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An Inter-laboratory Study on EPA Methods 537.1 and 533 for Potable and Non-Potable Water PFAS Analyses

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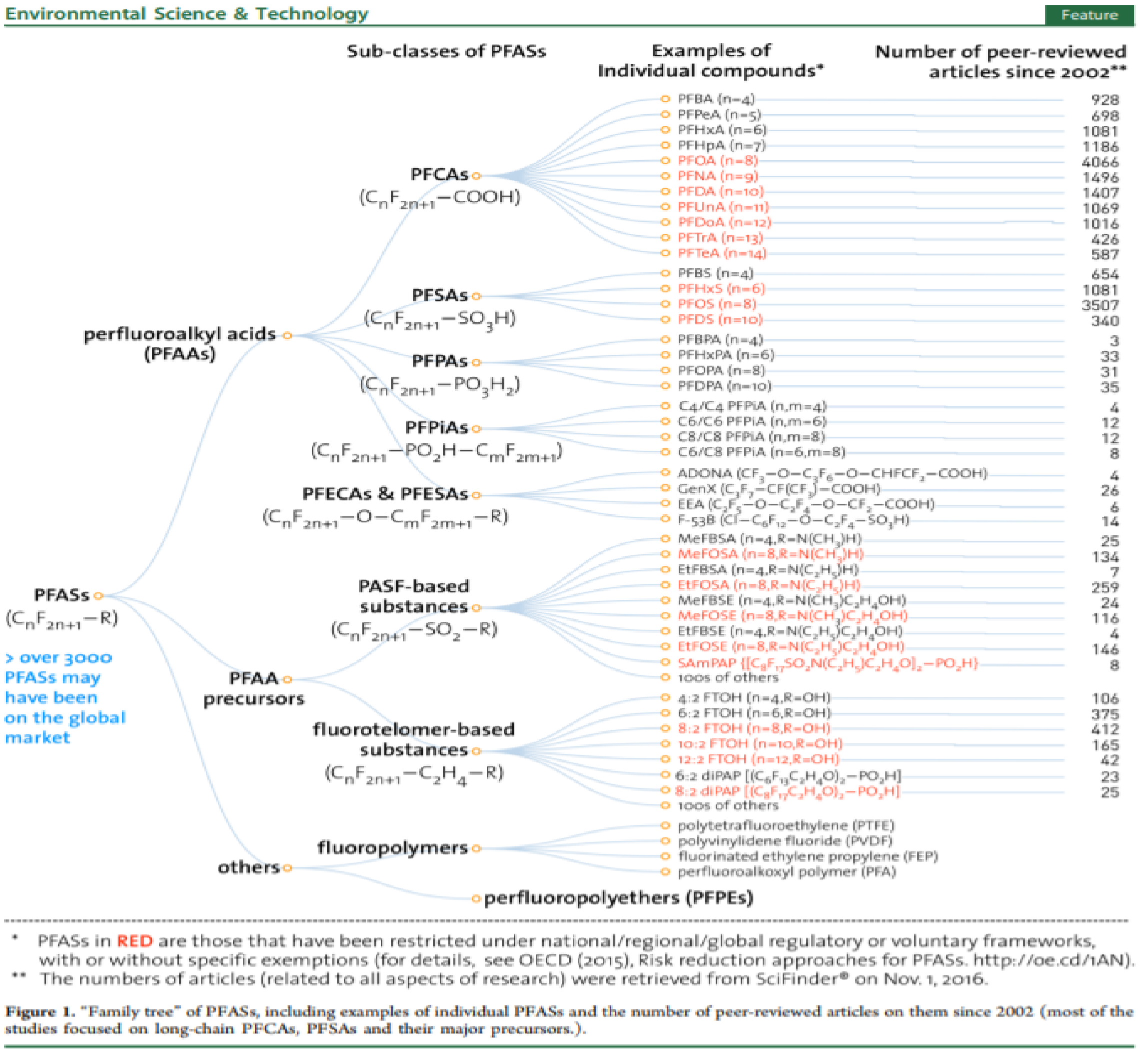
More than 3000 per- and polyfluoroalkyl substances (PFASs) are, or have been, on the global market……

Courtesy to Wang, DeWitt, Higgins & Cousins, *Environ. Sci. Technol.* 2017, 51(5), 2508-2518.



Environmental Science & Technology

Feature

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* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors.).

