EPA Method 1621

Determination of Adsorbable Organic Fluorine in Aqueous Matrices by Combustion Ion Chromatography

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Thank you!

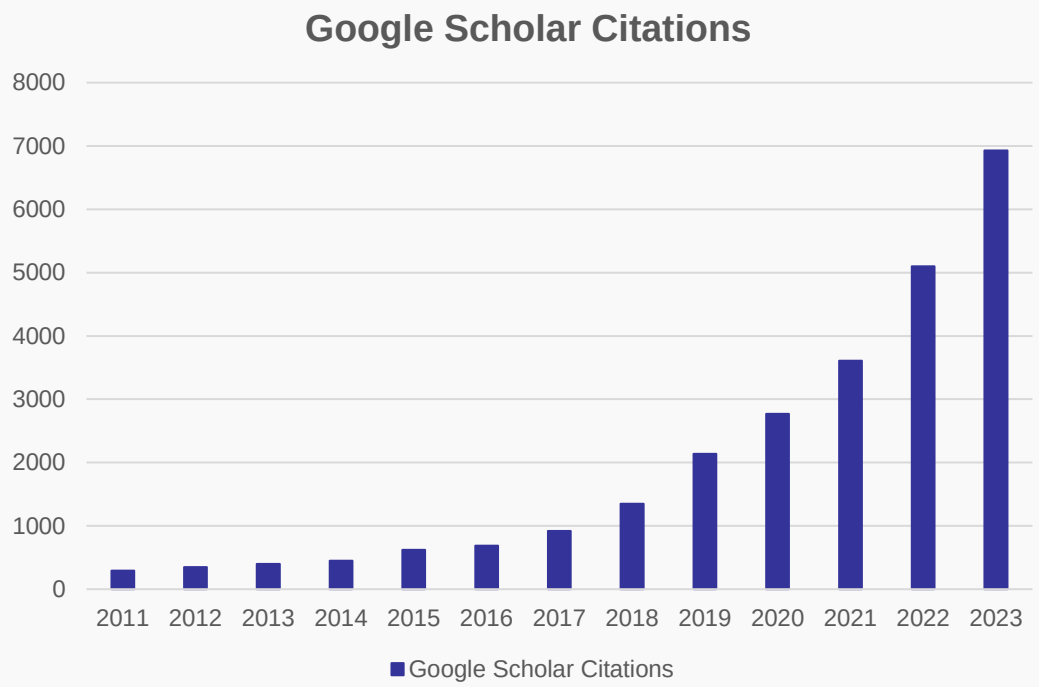
The EPA acknowledges the support of the several organizations and individuals who participated in the validation of Method 1621, including members of the EPA's workgroup, the laboratories that participated in the study, the organizations that provided the bulk samples of wastewater, and the EPA's support contractor staff who oversaw the day-to-day operations during the study and assisted in the preparation of study reports and method documents. At a minimum, that includes the following:

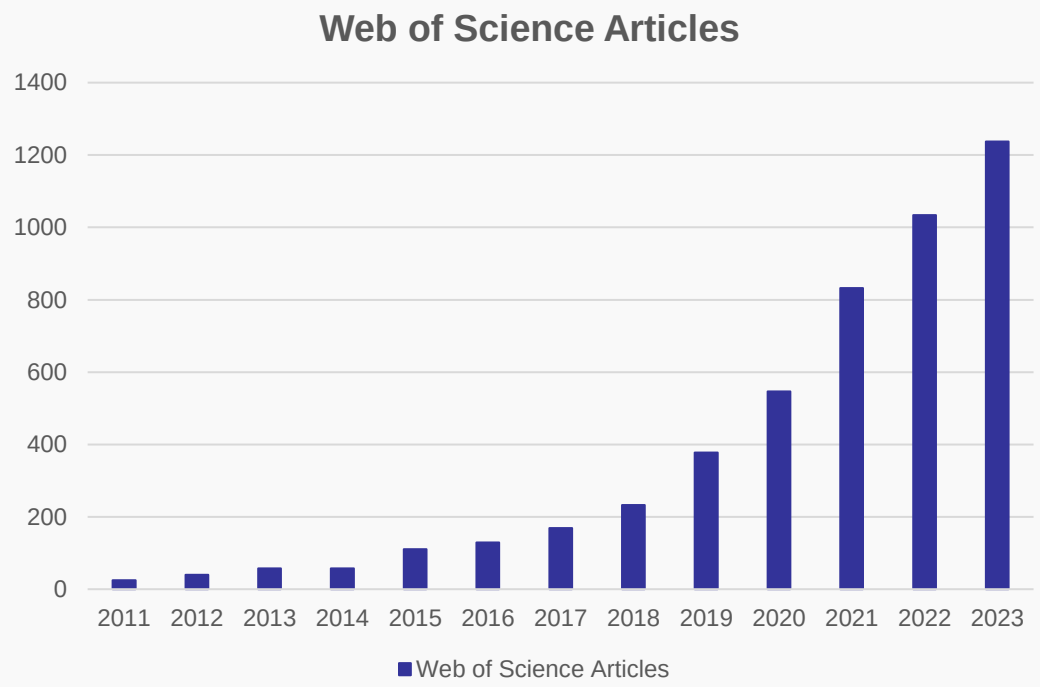
Thank you!

