First separate analytes in solution by liquid chromatography
- Triple Quadrupole or Tandem Mass Spec
  - Q1/MS1 separates the precursor ion(s) from everything else in the sample and allows them into the collision cell
  - Q2 is the collision cell, ions are fragmented forming product ions
  - Q3/MS2 allows only selected product ions to pass through to the detector



Analytical Methods: Adsorbable Organic Fluorine

- Good potential for quickly understanding total fluorine, EPA Method 1621 (2024)
- Challenges
  - Fluorine background
  - Reporting limits 100-1000 times higher than LC-MS/MS
  - No chain length information

Technique for estimating organic fluorine in a sample by combustion ion chromatography.



Science of The Total Environment **673**, 384–391 (2019).

Note:
Ultrashorts PFAAs such as TFA not detected using AOF using USEPA 1621

Ref: Ian Ross, CDM Smith, August 2024

Ultra Short Chain PFAS

Ultrashort “PFAS”

Ultrashort: Carbon chain length < 4

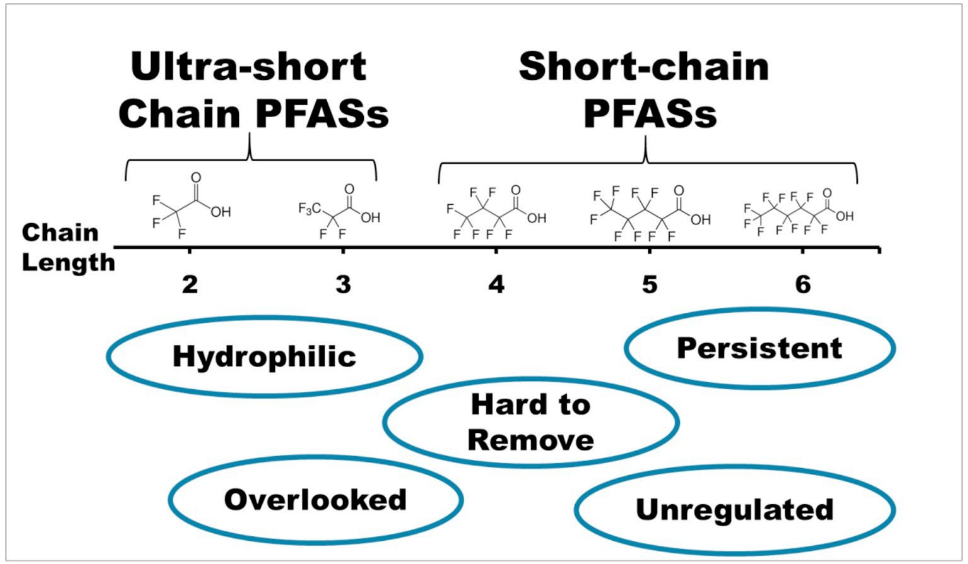


Image from Ateia et al.2019

USEPA

- At least two continuous carbons containing fluorine where one carbon is fully fluorinated and the other is at least partially fluorinated.
- **Update: Case by case (August 2023)!**

OECD

- At least one fully fluorinated CF_3 or CF_2

Canada

- At least one fully fluorinated CF_3 or CF_2

Trifluoroacetic acid and Trifluoromethanesulfonic acids are likely not PFAS in the US, but PFAS in Canada/Europe

Ultrashorts Target List

Analytes	Shorthand	Formula	Surrogate Standard
Carboxylates (PFCA)			
Trifluoroacetic acid	TFA or PFEtA	CF_3-COOH	$^{13}C_2$-PFEtA
Pentafluoropropionic acid	PFPrA	CF_3-CF_2-COOH	$^{13}C_3$-PFPrA
Sulfonates (PFSA)			
Trifluoromethanesulfonic acid	TFMS or PFMeS	CF_3-SO_4H	$^{13}C_3$-PFPrA
Pentafluoroethane-sulfonic acid	PFEtS	CF_3-CF_2-SO_4H	$^{13}C_3$-PFPrA
Heptafluoropropane-sulfonic acid	PFPrS	CF_3-CF_2-CF_2-SO_4H	$^{13}C_3$-PFPrA

- Focusing on 5 perfluorinated alkyl acids
- Extendable to polyfluorinated acids as needed

- Note: Bistriflimide (TFSI) also considered an ultra-short chain (C2) but amenable to 1633 analysis

Concerns around ultrashort PFAS are NOT new!

I&E

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14. Jordan, A.; Frank, H. Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFCs. *Environ. Sci. Technol.* **1999**, *33*, 522–527, DOI: 10.1021/es980674y [ACS Full Text], [CAS], [Google Scholar] open URL

15. Berg, M.; Müller, S. R.; Mühlemann, J.; Wiedmer, A.; Schwarzenbach, R. P. Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. *Environ. Sci. Technol.* **2000**, *34*, 2675– 2683, DOI: 10.1021/es990855f [ACS Full Text], [CAS], [Google Scholar] open URL

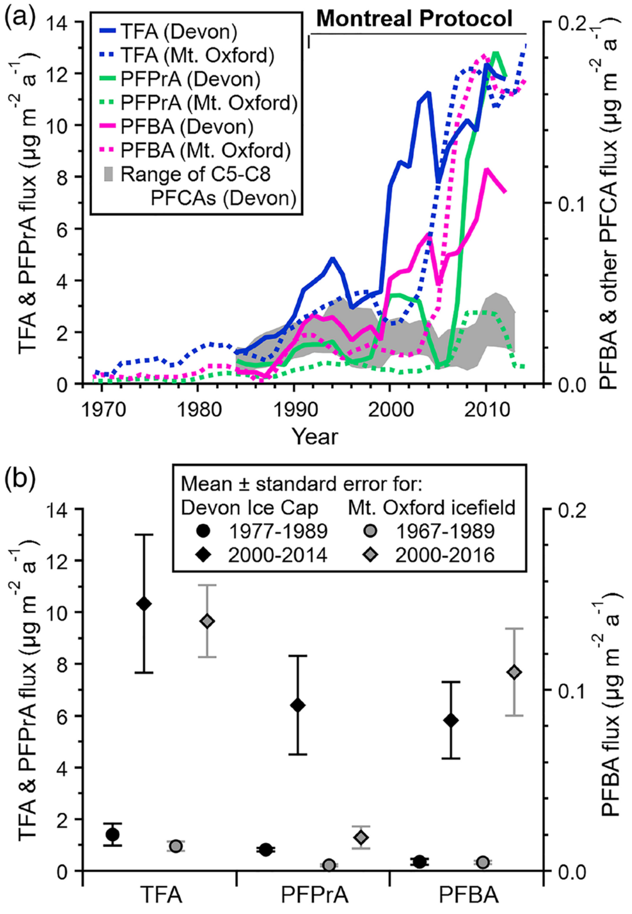
16. Rompp, A.; Klemm, O.; Fricke, W.; Frank, H. Haloacetates in fog and rain. *Environ. Sci. Technol.* **2001**, *35*, 1294– 1298, DOI: 10.5555/es0012220 [ACS Full Text], [CAS], [Google Scholar] open URL

