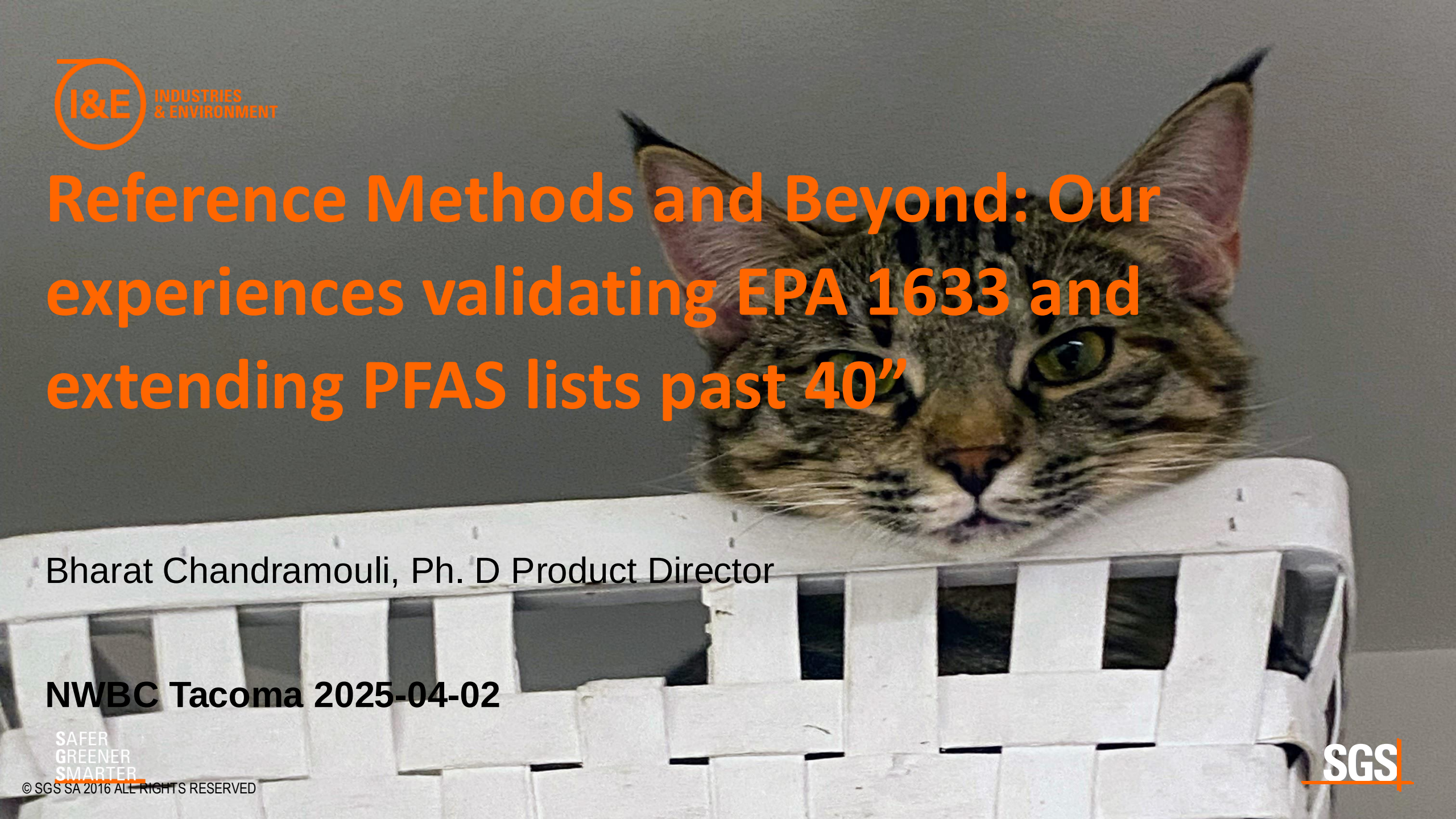

I&E INDUSTRIES & ENVIRONMENT

Reference Methods and Beyond: Our experiences validating EPA 1633 and extending PFAS lists past 40”

