



Ultrashort PFAS:

*Understanding Their Measurement and
Relevance for Remediation Monitoring*

PFAS Definitions



USEPA

- A structure that contains the unit $\text{R-CF}_2\text{-CF(R')R''}$, where R, R', and R'' do not equal "H"
- The carbon-carbon bond is saturated
- Branching, heteroatoms, and cyclic structures are included
- Multiple definitions, **none include only one CF_3**

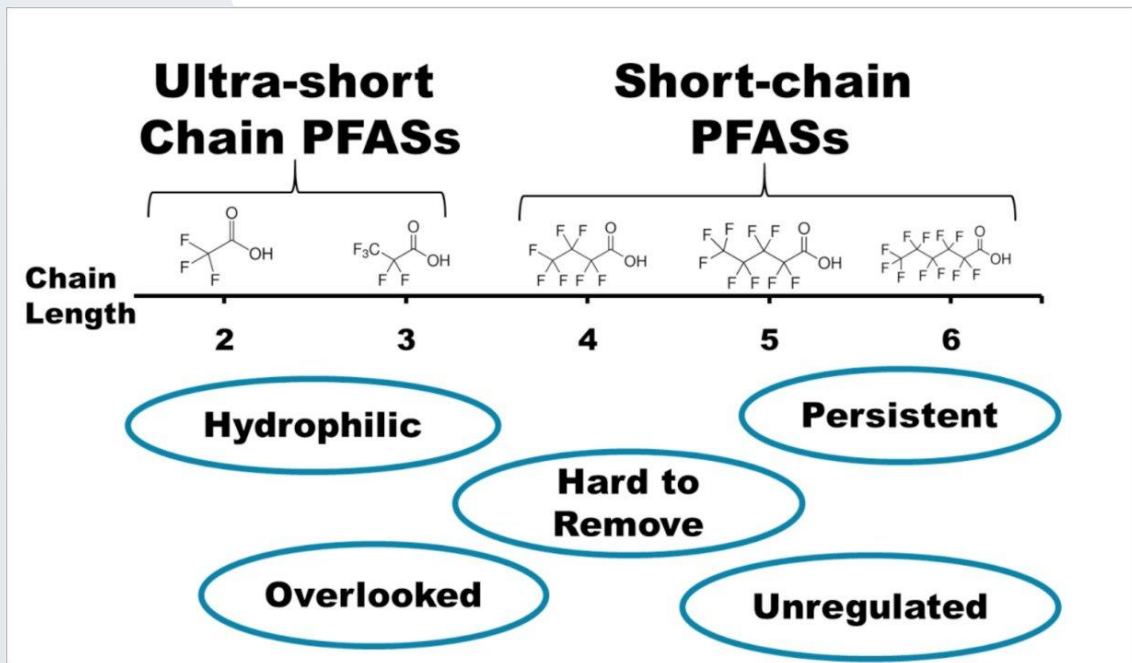
OECD

- Any chemical with at least a perfluorinated methyl group ($-\text{CF}_3$) or a perfluorinated methylene group ($-\text{CF}_2-$)
- At least **one fully fluorinated CF_3** or CF_2

Canada

- Any chemical with at least a perfluorinated methyl group ($-\text{CF}_3$) or a perfluorinated methylene group ($-\text{CF}_2-$)
- At least **one fully fluorinated CF_3** or CF_2

Ultra-short PFAS



Source: Ateia *et al.*: "The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review". *Chemosphere* 220 (2019) pp 866-882

"Ultrashort" = carbon chain length < 4

Using current definitions, trifluoroacetic acid (TFA) and Trifluoromethanesulfonic acid (TFMS) are not PFAS in the US, but PFAS in Canada/Europe

- Concerns around ultrashorts are emerging given multiple possible sources
- Contribute a significant proportion of the total PFAS measured at landfill sites (*The missing link in PFAS mass in landfill leachates?*)
- "New" chromatographic approaches make analyses almost routine
- Currently measurement of ultrashort PFAS is an independent method from 1633
- Extension of the PFAS analyte list to include ultrashorts has the potential to enhance the utility of the TOP assay

Concerns around ultrashort PFAS are NOT new...