Types of PFAS

- PFAS
  - Perfluoroalkyl substances
  - Polyfluoroalkyl substances

- PFAS
  - Non-polymeric substances
    - Perfluoroalkyl acids
    - Perfluoroalkane sulfonyl fluoride-based substances
    - Fluorotelomer-based substances
    - Per & polyfluoroalkyl ether–based substances
  - Polymeric substances
    - Fluoropolymers
    - Side-chain fluorinated polymers
    - Perfluoropolyethers

- PFAS
  - Perfluoroalkyl acids (PFAAs)
  - Perfluoroalkyl acid (PFAA) precursors
    - Sulfonamides
    - Sulfonamidoacetic acids
    - Fluorotelomer sulfonic acids
    - Fluorotelomer alchols
    - Certain per- and polyfluoroalkyl ether carboxylic acids
  - Others
    - Fluoropolymers
    - Perfluoropolyethers

- PFAS
  - Amenable to LC/MS/MS
  - Not amenable to LC/MS/MS

Wang et al. (2017). *ES&T*, 51(5), 2508-2518.
OECD (2018). ENV/JM/MONO(2018)7. 2018

Current PFAS Method Summary

Method	EPA 537/537.1	EPA 533	SW-846 EPA 8328	SW-846 EPA 8327	ASTM D7979-17	DoD/DoE QSM 5.3	Lab Methods	TOP Assay	TOF Assay
Techniques	RP-SPE LC/MS/MS IS CAL	WAX-SPE LC/MS/MS ID CAL	WAX-SPE LC/MS/MS ID CAL	1:1 MeOH LC/MS/MS Ext CAL	1:1 MeOH LC/MS/MS Ext CAL	WAX-SPE LC/MS/MS ID CAL	WAX-SPE LC/MS/MS ID CAL	Oxidation SPE LC/MS/MS	Combustion IC
Availability	2009 (v1.1)/ 2020 (v2)	2019	Draft	2019	2017	2019	Varies	Varies	Varies
Type of Water	Potable	Potable	Non-potable	Non-potable	Non-potable	Non-potable	Non-potable	Non-potable	Non-potable
Type of PFAS	14/18 analytes	25 analytes	24 analytes?	24 analytes	14+7 analytes	25 analytes	~40 analytes	All perfluoro-alkyl acids	All organo-fluorine
Type of analysis	Quantitative	Quantitative	Quantitative	Quantitative	Quantitative	Quantitative	Quantitative	Semi-quant. Screening	Semi-quant. Screening
Pros & Cons	Validated Limited S.C.	Validated Limited L.C.	Draft	Validated Faster Higher RLs	Validated Faster Higher RLs	Validated	More PFAS Inconsistent	All perfluoro-alkyl acids	Surrogate of all fluorine compounds
MRLs	~2 ng/L	~2 ng/L	~2 ng/L	10-50 ng/L	10-50 ng/L	~2 ng/L	~2 ng/L	ng-µg/L	µg-mg F/L

PFAS Have Been around for a Long Time.

PFOS Produced, 1949

AFFF Implemented, 1969

Phase out PFOS EPA & 3M, 2002

EPA 537, 2008-2009

No buy/use PFOS DuPont, 2013

Lifetime HA, 2016

GenX, 2017

National Leadership Summit & Engagement, 2018

EPA 537.1, 2018

PFAS Action Plan, 2019

EPA 533, 2019

1940s | 1950s | 1960s | 1970s | 1980s | 1990s | 2000s | 2010s | 2020s

PFOA Produced, 1940s

Homologues Produced
1950s-1970s

PFAS by LC/MS/MS
1980s-1990s

L.C. PFAS Replaced with S.C. PFAS, 2002

2010-2015 PFOA Stewardship Program

CCL3 & UCMR3 (6 PFAS)
2013-2015

UCMR5
2023-2025

Federal MCLs?