17. Scott, B. F.; Mactavish, D.; Spencer, C.; Strachan, W. M. J.; Muir, D. C. G. Haloacetic acids in canadian lake waters and precipitation. *Environ. Sci. Technol.* **2000**, *34*, 4266– 4272, DOI: 10.1021/es9908523 [ACS Full Text], [CAS], [Google Scholar] open URL

18. Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G. Poly and Perfluorinated Carboxylates in North American Precipitation†. *Environ. Sci. Technol.* **2006**, *40*, 7167– 7174, DOI: 10.1021/es061403n [ACS Full Text], [CAS], [Google Scholar] open URL

SGS

Sources of TFA and PFPrA



Pickard et al. 2020

- Ice core records in the Arctic show TFA and PFPrA are increasing in reference environments after Montreal Protocol
- Several sources are likely responsible though most TFA is likely perfluoroacyl halide hydrolysis
  - HCFC-124
  - HFC-134
- Sources in polluted environments include
  - Precursor transformation in fire suppression/AFFF PFAS (heptafluoropropane HFC-227ea and perfluoro-2-methyl-3-pentanone)
  - General fluorotelomer transformation

Rainwater TFA Estimates high ng/L background

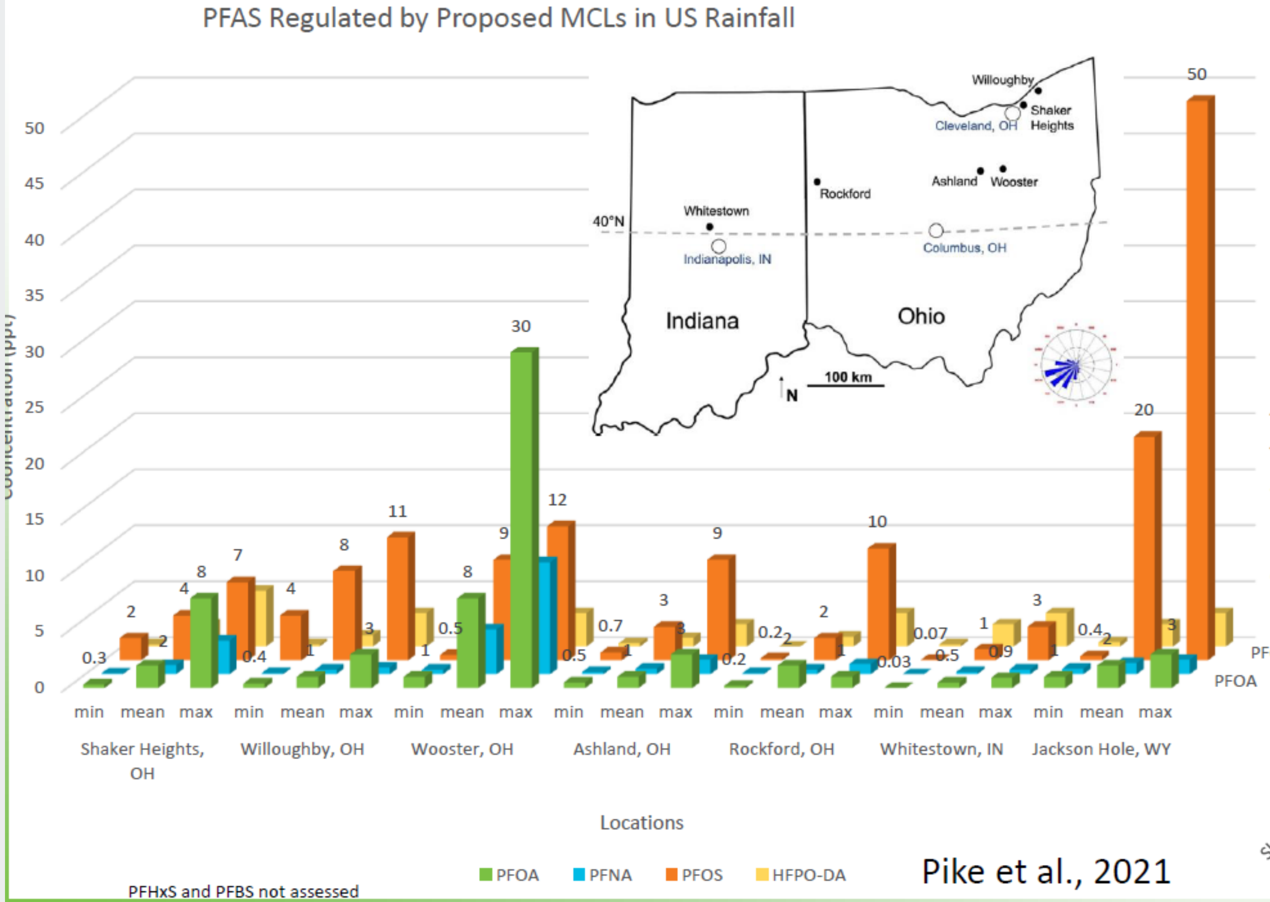
Table 1. Summary of Model Results for HFO-1234yf and TFA