13. Franklin, J. The atmospheric degradation and impact of 1,1,1,2-Tetrafluoroethane (Hydrofluorocarbon 134a). *Chemosphere* **1993**, *27*, 1565–1601, DOI: 10.1016/0045-6535(93)90251-y [[Crossref](#)], [[CAS](#)], [[Google Scholar](#)] [open URL](#)

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](#)

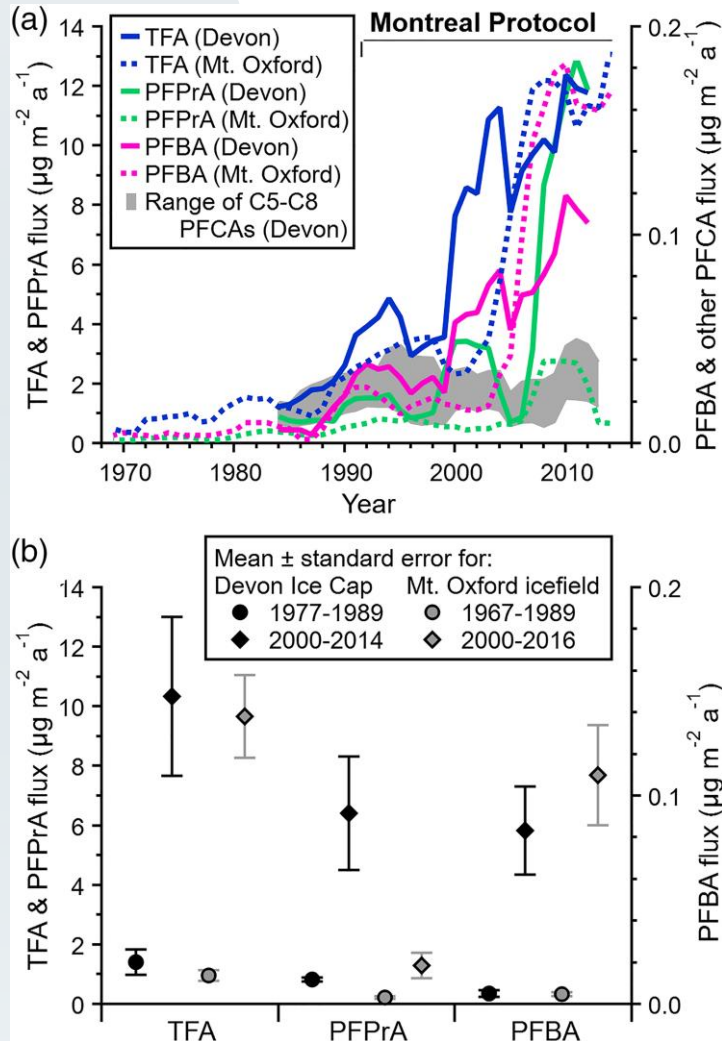
15. Berg, M.; Müller, S. R.; Mühlemann, J.; Wiedmer, A.; Schwarzenbach, R. P. Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. *Environ. Sci. Technol.* **2000**, *34*, 2675–2683, DOI: 10.1021/es990855f [[ACS Full Text](#) , [[CAS](#)],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

Sources of TFA and PFPrA



- Ice core records in the Arctic show TFA and PFPrA are increasing in the studied environments
- Several sources are likely, but it is suggested that TFA likely stems from perfluoroacyl halide hydrolysis of specific PFAS, e.g.,
 - HCFC-124
 - HFC-134
- Other sources in polluted environments include:
 - Precursor transformation of specific PFAS in AFFF, e.g., heptafluoropropane, HFC-227ea and perfluoro-2-methyl-3-pentanone
 - General fluorotelomer transformation

Source: Pickard *et al*: *Geophysical Research Letters*, **47**(10) 2020

Rainwater TFA Estimates – High ng/L Background

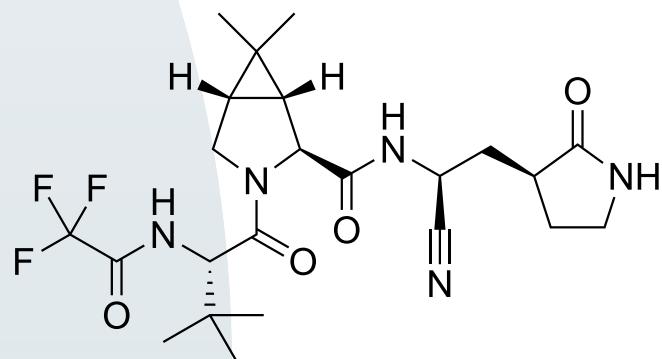


Table 1. Summary of Model Results for HFO-1234yf and TFA

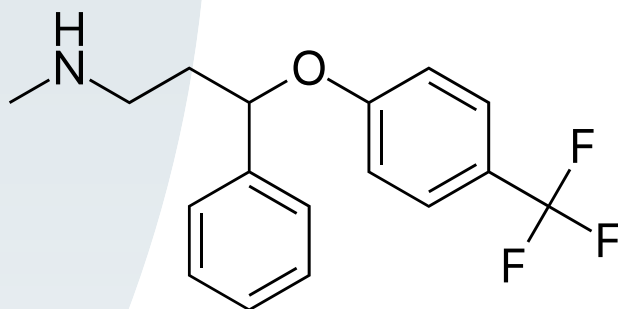
	CH annual ^a	US annual ^a	US summer ^a	US summer ^b by Luecken et al ²³	EU annual ^a
HFO emissions (Gg)	42.65	24.53	15.21	15.21	19.16
mean HFO (pptv)	2.62	2.20	4.19	7.40	2.73
max HFO (pptv)	30.96	19.44	40.95	300.00	19.08
mean TFA (pptv)	0.48	0.33	0.83	na	0.42
max TFA (pptv)	3.77	1.15	3.26	>0.8	1.78
mean 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