- EPA ORD/CESER
- EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK
- Delaware River Basin Commission
- Hampton Roads Sanitation District
- Massachusetts Water Resources Authority
- Los Angeles City Sanitation
- ASTM D19
- General Dynamics Information Technology
- Pace Analytical Services, MA
- Enthalpy Analytical
- Eurofins, Lancaster, PA
- Mandel Scientific Inc.
- SGS AXYS, Canada
- Thermo Fisher, IC Applications Lab
- Trace Elemental Instruments
- University of North Carolina at Charlotte

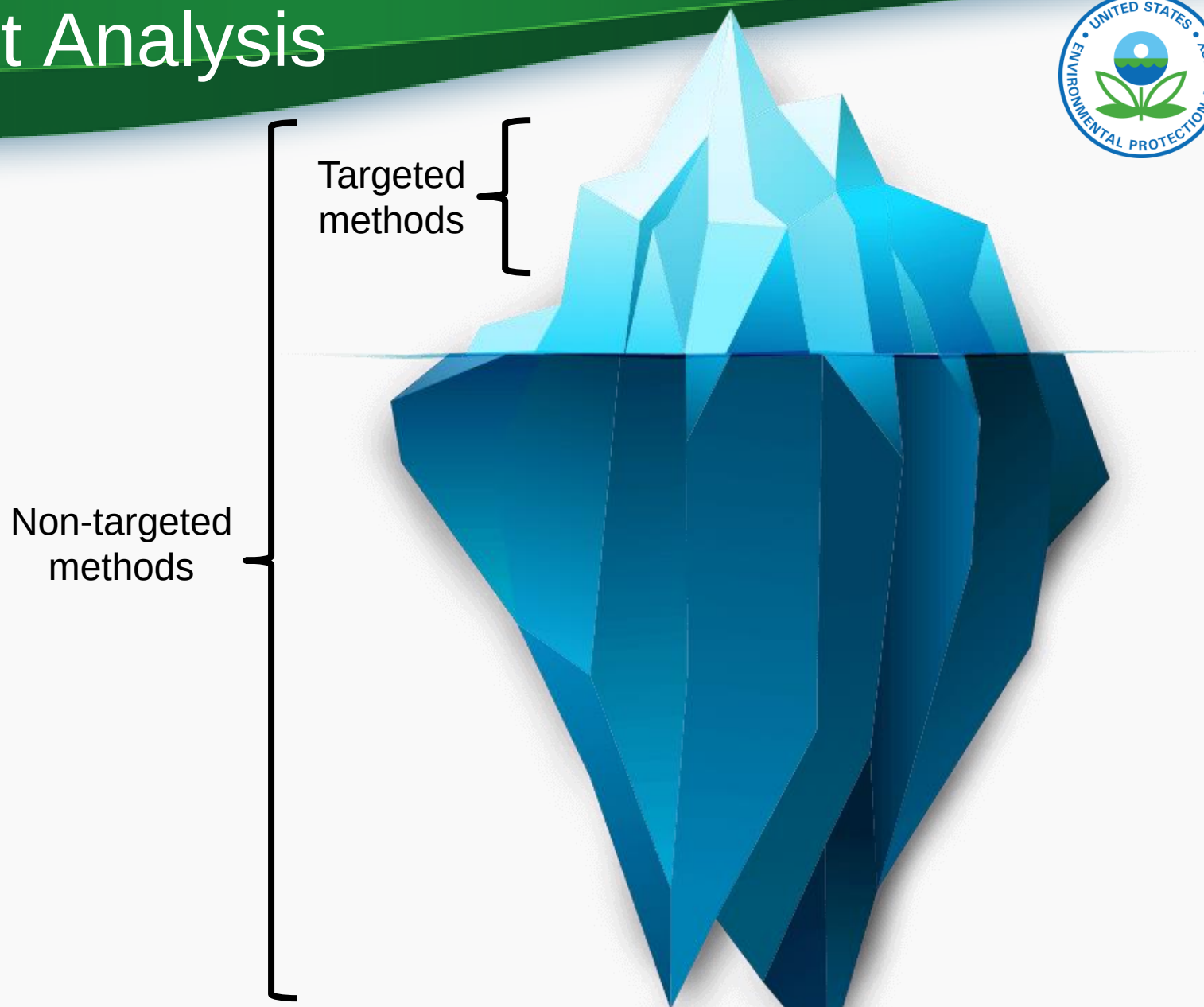
Have you heard of PFAS?