	CH annual[a]	US annual[a]	US summer[a]	US summer[b] by Luecken et al[23]	EU annual[a]
HFO emissions (Gg)	42.65	24.53	15.21	15.21	19.16
mean HFO (pptv)	2.62	2.20	4.19	7.40	2.73
max HFO (pptv)	30.96	19.44	40.95	300.00	19.08
mean TFA (pptv)	0.48	0.33	0.83	na	0.42
max TFA (pptv)	3.77	1.15	3.26	>0.8	1.78
mean TFA deposition ($kg\ km^{-2}\ yr^{-1}$)	0.96	0.45	0.59	0.48	0.52
max TFA deposition ($kg\ km^{-2}\ yr^{-1}$)	7.94	2.12	2.90	2.34	2.95
mean rainwater conc of TFA ($ng\ L^{-1}$)	638	480	1277	500[b]	620
max rainwater conc of TFA ($ng\ L^{-1}$)	22 574	4485	15 417	1264[b]	2099

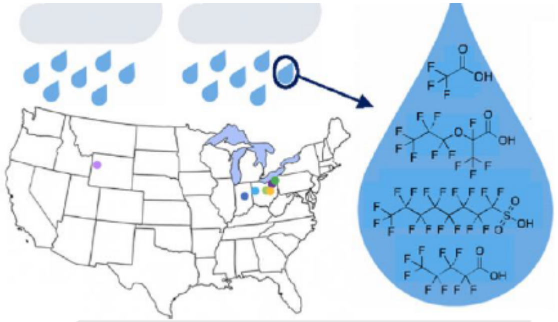