Source: Wang et al: *Environ Sci Technol*, **52**(5) 2018

Drugs, Agrichemicals and Trifluoromethylation



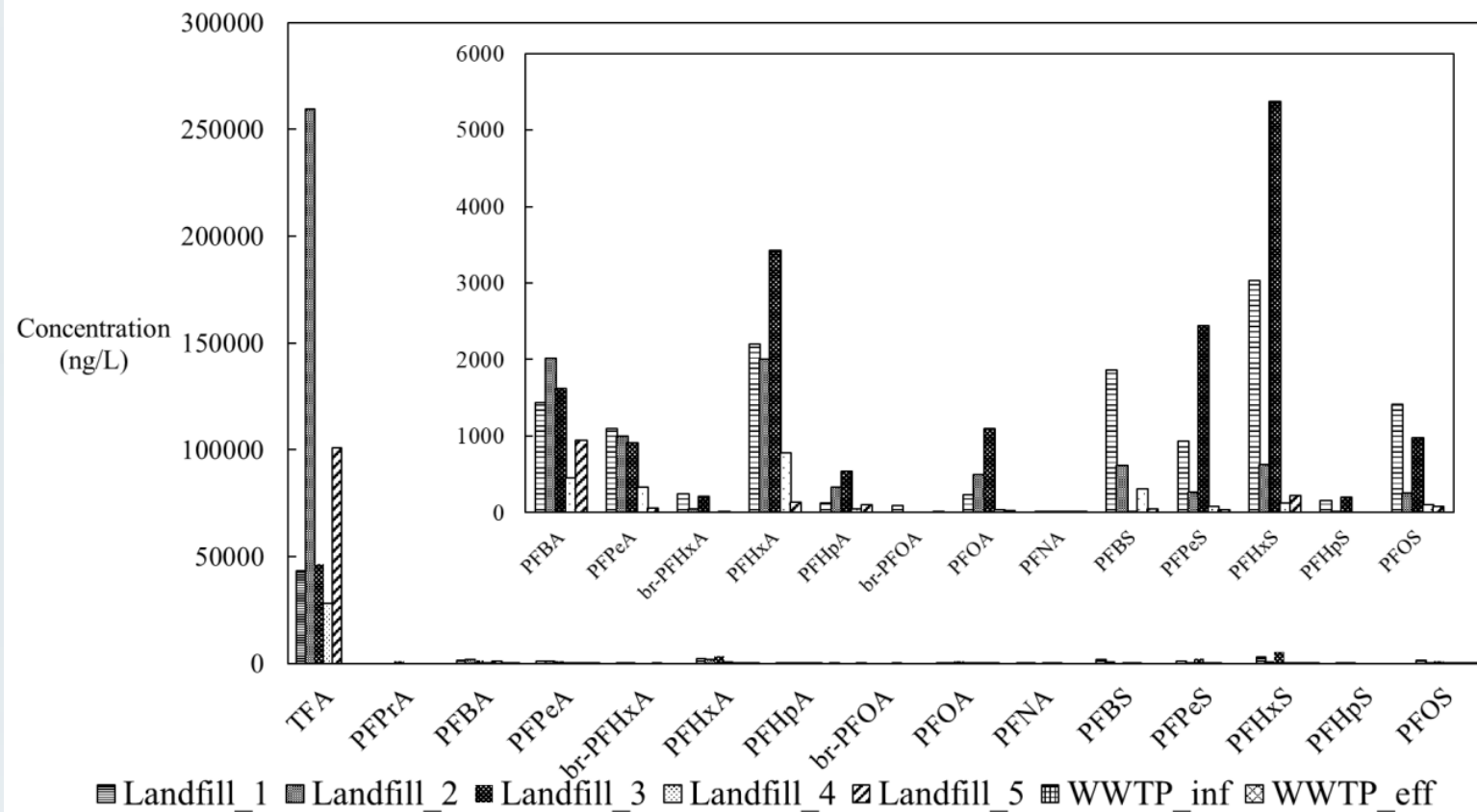
Fluoxetine (Prozac)



Paxlovid constituent

- Adding a CF₃ 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 CF₃ group breaks off to form TFA