Increasing body of literature for PFAS, including human health and ecotoxicology, treatment technologies, occurrence, and analytical methods





Target vs. Non-target Analysis



Target vs. Non-target Analysis

- Target:
  - Only find what you're looking for
  - Known analytes
  - Standards available
- Non-target:
  - Known and unknown analytes
  - Data can be reanalyzed

Analytical challenges of PFAS

- State, local and International regulatory agencies taking action to address release of PFAS
- Thousands of PFAS in use
- Challenging and expensive to develop targeted methods
  - ~100 PFAS standards
- Stakeholder need for aggregate methods

Adsorbable Organic Fluorine

- Increasing demand for aggregate methods like AOF
- Naturally occurring organofluorines are rare
- Collaborated with ASTM D19 and EPA ORD on single-laboratory validation of Draft Method 1621 for AOF

Timeline

Jun. 2019
First draft study plan

Aug. 2020
EPA Workgroup formed

May 2021
SLV study plan finalized

Apr. 2022
Draft Method 1621 posted to website

Sep. 2022
MLV study plan finalized

Jan. 2024
Final Method 1621 posted to website

AOF, Method 1621 (cont.)

- The main objective of the validation was to develop and characterize the performance of a new method for adsorbable organofluorine that:
  - Provided an aggregate response for adsorbable organofluorine compounds using CIC
  - Could measure AOF at levels useful as a screening tool
  - Could be implemented in a typical environmental laboratory using commercially available materials and instrumentation

AOF, Method 1621 (cont.)

- Sample matrix selection:
  - Total suspended solids (TSS) > 40 mg/L
  - Total dissolved solids (TDS) > 100 mg/L
  - Oil and grease (O&G) > 20 mg/L
  - Conductivity as NaCl > 120 mg/L
  - Hardness as CaCO3 > 140 mg/L

- Aqueous matrices included across both the SLV and MLV:
  - POTWs
  - Bus washing station
  - Hospital effluent
  - Metal finisher
  - Industrial discharger
  - Chemical manufacturer
  - Surface water
  - Dairy effluent
  - Pharmaceutical effluent

AOF, Method 1621 (cont.)

- Single-Laboratory Validation completed April 2022:
  - Calibration and sorbent testing
  - Recovery ranged from about 40-200% for analytes tested:
    - 36 individual PFAS
    - 3 different mixed PFAS standards
    - 3 fluorinated pharmaceuticals
    - 3 fluorinated pesticides
  - IPR and MDL studies
  - Ten wastewater and surface water matrices were tested at two spike concentrations

https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

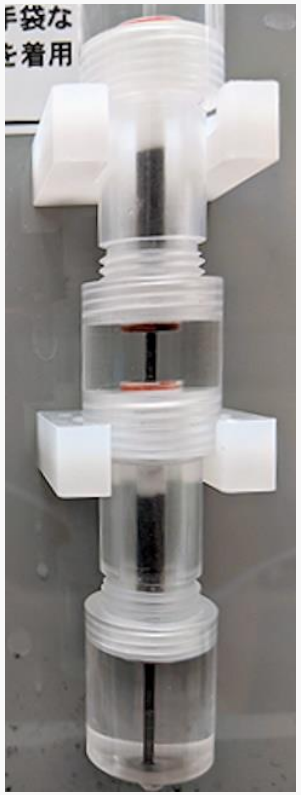
AOF, Method 1621 (cont.)