Wang et al. 2018

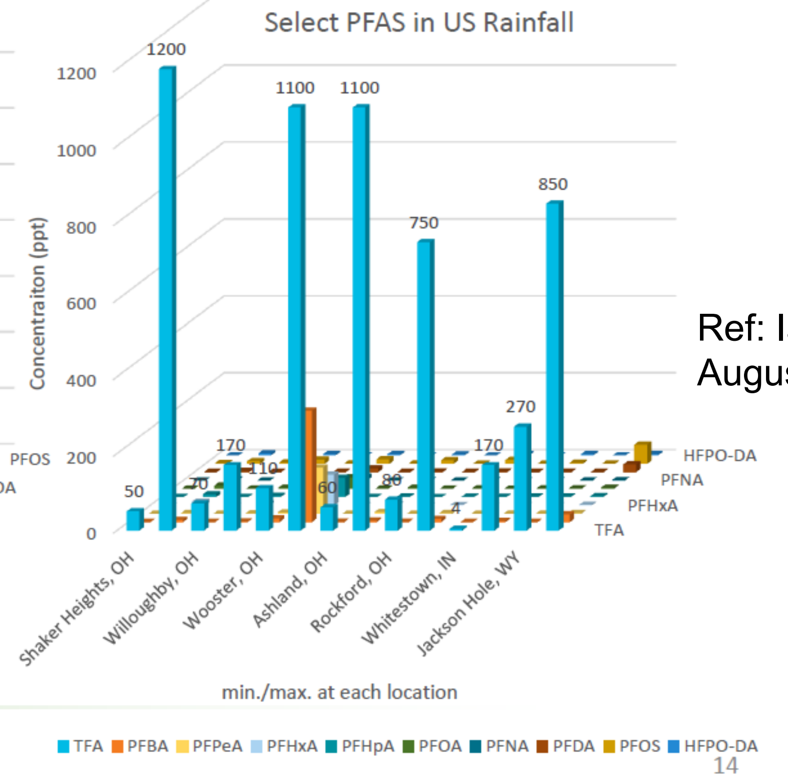
Rainwater PFAS Estimates

Select PFAS in US Rainfall



Pike et al., 2021

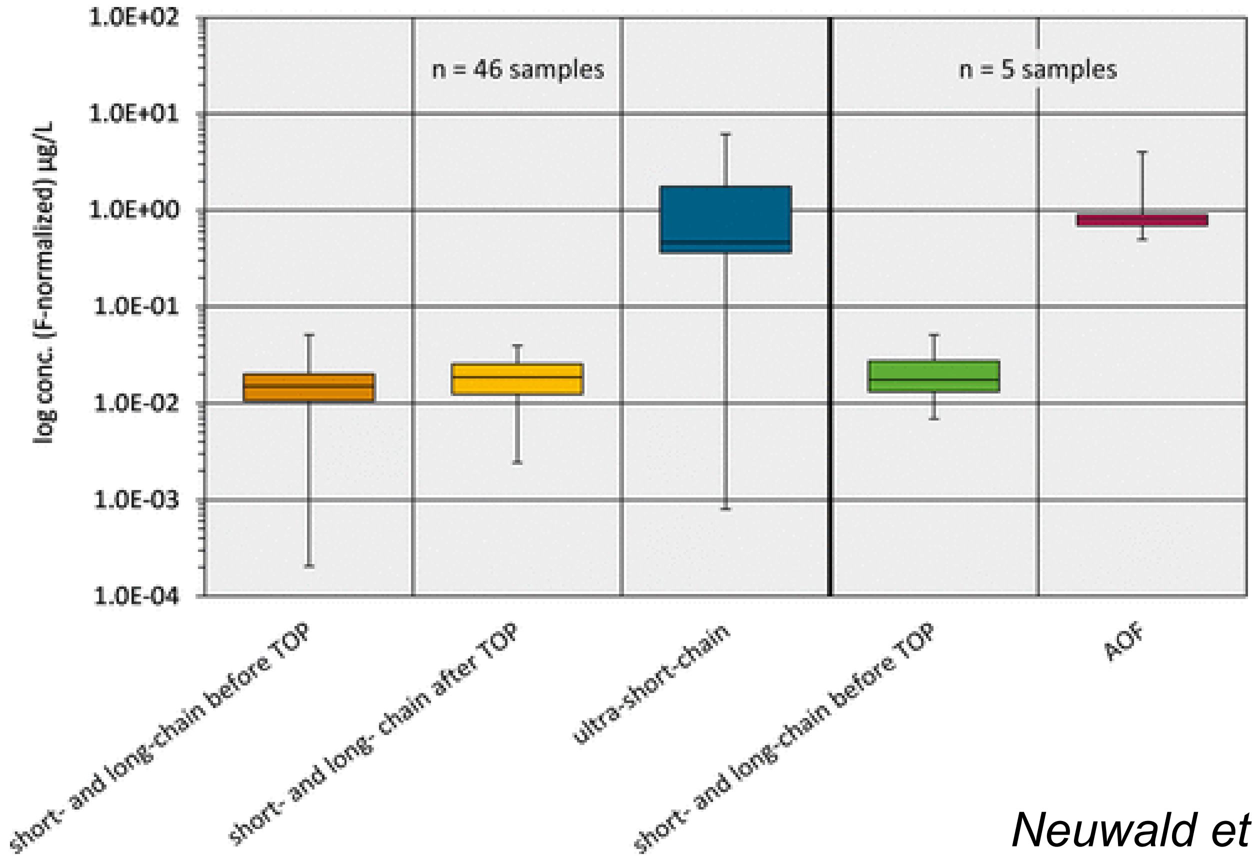


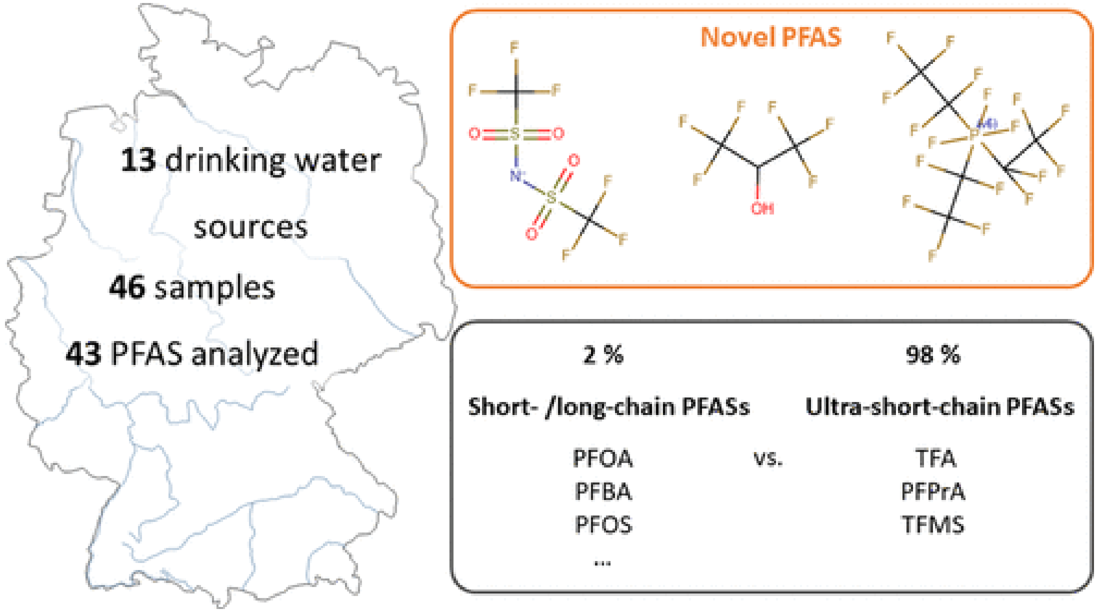


Ref: Ian Ross, CDM Smith, August 2024

Follow up study (Kim et. al., 2022) found estimated ΣPFAS16,400 ppt in rain at Wooster, Ohio, as maximum detected

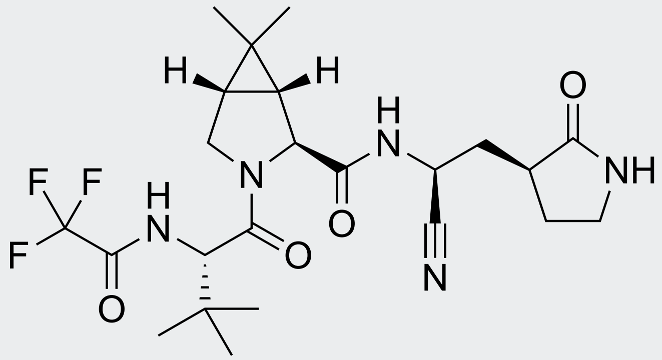
98% of German Target Drinking Water PFAS is ultrashorts



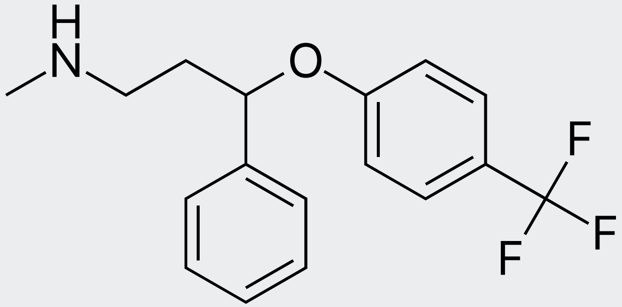


Neuwald et al. 2023

Drugs, Agrochemicals and Trifluoromethylation



Fluoxetine (Prozac)