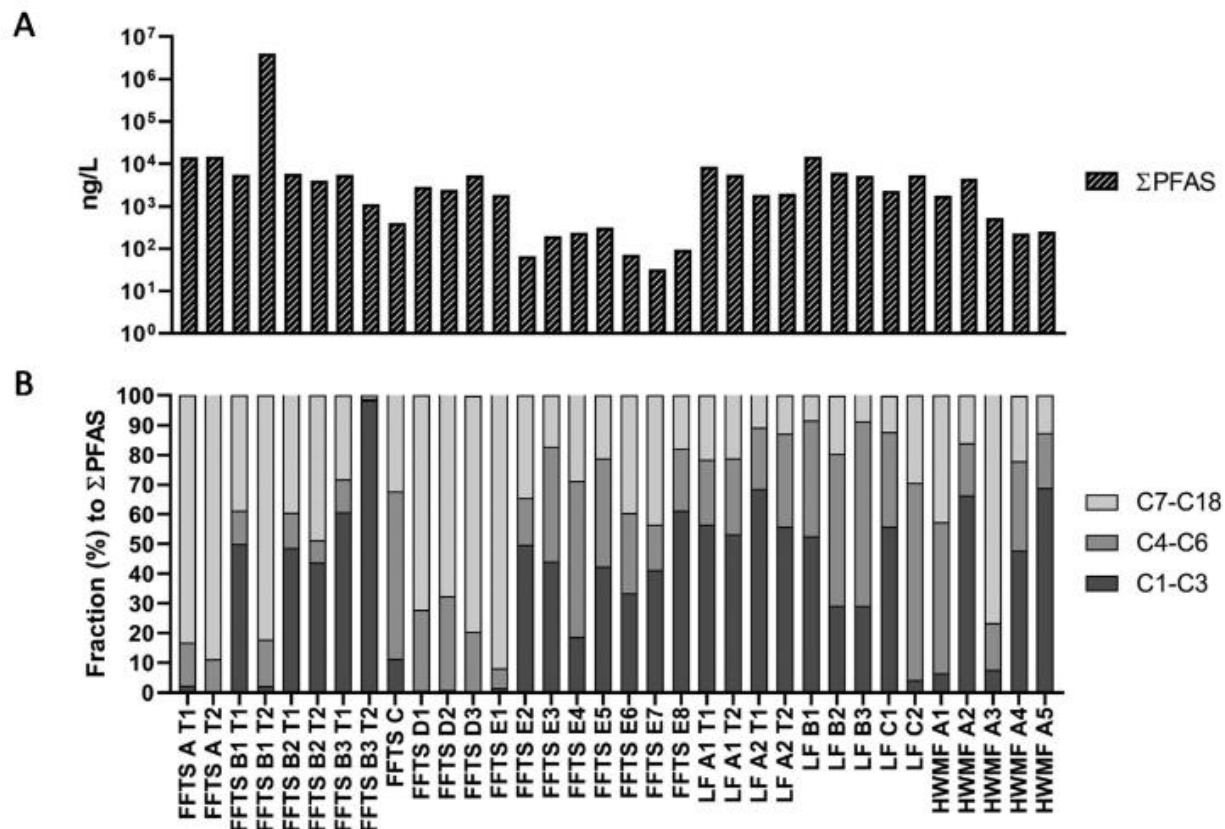
TFA Predominates Among PFAAs in US Landfills



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

Source: Tsou et al: *Environ Sci Technol Water*, **3** 2023

Occurrence of Ultrashort Chain Sulfonates



- 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) recently 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? More study is needed