Granular Activated Carbon Column Vendor Comparison						
Vendor	Capping Material	Replicate 1	Replicate 2	Replicate 3	Mean	Std Dev
GAC + Capping Material (µg F^-/L)						
Nittoseiko-Mandel	Glass wool	0.245	0.145	0.371	0.254	0.113
CPI	Glass wool	0.035	0.184	0.060	0.093	0.080
UCT Enviro-Clean	Glass wool	0.180	0.224	0.360	0.255	0.094
Analytik-Jena (AOX/TOX)	Glass wool	8.51	9.27	11.02	9.60	1.29
Analytik-Jena (Low Fluorine)	Cellulose acetate	0.201	0.165	0.465	0.277	0.164
Sigma-Aldrich	Cellulose acetate	0.289	-0.148	-0.154	-0.004	0.254
GAC Only (µg F^-/L)						
Nittoseiko-Mandel		0.361	0.401	0.242	0.335	0.083
CPI		-0.018	-0.017	-0.042	-0.026	0.014
UCT Enviro-Clean		-0.029	0.096	-0.027	0.013	0.072
Analytik-Jena (AOX/TOX)		0.770	0.822	0.740	0.777	0.041
Analytik-Jena (Low Fluorine)		0.088	-0.003	-0.021	0.021	0.058
Sigma-Aldrich		0.095	0.132	0.088	0.105	0.024

AOF, Method 1621 (cont.)

Background Fluorine Contribution by Column Capping Material				
Vendor	Average µg F^-/L			% F^- Added by Capping Material
	GAC	GAC + Capping	Capping Material	
Nittoseiko-Mandel	0.335	0.254	-0.081	**0**
CPI	-0.026	0.093	0.093	**100.0**
UCT Enviro-Clean	0.013	0.255	0.242	**94.9**
Analytik Jena (Low Fluorine)	0.021	0.277	0.256	**92.4**

AOF, Method 1621 (cont.)

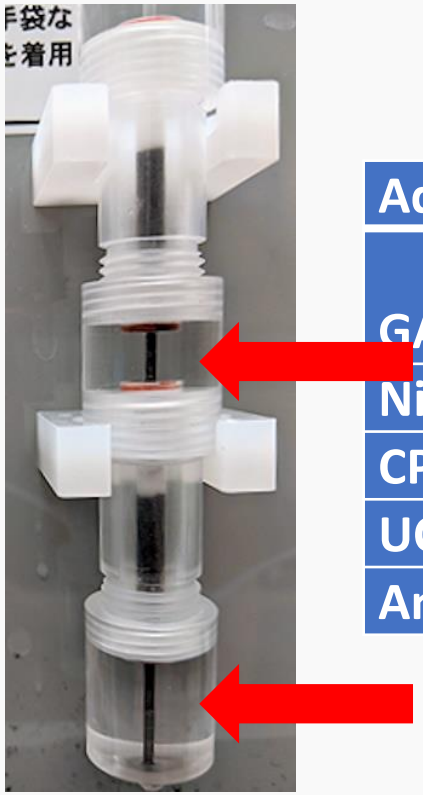


Carbon Migration from GAC Columns

Adsorption of PFBS at 600 ng per GAC Vendor						
GAC Vendors	Percent Recoveries					RSD (%)
	Rep 1	Rep 2	Rep 3	Rep 4	Mean	
Nittoseiko-Mandel*	67.7	82.1	88.7	91.3	82.5	12.8
CPI*	118.6	70.7	74.7	81.2	86.3	7.7
UCT Enviro-Clean*	64.7	73.1	77.4	173.1	97.1	52.5
Analytik-Jena (Low Fluorine)	82.9	93.2	91.4	100.1	91.9	7.7

*Issues with capping material during elution

AOF, Method 1621 (cont.)