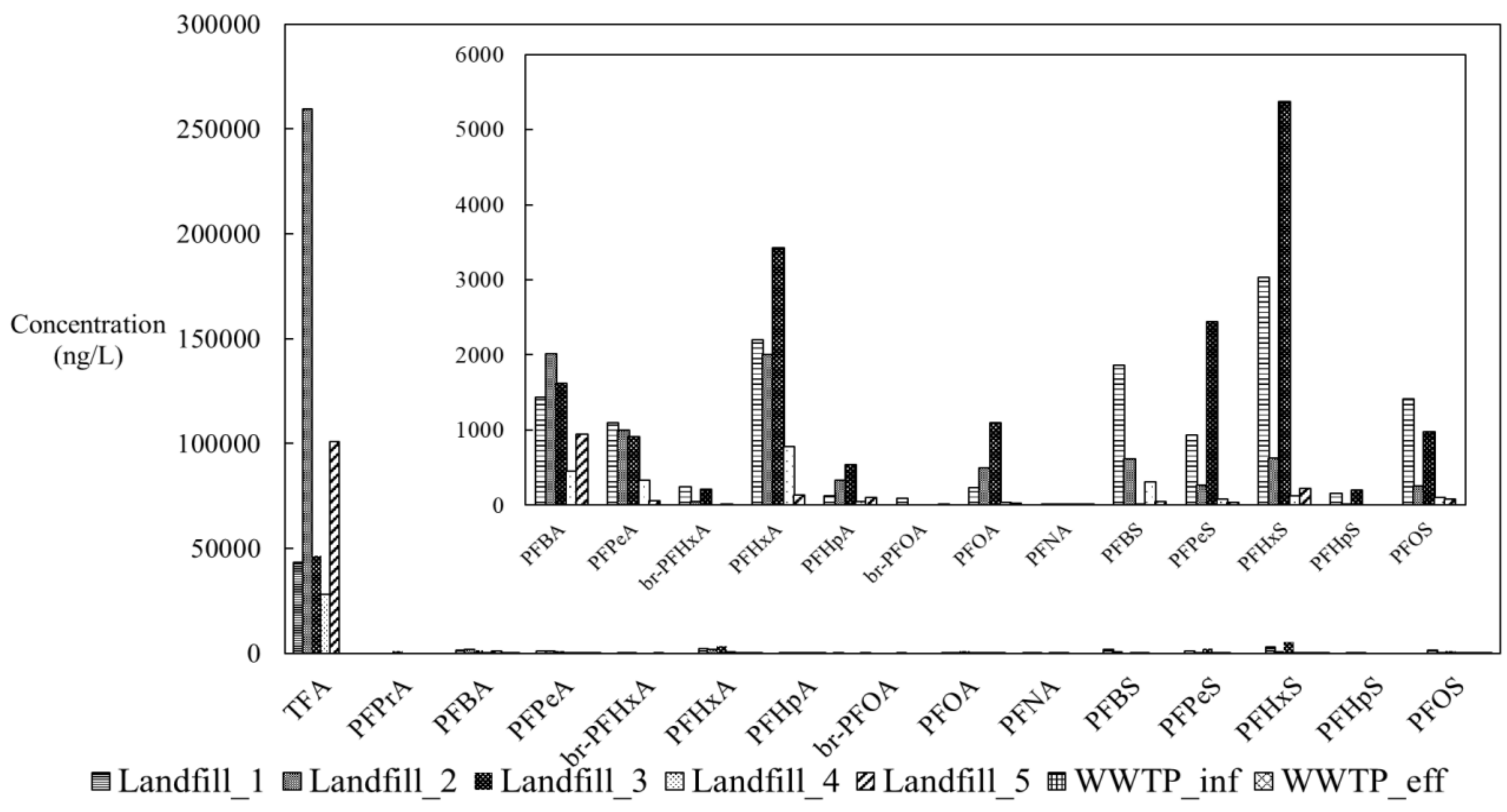


Paxlovid constituent

- Adding a CF_3 group to a molecule (trifluoromethylation) is a well-known technique to improve biological activity, chemical or metabolic activity, and chemical or metabolic stability
- 15-20% of all FDA-licensed drugs and >50% of bestselling drugs contain fluorine
- Also common herbicides such as trifluralin
- This CF_3 group breaks to form TFA

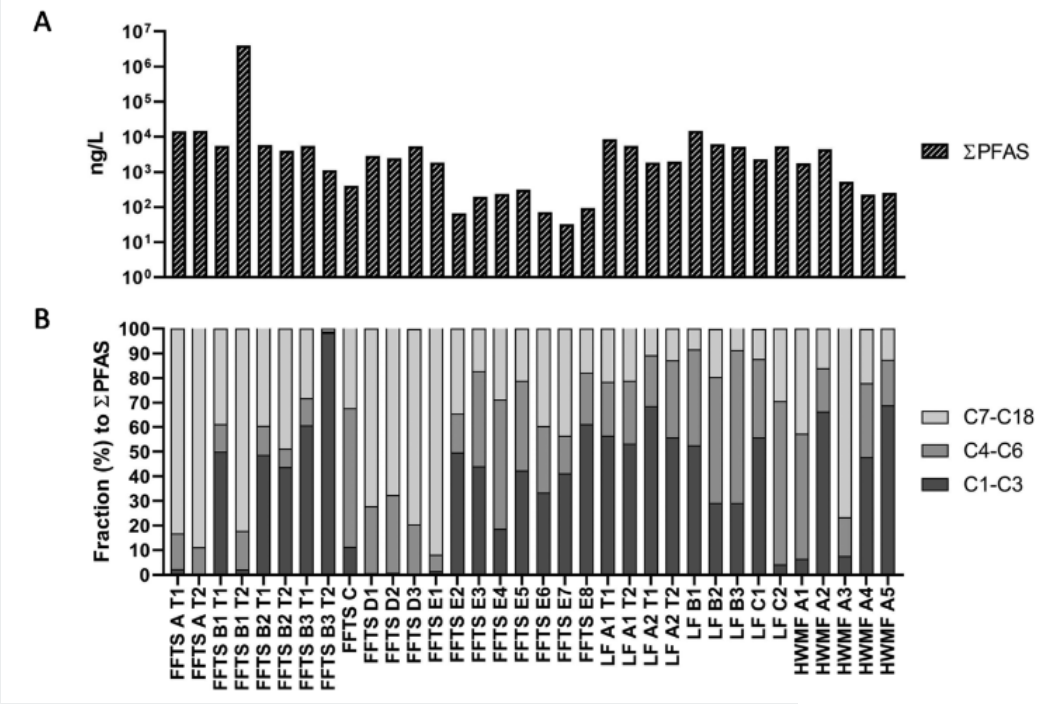
TFA predominates among PFAAs in US landfill leachate

- High levels of TFA most likely from fluorotelomer transformation and chain shortening



Tsou et al. 2023

Occurrence of ultrashort chain sulfonates



Björnsdotter et al. (2019)

- Presence of PFEtS (C2) PFPrS (C3) sulfonates noted in legacy 3M AFFF (Barzon-Hanson and Field 2015)
  - PFEtS 7-13 mg/L
  - PFPrS 120-270 mg/L
- Björnsdotter et al. (2019) published on occurrence in Sweden
  - Detection frequencies 94, 71 and 88% for C1, C2, C3
  - TFMS up to 1000 ng/L, PFEts and PFPrS up to 1700 and 15000 ng/L
  - AFFF sites main source
- Other sources? Ionic Liquids? Battery fluids? More study is needed