Source: Björnsdotter *et al.*: *Environ Sci Technol Water*, **53**(19) 2019

Regulatory Drivers



- EPA Regional Screening Levels (RSLs) for TFSI and PFPrA

Contaminant		Screening Levels									
Analyte	CAS No.	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	key	Resident Air (ug/m³)	key	Industrial Air (ug/m³)	key	Tap Water (ug/L)	key
~Ammonium perfluorooctanoate	3825-26-1	1.9E-05	c*	7.8E-05	c*					2.7E-06	c*
~Bis(trifluoromethylsulfonyl)amine (TFSI)	82113-65-3	2.3E+00	n	3.5E+01	n					5.9E-01	n
~Hexafluoropropylene oxide dimer acid (HFPO-DA)	13252-13-6	2.3E-02	n	3.5E-01	n					1.5E-03	n
~Perfluorodecanoic acid (PFDA)	335-76-2	1.3E-05	n	1.6E-04	n					4.0E-06	n
~Perfluorododecanoic acid (PFDoDA)	307-55-1	3.2E-01	n	4.1E+00	n					1.0E-01	n
~Perfluorohexanesulfonate	108427-53-8	1.3E-01	n	1.6E+00	n					3.9E-02	n
~Perfluorohexanesulfonic acid (PFHxS)	355-46-4	1.3E-01	n	1.6E+00	n					3.9E-02	n
~Perfluorohexanoate	92612-52-7	3.2E+00	n	4.1E+01	n					6.1E-01	n
~Perfluorohexanoic acid (PFHxA)	307-24-4	3.2E+00	n	4.1E+01	n					9.9E-01	n
~Perfluorononanoate	72007-68-2	1.9E-02	n	2.5E-01	n					5.9E-03	n
~Perfluorononanoic acid (PFNA)	375-95-1	1.9E-02	n	2.5E-01	n					5.9E-03	n
~Perfluorooctadecanoic acid (PFODA)	16517-11-6	2.5E+02	n	3.3E+03	n					8.0E+01	n
~Perfluorooctanesulfonate	45298-90-6	6.3E-04	n	8.2E-03	n					2.0E-04	n
~Perfluorooctanesulfonic acid (PFOS)	1763-23-1	6.3E-04	n	8.2E-03	n					2.0E-04	n
~Perfluorooctanoate	45285-51-6	1.9E-05	c*	7.8E-05	c*					2.7E-06	c*
~Perfluorooctanoic acid (PFOA)	335-67-1	1.9E-05	c*	7.8E-05	c*					2.7E-06	c*
~Perfluoropropanoic acid (PFPrA)	422-64-0	3.9E+00	n	5.8E+01	n					9.8E-01	n
~Perfluorotetradecanoic acid (PF14tDA)	376-06-7	6.3E+00	n	8.2E+01	n					2.0E+00	n
~Perfluoroundecanoic acid (PFUDA)	2058-94-8	1.9E+00	n	2.5E+01	n					6.0E-01	n
~Potassium perfluorobutanesulfonate	29420-49-3	1.9E+00	n	2.5E+01	n					6.0E-01	n

Source: USEPA - <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>

Ultrashort Target Compound List



Analytes	Acronym	Formula	Aqueous Reporting Limit (ng/L at 0.02 L)	Solid Reporting (ng/g)	Surrogate Standard
Carboxylates (PFCA)					
Trifluoroacetic acid	TFA or PFEtA	CF ₃ -COOH	100	1.6	¹³ C ₂ -PFEtA
Pentafluoropropionic acid	PFPrA	CF ₃ -CF ₂ -COOH	20	0.32	¹³ C ₃ -PFPrA
Sulfonates (PFSA)					
Trifluoromethanesulfonic acid	PFMeS	CF ₃ -SO ₄ H	10	0.16	¹³ C ₃ -PFPrA
Pentafluoroethanesulfonic acid	PFEtS	CF ₃ -CF ₂ -SO ₄ H	5	0.08	¹³ C ₃ -PFPrA
Heptafluoropropanesulfonic acid	PFPrS	CF ₃ -CF ₂ -CF ₂ -SO ₄ H	5	0.08	¹³ C ₃ -PFPrA