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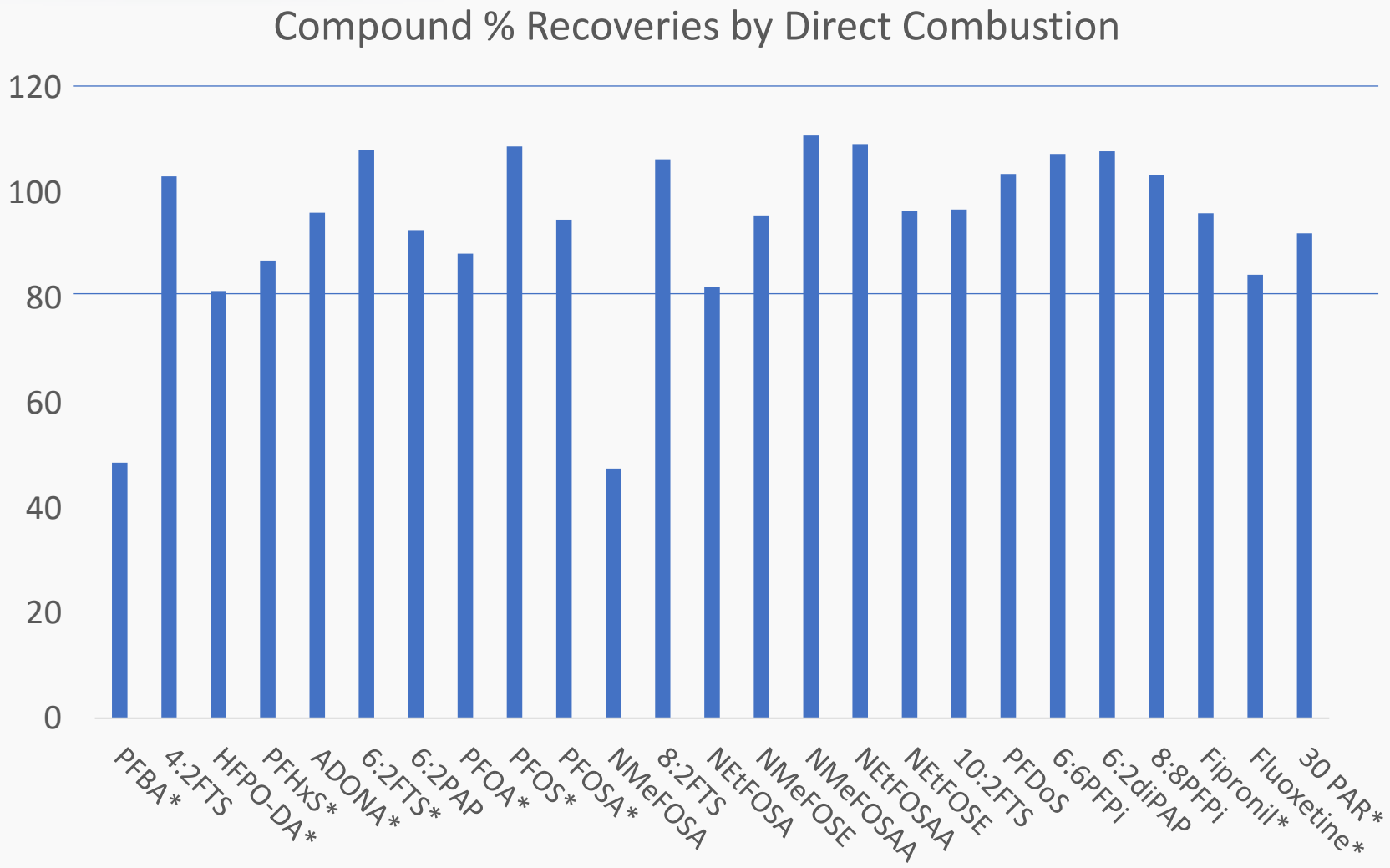
AOF, Method 1621 (cont.)

- During the SLV, we also tested:
  - Background levels of inorganic fluorine with two forms of nitrate washes
    - $NaNO_3$
    - KNO_3
- Compound recoveries by direct combustion

AOF, Method 1621 (cont.)