Method Objectives

01

Develop and validate an isotope-dilution LC-MS/MS approach for ultrashorts

02

Test fit with EPA 1633/typical PFAS method for short/long chain

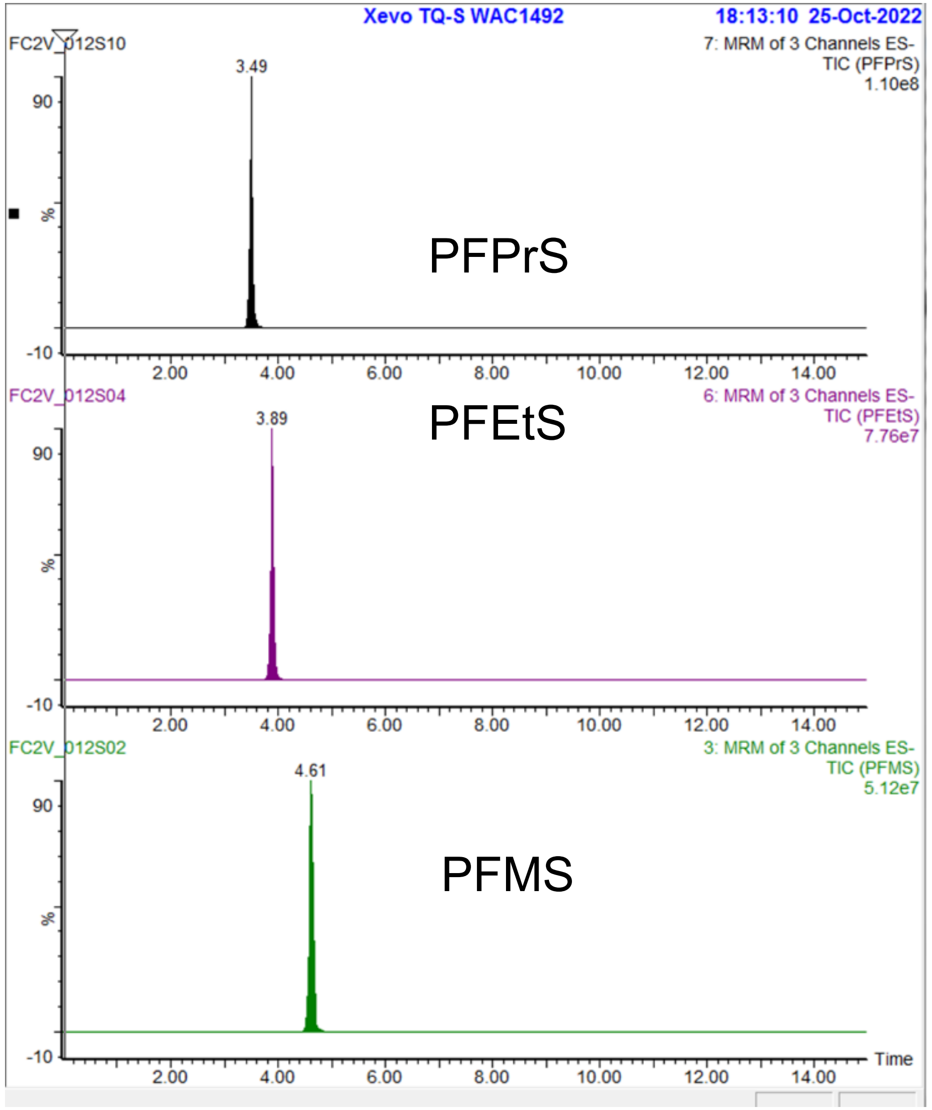
03

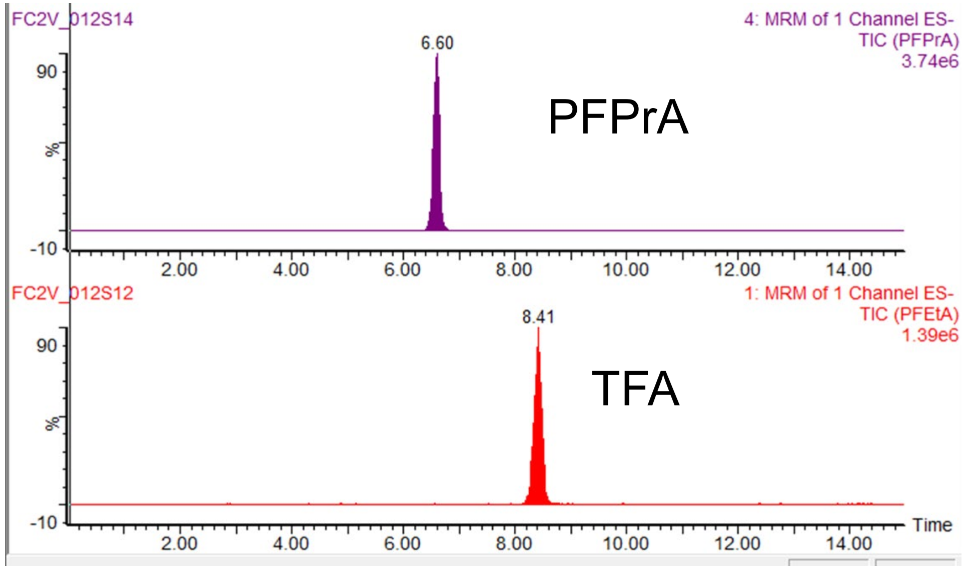
Test with complex samples for limitations and interferences

04

Test the method to extend the Total Oxidizable Precursor Assay (TOP)

Method Choices: Chromatography





- We tried two columns and finalized on a RESTEK Polar X 2.7 µm column with HILIC and Ion-Exchange
- 15-minute run time
- Good retention for targets (reversed from the C-18) and generally stable performance

Making Ultrashorts work

Pre-Preparation

- Sample up to 500 mL
- Spike with isotopically labeled standards
- Aqueous: pH Adjustment to 6-7

Preparation

- Use of Weak Anion Exchange (WAX) cleanup for all analysis
- Use of dispersive carbon cleanup
- No Evaporation of 1633 extract
- Portion of extract evaporated to dryness to remove ammonia prior to ultrashorts analysis

LC-MS/MS Analysis with Isotope Dilution/Surrogate Standard Quantitation

- Use of multiple transitions/ratio checks for interference monitoring
- Use of injection internal standards for surrogate recovery monitoring