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

Extending TOP Analysis

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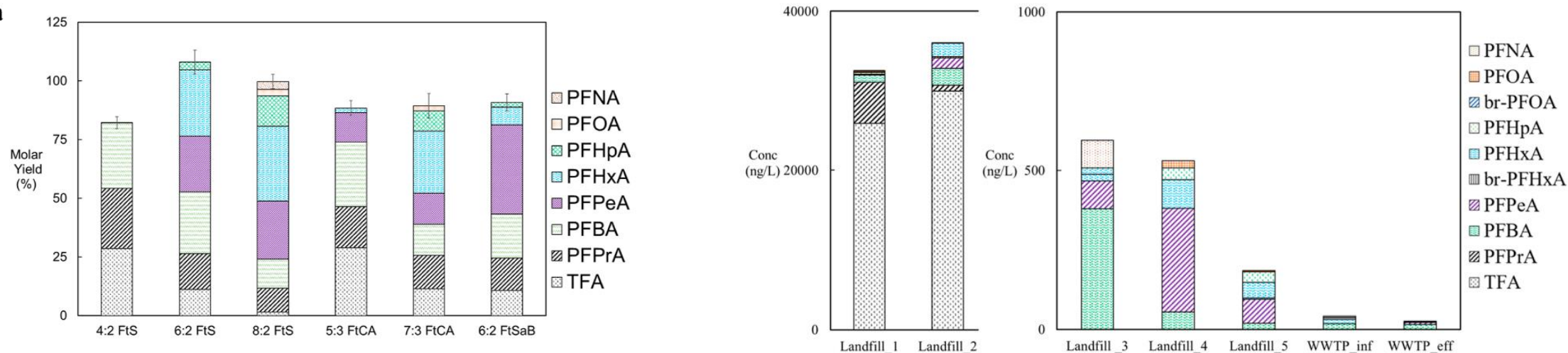
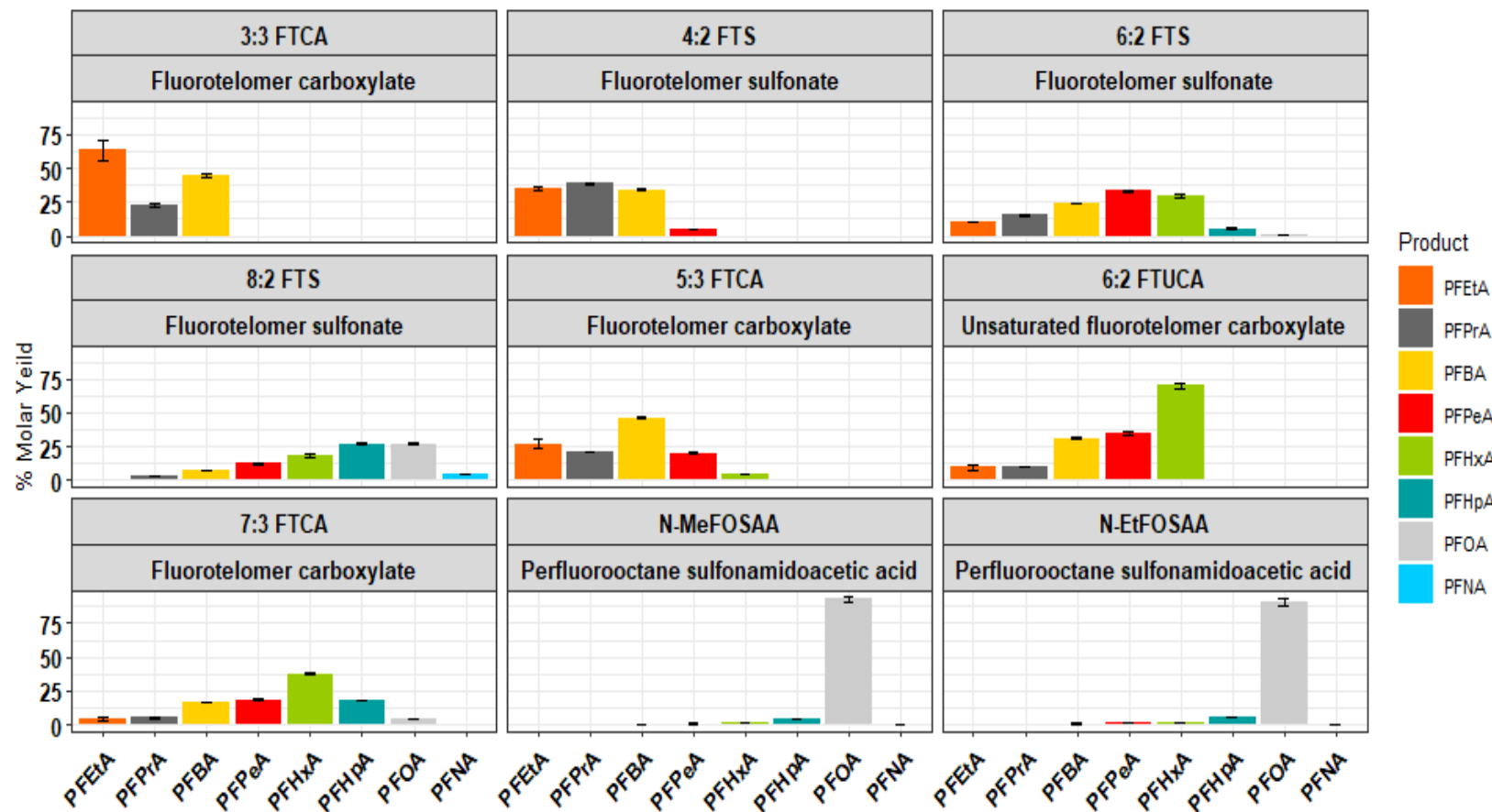


Figure 4. Concentration of precursors (Δ PFCAs) produced in the TOP assay for landfill leachates and wastewater treatment plant samples. Raw data from these samples can be found in [Tables S3 and S4](#).

Source: Tsou *et al*: *Environ Sci Technol Water*, **3** 2023

- Extending TOP assay to cover TFA and PFPrA uncovers much of that “missing” mass fluorotelomer PFAS

Conversion of Selected PFAS to Ultrashort PFAS



- TOP oxidation produces significant ultrashort PFAS.
- The values agree with those generated by Tsou *et al.* 2023