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SGS

SGS PFAS CAPABILITIES

Drinking Water	Ambient and contaminated sites monitoring, due diligence	Wastewater, biosolids, leachates, NPDES	Tissues and Serum	Remediation Project Support	Method Development and Customization	Forensics and Beyond 1633 Target PFAS	Air and Emissions	Products and Industrial
EPA 537.1	EPA 1633	EPA 1633	EPA 1633	Experienced analytical partner on SERDP/ESTCP projects	Developer of EPA 1633	Up to 90 target PFAS	High-Volume TO-9 type ambient monitoring for sub pg/m^3 reporting limits	AFFF product testing
EPA 533	High-capacity DoD project experience	EPA1621 organic fluorine AOF	Expert in fish, milk, other animal and plant tissue	Isotope dilution methods with list customization	Unquestioned leader on method development	Extended branched PFAS estimation	OTM-45 modified PFAS stack testing	Consumer and industrial product testing
UCMR5 Approved!	Screening methods 8327, 8421 and 8535		Extensive human monitoring experience	Extraction modifications	Industry leading PFAS experts for project support and customization	TOP assay		
						AOF EPA 1621, EOF, TF		
						Fluorotelomer alcohols		
						TFA and ultrashort PFAS		
						Non-Target Analysis		

Lists of US Interest Expanding in regulation and methods

	UCMR3	EPA 537 1.1	EPA 537.1	EPA 533	UCMR5	EPA 1633
Perfluoroalkyl carboxylates	C_7, **C_8** and C_9	C_6-C_{14}	C_6-C_{14}	C_4-C_{12}	C_4-C_{14}	C_4-C_{14}
Perfluoroalkyl sulfonates	C_4, C_6 and **C_8**	C_4, C_6 and C_8	C_4, C_6 and C_8	C_4-C_8	C_4-C_8	C_4-C_{10}, C_{12}
Fluorotelomer sulfonates				4:2, 6:2 and 8:2	4:2, 6:2 and 8:2	4:2, 6:2 and 8:2
Fluorotelomer carboxylates						3:3, 5:3 and 7:3
Perfluorooctane sulfonamides						FOSA, EtFOSA and MeFOSA
Perfluorooctane sulfonamidoacetic acids		EtFOSAA, MeFOSAA	EtFOSAA, MeFOSAA		EtFOSAA, MeFOSAA	EtFOSAA, MeFOSAA
Perfluorooctane sulfonamide ethanols						EtFOSE, MeFOSE
Per- and polyfluoroether carboxylates			HFPO-DA, ADONA	HFPO-DA, ADONA, PFMBA, PFMPA, NFDHA	HFPO-DA, ADONA, PFMBA, PFMPA, NFDHA	HFPO-DA, ADONA, PFMBA, PFMPA, NFDHA
Ether sulfonates			F-53B (2)			F-53B (2), PFEESA
Total	**6**	**14**	**18**	**25**	**29**	**40**

Available EPA/ASTM (Reference) Methods Summary

Method	Matrix	Instrument	Remarks
537.1 (Final)	Drinking Water	LC-MS/MS	18 targets
533 (Final)	Drinking Water	LC-MS/MS	24 Targets
1633 (In promulgation)	NPW, solids, tissue, waste	LC-MS/MS	40 targets
8327 (?)	Water	LC-MS/MS	24 targets
1621 (In promulgation)	Water	Combustion Ion Chromatography	“Total” organic fluorine screening
ASTM D8421(In Promulgation)	Water	LC-MS/MS	Up to 44 targets
OTM-45 (Review)	**Air** Stack Emissions	LC-MS/MS	Up to 49 targets
OTM-50 (Review)	Air Emissions	GC-MS	