Method Validation in Drinking Water

I&E

Target	Mean	%RSD	Clean Water Reporting Limit (ng/L at 500 mL)
TFA	101	14%	20
PFPrA	75	3%	4.2
PFMS	59	4%	2.0
PFEtS	69	4%	1.0
PFPrS	66	4%	1.0
$^{13}C_2$-PFEtA	102	18%	
$^{13}C_3$-PFPrA	124	4%	

- Pre-existing literature indicates significant challenges on WAX
- Initial validation in aqueous samples only
- Samples run from a portion of the Method 1633 extract
- More appropriate labeled standards needed for PFSA
- Optimization options limited by combination with 1633
  - pH of sample loading at 6-7
  - Capacity of ion-exchange mode for ultrashorts
  - Need for a separate method

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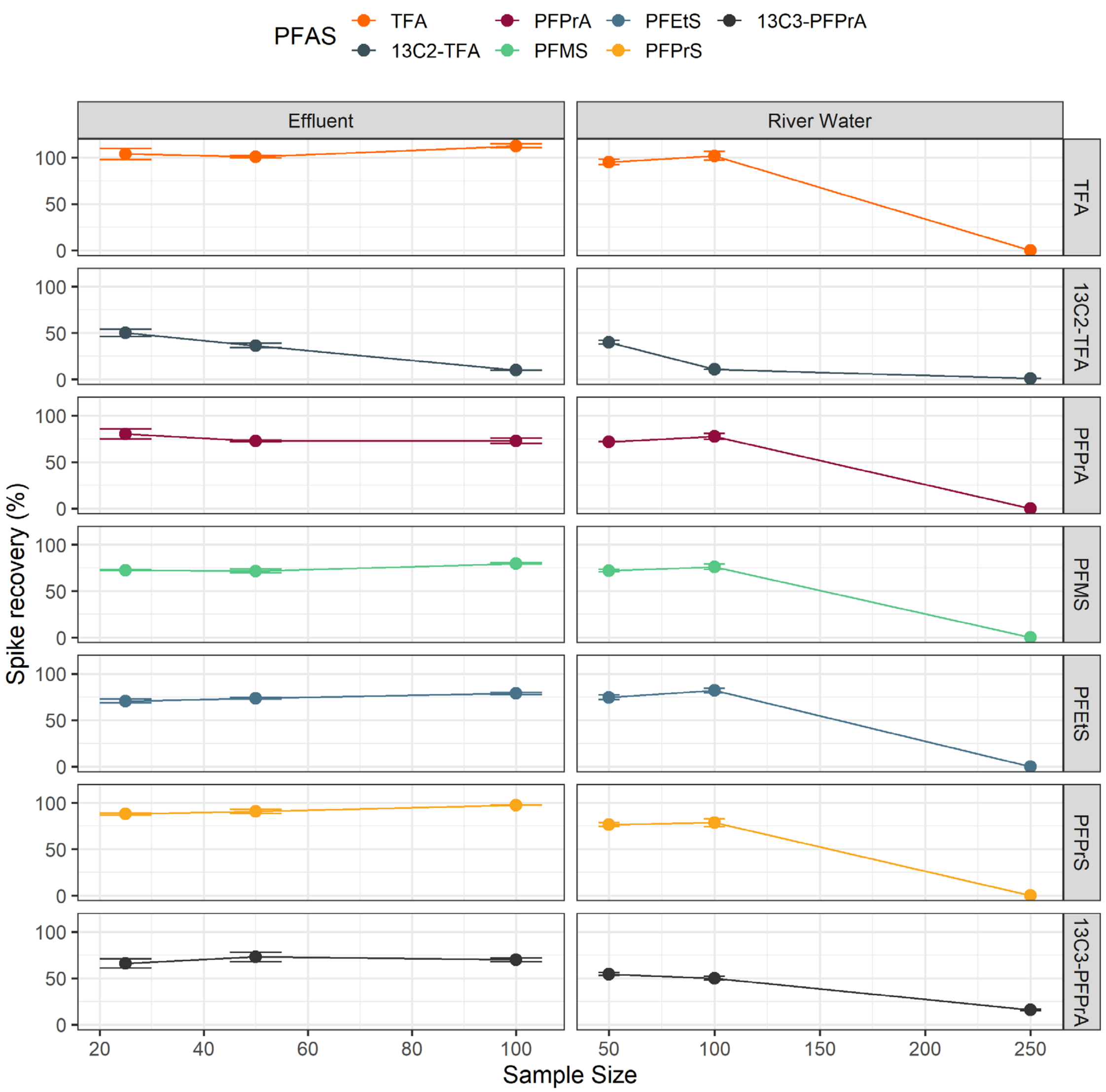
Method Robustness

- Robustness tested with spike experiments in real samples
- The recovery of $^{13}C_2$-TFA was heavily sample size dependent due to lack of retention on cartridge
- Sample sizes >100 ml resulted in very unusable data
- This complicates easy combination with EPA 1633 (default sample 500 mL). However, no issues as a standalone test

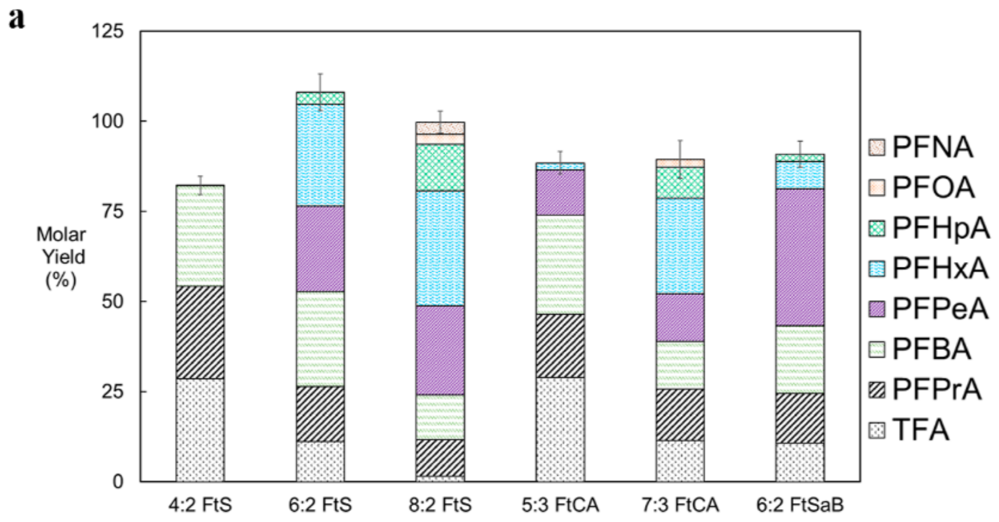


Final Standalone Method Attributes

Target	Standalone Method RLs (20 mL Sample)	Recovery Specifications (labeled all samples, targets in LCS)
TFA	100	50-150
PFPrA	20	50-150
PFMS	10	50-150
PFEtS	5	50-150
PFPrS	5	50-150
$^{13}C_2$-PFEtA		50-150
$^{13}C_3$-PFPrA		50-150