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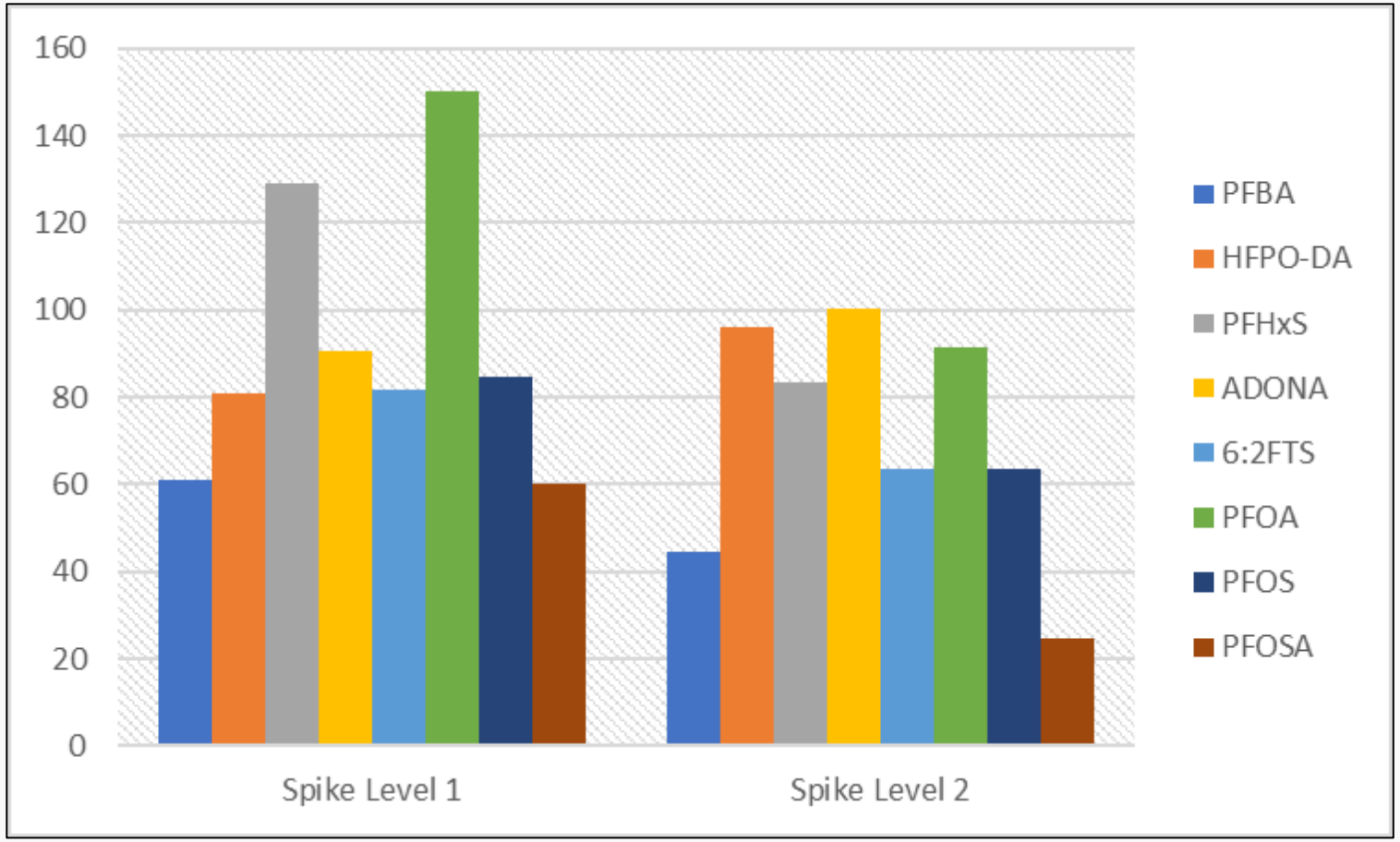
- Compound recoveries by direct combustion
- Adsorption of individual PFAS compounds at 6 µg F-/L and 19 µg F-/L
  - subset of eight individual PFAS selected after extensive method validation at ORD that included 35 individual PFAS, two fluorinated pharmaceuticals and two fluorinated herbicides

AOF, Method 1621 (cont.)