PFAS Analytical Methods Development and Sampling Research | US EPA

ORIGIN OF 1633

Lack of PFAS measurement Standardization flagged as major concern

EPA starts internal development process with 8000 series methods 8327 and 8328

Isotope dilution method 8328 stalls and EPA Office of Water takes over

SGS AXYS selected for validation by EPA and DoD team due to long history of work on isotope dilution mass spectrometry methods for the EPA

EPA 1633 PROGRESS

SGS AXYS Phase1
- Validation and method detection limits in aqueous, solids and tissue

SGS AXYS Phase2
- Analysis of spiked and unspiked samples, 3 each of groundwater, surface water, wastewater, leachate, soil, sediment, biosolid, and tissue
- Holding time studies

Draft 1633 publication
- For review and recommended use in all applications including NPDES

Multi-lab validation
- Starting Q4 2021 and into 2022

Final Method and validation report

Comments and Promulgation

[EPA Announces First Validated Laboratory Method to Test for PFAS in Wastewater, Surface Water, Groundwater, Soils | US EPA]

EPA 1633

Extraction

- Spike with isotopically labeled standards
- Solids:, Sequential basic* extraction
- Aqueous: pH Adjustment
- Tissue: Sequential/extended basic extraction

Cleanup: Weak Anion Exchange + Carbon

- Use of WAX cleanup for all analysis to deal with complex matrices
- Use of carbon cleanup

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
- Use of bile acid check standards in tissue analysis

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EPA 1633 is being promulgated!

Regulations.gov

We're done right? There's no more PFAS analytical work to do. 1633 takes care of it all!

LOL J/K The work never stops

Contaminant		Screening Levels											Protection of Groundwater SSLs		
Analyte	CAS No.	Resident Soil (mg/kg)	key	Industrial Soil (mg/kg)	ke	Resident Air (ug/m3)	k	Industrial Air (ug/m3)	k	Tap Water (ug/L)	k	MCL (ug/L)	Risk-based SSL (mg/kg)	k	MCL-based SSL (mg/kg)
~Bis(trifluoromethylsulfonyl)amine (TFSI)	82113-65-3	2.3E+01	n	3.5E+02	n					5.9E+00	n		1.9E-03	n	
~Perfluorooctadecanoic acid (PFODA)	16517-11-6	2.5E+03	n	3.3E+04	n					8.0E+02	n		2.2E+02	n	
~Perfluoropropanoic acid (PFPrA)	422-64-0	3.9E+01	n	5.8E+02	n					9.8E+00	n		2.1E-03	n	