- A 20 mL sample provides good accuracy and precision in samples with matrix interference
- Given typical expected levels of these targets and background (high ng/L TFA in rainwater for example), these RLs are fit for purpose
- Flow rate adjusted to extend retention time on column

Extending TOP Analysis (*Tsou et al. 2023)*



- Extending TOP to cover TFA and PFPrA uncovers most of that "missing" mass fluorotelomer PFAS

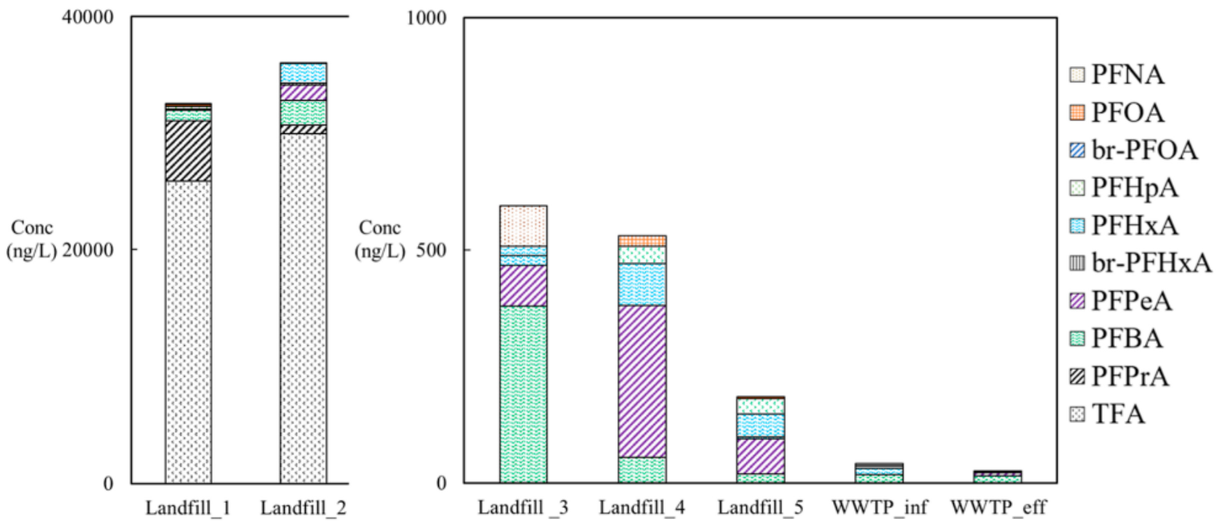


Figure 4. Concentration of precursors (ΔPFCAs) produced in the TOP assay for landfill leachates and wastewater treatment plant samples. Raw data from these samples can be found in Tables S3 and S4.

Simple Direct Injection Approach (similar to Method D8421)

I&E

1 mL of sample + surrogates + methanol

Filter

- Syringe filter 0.2 um

LC-MS/MS Analysis

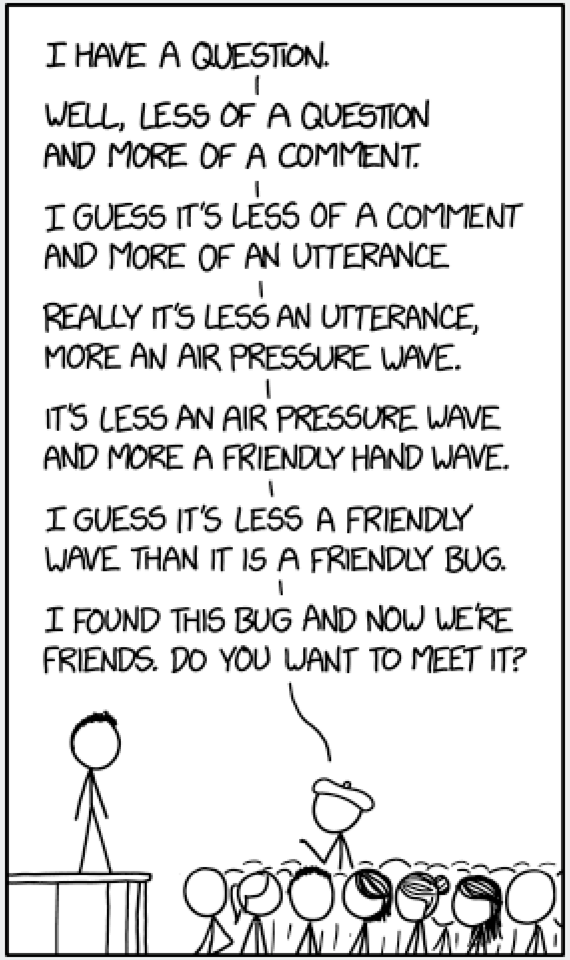
- Use of multiple transitions/ratio checks for interference monitoring
- Use of injection internal standards for surrogate recovery monitoring

RLs

- TFA – 133 ng/L
- PFPrA – 28 ng/L
- TFMS – 13 ng/L
- PFEtS – 7 ng/L
- PFPrS – 7 ng/L

Summary

Summary



https://xkcd.com/2191/

- Complex Analysis
- Develop method-specific technical (and robust QC) requirements
- Look for additions of Ultra Short Chain PFAS as Target Compounds into existing methods and regulations
- PFPrA can be measured by 1633 however, peak shapes are poor as it does not contain a secondary transition – leads to unreliable results
- SGS has created a Work Item at ASTM D -19.06 WK88987 for measuring Ultrashort PFAS

Thank you!

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