Average % recoveries for adsorption capacity of select individual compounds at (~6 and ~19 µg F-/L)



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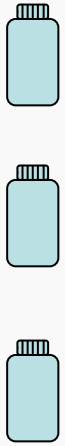
- Compound recoveries by direct combustion
- Adsorption of individual PFAS compounds at 6 µg F-/L and 19 µg F-/L
- % breakthrough from top GAC to bottom GAC
- Analytical interferences
  - Inorganic fluorine: adding nitrate to sample increased allowable inorganic fluorine to 8 mg/L
  - Inorganic chloride: tested 100, **500**, and 1000 mg Cl-/L

AOF, Method 1621 (cont.)

- Method defined parameter
- Sample preparation



- 100 mL
- 90 days @ 0-6˚ C
- Measure TSS
- Verify sample pH ≥ 5
- Check for chlorine and dechlorinate if needed
- Determine concentration of inorganic fluoride
- Sample volume determined by weight
- Add 0.5 mL of 2M sodium nitrate
- Slowly load sample onto GAC columns
- Wash GAC columns with 25 mL of 0.01 M sodium nitrate
- Rinse with 20 mL reagent water
- Dry columns
- Transfer carbon to combustion boats
- Sample ready for combustion and analysis

AOF, Method 1621 (cont.)

- Multi-Laboratory Validation completed January 2024:
  - 10 labs, 9 wastewaters and surface water matrices were tested at three spike concentrations
  - Calibration testing (including extended range up to 100 µg F-/L)
  - PFHxS used in every test matrix; PFBA, PFOS, and a mixed standard were also tested
  - Initial precision and recovery and method detection limit
  - % breakthrough was ≤ 50% for 94% of the 475 detected results across the nine wastewater matrices tested

AOF, Method 1621 (cont.)

- 10 lab pooled MDL_s was 1.5 ppb
  - Maximum MDL_s was 2.9 ppb, maximum MDL_b was 3.2 ppb

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  - IPR recovery: 80 – 120%, with an RSD < 20%
  - OPR recovery: 70 – 130%
  - MS/MSD recovery: 50-150%, with an RPD ≤ 30%

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  - 97% of study data fell below this limit

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AOF, Method 1621 (cont.)

Recoveries for Different Standards Spiked into Sample #7						
Spiking Standard	# of Results	Nominal Spike Conc. (µg F^-/L)	% Recovery			RSD (%)
			Mean	Min	Max	
PFBA	18	10	64.1	41.0	86.9	23.9
	18	30	63.6	22.8	107.8	27.5
PFOS	18	10	93.6	41.1	145.0	23.6
	18	30	84.5	33.3	102.3	23.8
Mixed PFAS	18	10	83.1	36.9	107.7	22.6
	18	30	83.1	53.7	95.2	11.7

AOF, Method 1621 (cont.)

Comparison of Inorganic vs. Organic Standard Calibrations			
Calibration Std	Concentration (µg F^-/L)	Recovery (%)	
		NaF	PFHxS
CS-1	1.0	99.0	97.8
CS-2	2.0	102.7	105.0
CS-3	5.0	98.9	99.9
CS-4	10.0	98.8	98.5
CS-5	25.0	100.7	96.7
CS-6	50.0	99.9	102.6
	%RSE	2.0	4.1

AOF, Method 1621 (cont.)

Combustion Efficiencies of Standards by Direct Combustion				
Standard	Inorganic Calibration		Organic Calibration	
	Mass (ng F^-)	% Recovery	Mass (ng F^-)	% Recovery
NaF	1000	99.5	1000	95.9
PFBA	302	48.6	304	98.3
PFOS	653	108.8	667	93.4
Mixed PFAS	742	94.6	745	99.2

AOF, Method 1621 (cont.)

Recoveries of Mixed PFAS Standard, Inorganic vs. Organic Calibrations				
Nominal Spike Conc (µg F^-/L)	Inorganic Calibration		Organic Calibration	
	Mean Recovery (%)	RPD (%)	Mean Recovery (%)	RPD (%)
10	100.5	14.5	93.0	3.2
30	91.6	1.8	91.5	3.1

Some Considerations

- Not all PFAS have same performance
  - % breakthrough higher for PFBA
  - Recoveries lower for short-chain and longer chain PFAS
- Not all GAC have same performance
- Differences in data quality possible with different adsorption units