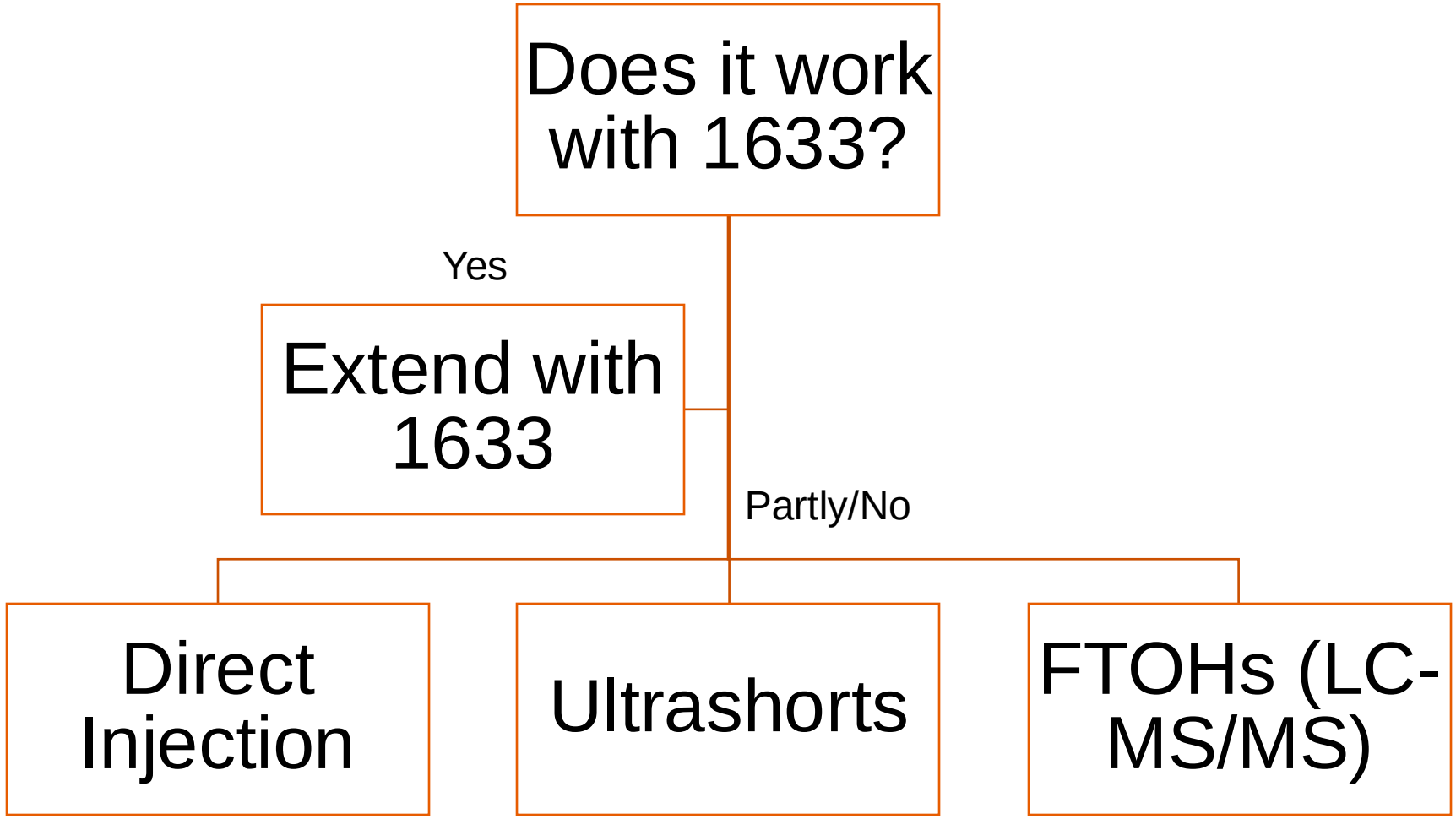
EPA Regional Screening Levels (RSLs) for TFSI, PFPrA and PFODA, famously not a part of EPA 1633's target list, and some sites needs these targets added

Nevermind the screening levels/reference limits getting lower

Target	1633 Reporting limit (ng/g)	Washington (saturated zone GW/SW protection)	Minnesota (new residential SRV)	EPA RSL
PFOS	0.16-0.4	0.01	1.3	0.03
PFOA	0.16-0.4	0.004	0.16	0.061
PFHxS	0.16-0.4	0.026	0.0054	0.0042
PFNA	0.16-0.4	0.005		0.042
HFPO-DA	0.64-1.6	0.0072	66	0.01

And of course, there’s so much more

The process


Does it work with 1633?
Yes
Extend with 1633
Partly/No
Direct Injection
Ultrashorts
FTOHs (LC-MS/MS)