Experimental – Study sites and Methods



- **Study sites: Two municipal solid waste landfills**

- I. Active site – **Site 1**

- In operation since the 1960s

- II. Closed site – **Site 2**

- Site inactive since around late 1980s

- **Analytical methods: – 5 methods, 79 analytes**

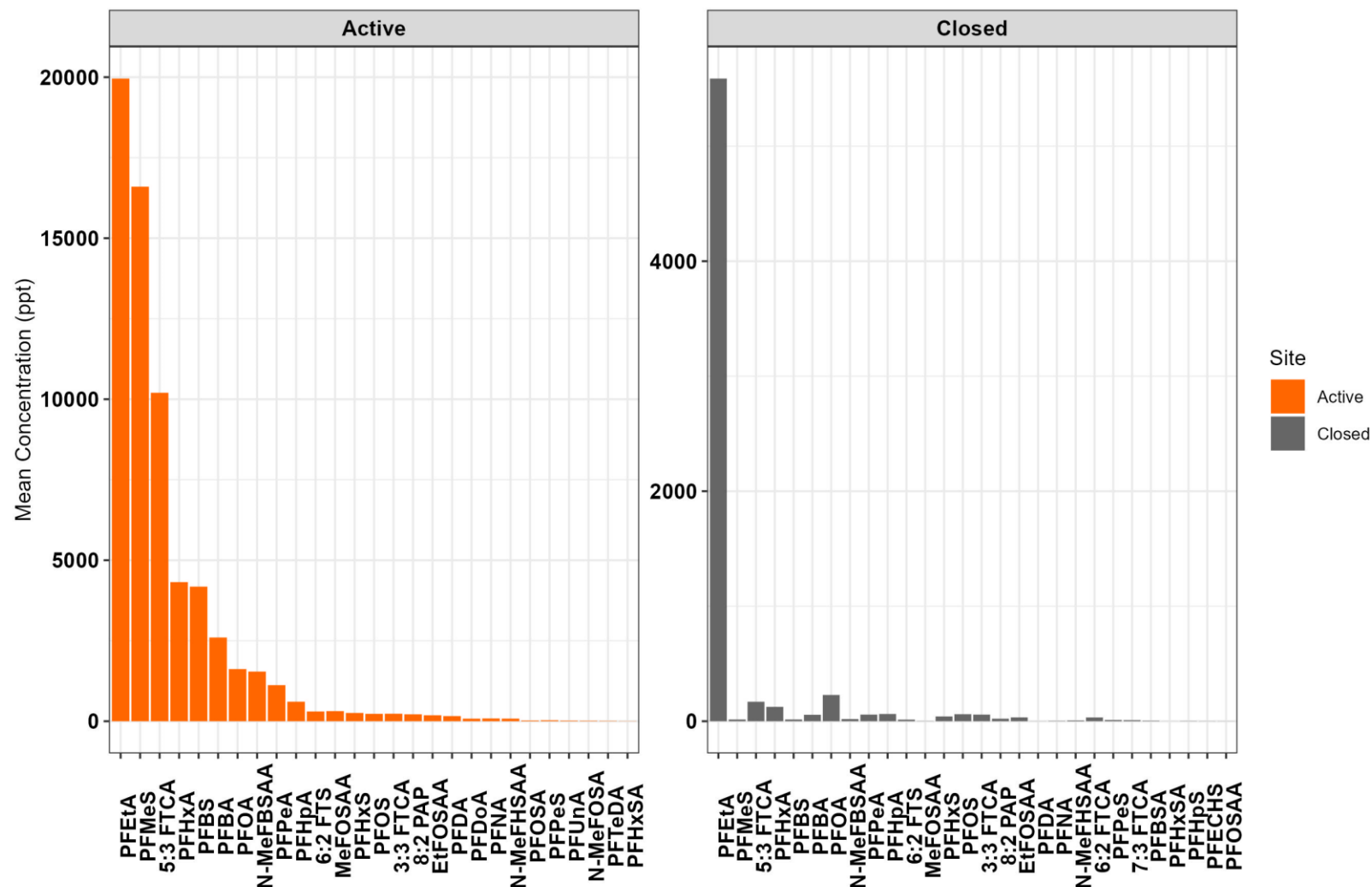
- I. Pre-oxidation

- SGS AXYS Method MLA-110 – US EPA method 1633 - 40 analytes
 - SGS AXYS Method MLA-120 – Ultrashort PFAS - 5 analytes
 - SGS AXYS method MLA-121 – Extended list of PFAS - 34 analytes