Images provided by EPA ORD

Some Considerations

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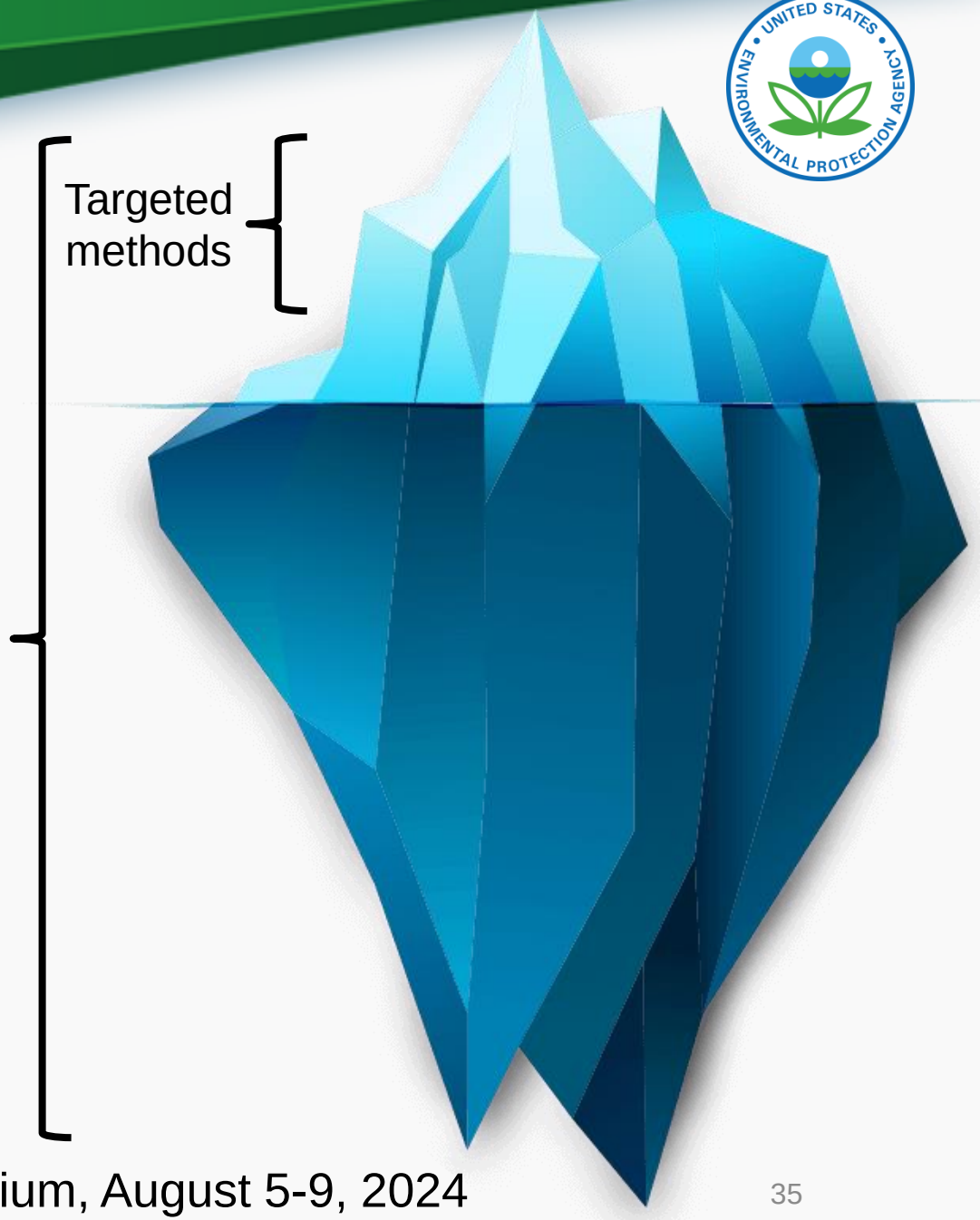
  - % breakthrough higher for PFBA
  - Recoveries lower for short-chain and longer chain PFAS
- Not all GAC have same performance
- Differences in data quality possible with different adsorption units
- Check your tubes

Images from MLV participant laboratories

Takeaways

- Aggregate methods are useful tool in the PFAS toolbox
- AOF is helpful to pinpoint samples which may require follow up analysis by targeted methods, such as Method 1633
- AOF detection limits are sufficiently sensitive for screening wastewater matrices for organofluorines



Thank you!

For more information or additional feedback, please contact:

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