Beyond 1633: The list

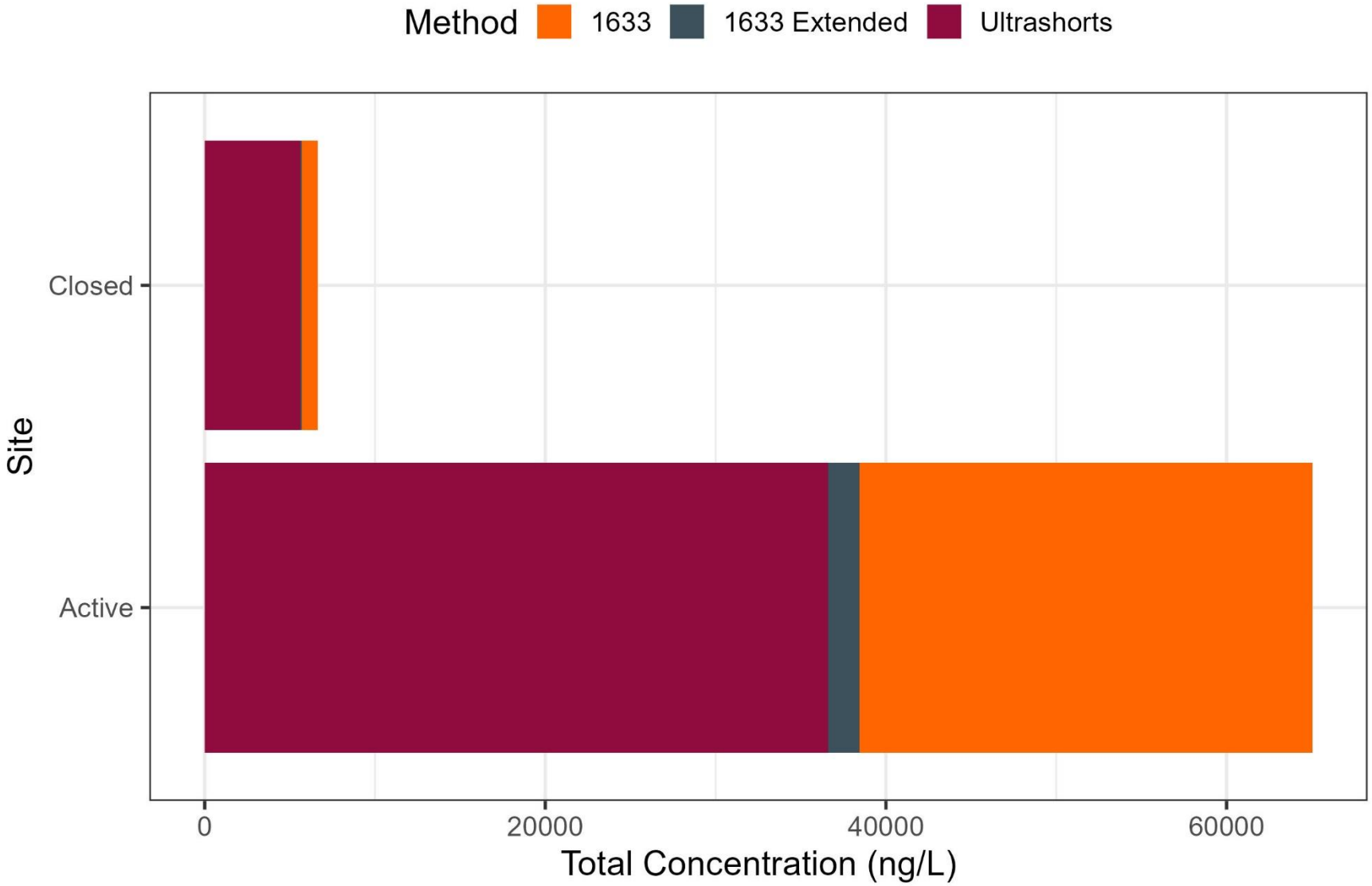
Perfluoroalkylcarboxylates	PFHxDA	Legacy	Perfluoroalkylsulfonamides	TFSI (HQ-115)	Lithium battery ionic liquid
	PFODA	Legacy		PFBSA	Replacement waterproofing/sidechain degradation
	PFPrA	Fluorotelomer degradation, refrigerants, more		PFDSA	Legacy waterproofing/sidechain degradation
	TFA (PFEtA)	Fluorotelomer degradation, refrigerants, more		PFHpSA	Legacy waterproofing/sidechain degradation
Perfluoroalkyl sulfonates	PFEtS	AFFF impurity		PFHxSA	Replacement waterproofing/sidechain degradation
	PFMeS	AFFF impurity, other sources	Sulfonamidoacetic acids	N-MeFBSAA	Replacement waterproofing/sidechain degradation
	PFPrS	AFFF impurity		N-MeFHSAA	Replacement waterproofing/sidechain degradation
Fluorotelomer sulfonates	10:2 FTS	Fluorotelomer intermediate		PFOSAA	Legacy waterproofing/sidechain degradation
Fluorotelomer carboxylates	10:2 FTCA	Fluorotelomer intermediate	Perfluoroether carboxylate	HydroEVE	Byproduct of Nafion
	6:2 FTCA	Fluorotelomer intermediate		PFMOAA	Ethers/PFOA replacements
	6:2 FTUCA	Fluorotelomer intermediate		PFO3OA	Ethers/PFOA replacements
	8:2 FTCA	Fluorotelomer intermediate		PFO4DA	Ethers/PFOA replacements
	8:2 FTUCA	Fluorotelomer intermediate		PFO5DoA	Ethers/PFOA replacements
Cyclic perfluorinated acid	PFECHS	PFOS Replacement, aviation		PFO6TeA	Ethers/PFOA replacements
			Perfluoroether sulfonates	Nafion BP1	ionic polymers in fuel cells
Perfluoroalkylphosphinate	6:6 PFPi	Defoamers, wetting agents		Nafion BP2	ionic polymers in fuel cells
	6:8 PFPi	Defoamers, wetting agents	Fluorotelomer betaines	5:1:2 FTAB	AFFF Agent
	8:8 PFPi	Defoamers, wetting agents		5:3 FTB	AFFF Agent
Perfluoroalkylphosphonic acid	PFDPA	Defoamers, wetting agents		6:2 FAB	AFFF Agent
	PFHxPA	Defoamers, wetting agents	Fluorotelomer alcohols	10:2 FTOH	Fluorotelomer building blocks, other
	PFOPA	Defoamers, wetting agents		12:2 FTOH	Fluorotelomer building blocks, other
Polyfluoroalkyl phophate di-ester	6:2 diPAP	Food packaging		4:2 FTOH	Fluorotelomer building blocks, other
	8:2 diPAP	Food packaging		6:2 FTOH	Fluorotelomer building blocks, other
Polyfluoroalkyl phophate mono ester	6:2 PAP	Food packaging		7:2 sFTOH	Fluorotelomer intermediate
	8:2 PAP	Food packaging		8:2 FTOH	Fluorotelomer building blocks, other