- II. Post-oxidation

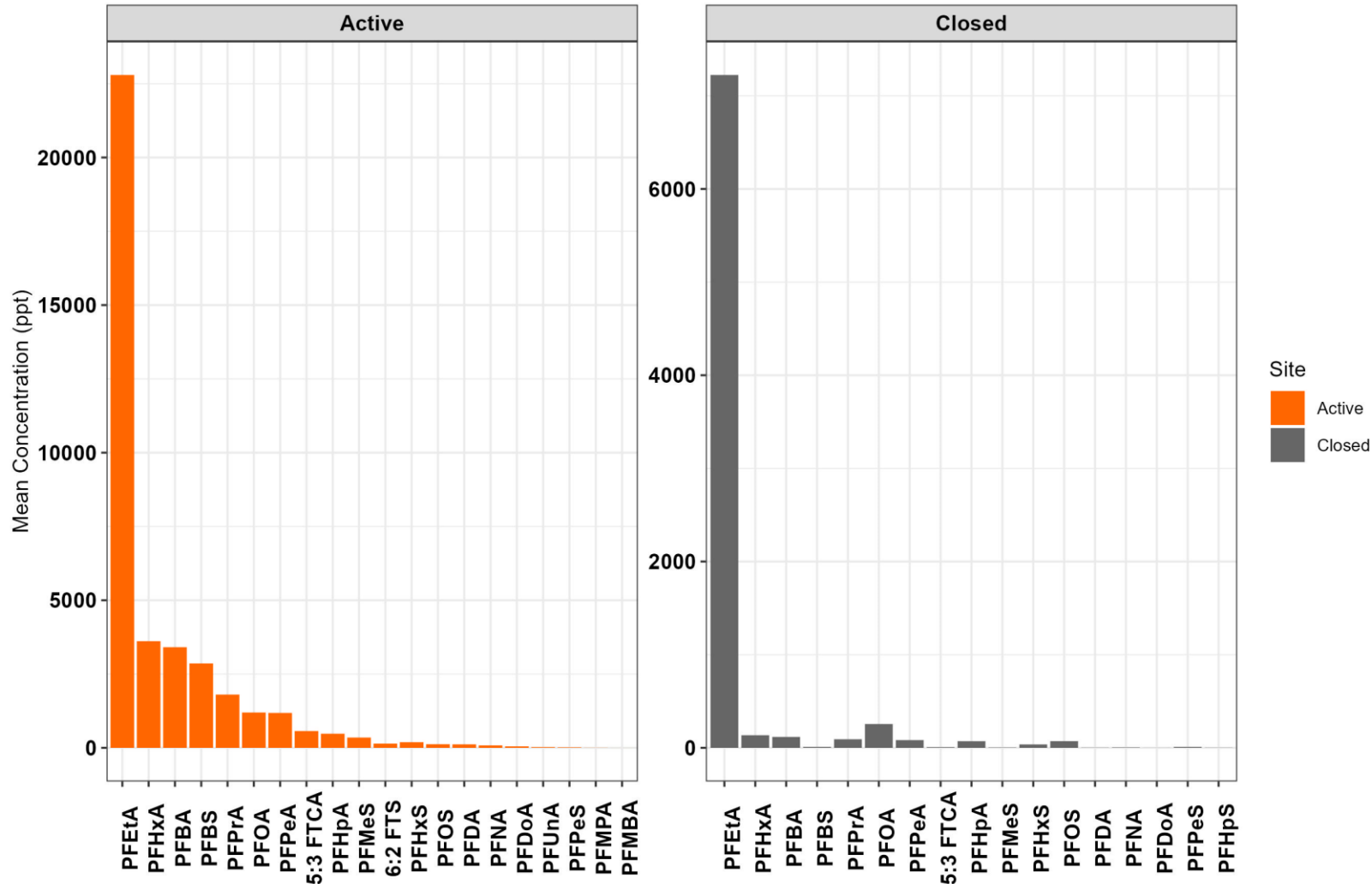
- SGS AXYS Method MLA-111 – TOP Assay protocol - 19 terminal acids
 - SGS AXYS method MLA-122 – TOP Assay for Ultrashort PFAS - 5 terminal acids

Results – Occurrence of PFAS – by Analyte



- PFEtA, i.e., TFA (20,000 ng/L and 5,588 ng/L) showed the highest conc. of any PFAS in leachates from both sites.
- PFMeS (16,600 ng/L), another ultrashort PFAS, showed the second highest conc in the leachate from the active landfill. It was not detected in the closed landfill.
- Excluding the ultrashort PFAS, the highest concentration was observed for 5:3 FTCA.
- *PFPrA was NOT detected in pre-oxidation TOP measurements.*

Results – Adding Ultrashorts to TOP



- The conc of PFEtA (TFA) increased by 14% in the active landfill and by 7% in the leachate from the closed landfill.
- The concentration of PFEtA (TFA), PFBA, PFHxA, PFPrA, PFPeA, and PFOA increased after top Oxidation
- PFMeS was not detected after TOP oxidation
- The significance of ultrashort PFAS is highlighted for both pre and post oxidation measurement of PFAS in landfill leachates.

To Conclude...



- Ultrashort PFAS contribute a significant proportion (>80%, and 30% at the closed and active sites by conc.) of the total PFAS measured at both the landfill sites studied and likely provide the missing link in PFAS mass in landfill leachates.
- Results demonstrate the importance of monitoring ultrashort PFAS in landfill leachate samples.
- PFMeS (a C1 ultrashort PFAS) was measured at the second highest concentration at the active landfill site. This analyte was not detected post-oxidation in the TOP measurements.
-
- PFPrA (a C3 ultrashort PFAS) was detected after oxidation in the TOP assay, but was not detected in the pre-oxidation samples
- Future study – we plans to investigate landfill leachates further using non-targeted analytical methods



Thank you!

Do you have any questions?

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