Validation Results

Type	Count	Reporting Limits (ng/L)	Sample Size
1633, A or Extended	35 (plus the 40 in 1633 = 75)	0.1 - 5	500 mL (or lower)
Direct Injection Only	4 (AFFF agents and Nafion BP1)	10-50	2 mL
Fluorotelomer Alcohols by LC-MS/MS	6	2-40	500 mL (or lower)
Ultrashorts	5	5-100	20 mL

- Most PFAS tested retained well on weak anion exchange and was amenable to a 1633 preparation followed by a second LC-MS/MS run
- This was developed before the PFPrA RSL, so PFPrA would work with the 1633 workflow (mostly)
- FTOHs are a fully separate workflow

Totals and Methods from a landfills pilot



- In each site, ultrashorts single largest class
  - 56% Active
  - 84% Closed
- 1633 presence indicates use state (precursors)
  - 41% Active
  - 14% Closed
- 1633 extended picks up some key precursors missed in 1633 (short chain sulfonamides)
  - 3% Active
  - 1% Closed

Conclusions

- EPA methods are maturing with EPA 1633(A) and more fully commercialized
- However, the challenge of additional PFAS and lower action levels means we need to keep expanding testing lists and lowering detection limits
- Though we did not talk about this methods like organic fluorine measurement can set a boundary around “total” PFAS
- Use of more sophisticated high-resolution mass spectrometry can expand universe to 100s more for forensic purposes