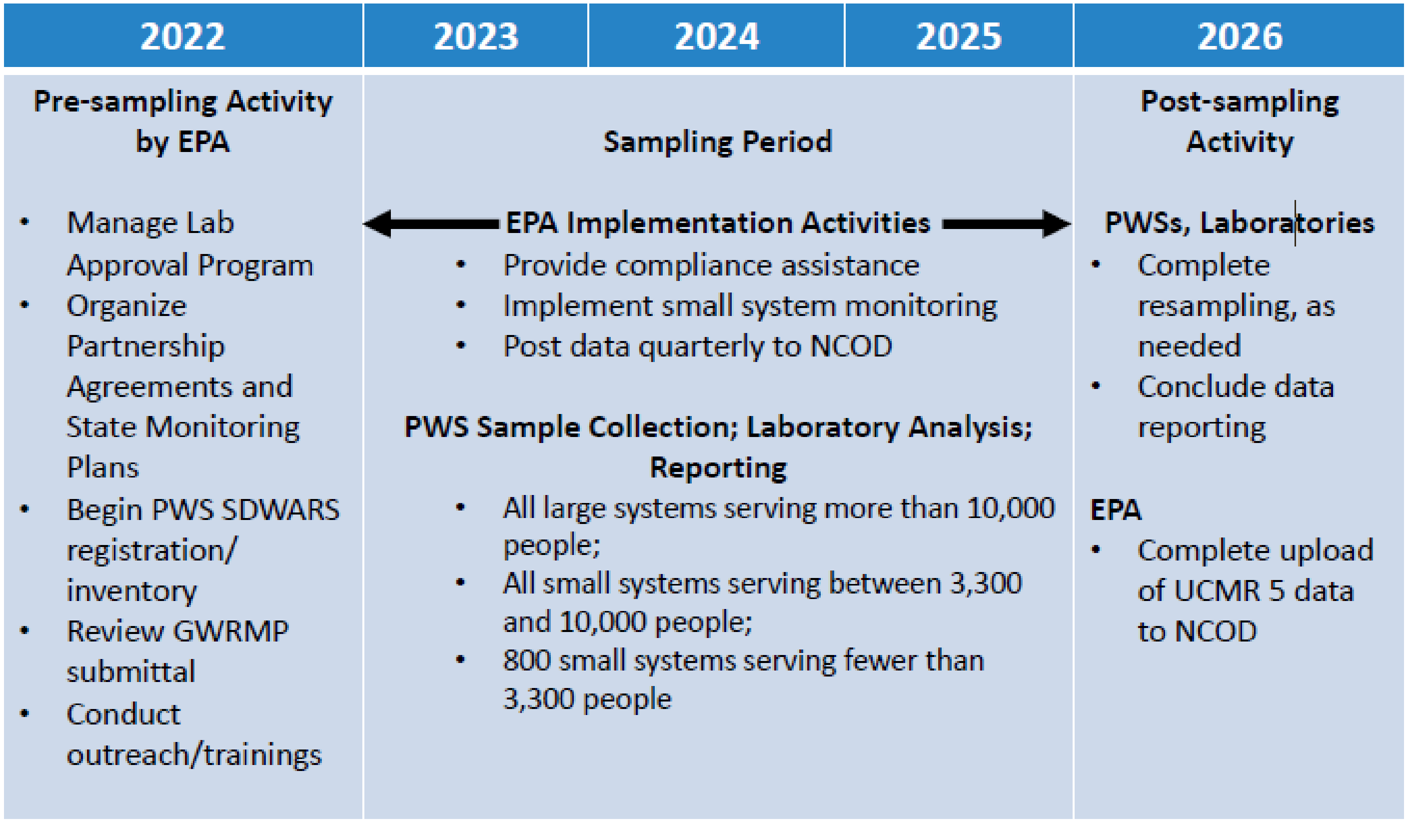
State Lists & Guidance Levels, 2009/2015 -

Source water assessments

Drinking Water PFAS Regulations

- **USEPA**
  - 2013-2015 UCMR3 for 6 PFAS with MRLs of 10-90 ng/L by EPA Method 537
  - Health Advisories (2016): PFOA/PFOS or PFOA + PFOS = 70 ng/L
  - 2023-2025 UCMR5 for 29 PFAS with MRLs of 2-8 ng/L by EPA Methods 537.1 and 533
  - MCLs for PFOA, PFOS, and other PFAS?
- **States with DW Regulations as June 30, 2021**
  - Established / interim / proposed MCL: NJ, NH, VT, MA, NY, WI, ME
  - Established NL: CA
  - Proposed HBV / AL / TL: MI, MN, OH, RI, NC, OR, CO, IL
- **Examples**
  - Individual PFAS — NJ MCL: PFNA = 13 ng/L, PFOA = 14 ng/L, PFOS = 13 ng/L
  - Sum of PFAS — MA MCL: PFOA + PFHxS + PFOS + PFHpA + PFNA + PFDA = 20 ng/L

Proposed UCMR5 Timeline of Activities



2022	2023	2024	2025	2026
Pre-sampling Activity by EPA • Manage Lab Approval Program • Organize Partnership Agreements and State Monitoring Plans • Begin PWS SDWARS registration/ inventory • Review GWRMP submittal • Conduct outreach/trainings	**Sampling Period** ⟵ **EPA Implementation Activities** ⟶ • Provide compliance assistance • Implement small system monitoring • Post data quarterly to NCOD **PWS Sample Collection; Laboratory Analysis; Reporting** • All large systems serving more than 10,000 people; • All small systems serving between 3,300 and 10,000 people; • 800 small systems serving fewer than 3,300 people			**Post-sampling Activity** **PWSs, Laboratories** • Complete resampling, as needed • Conclude data reporting **EPA** • Complete upload of UCMR 5 data to NCOD

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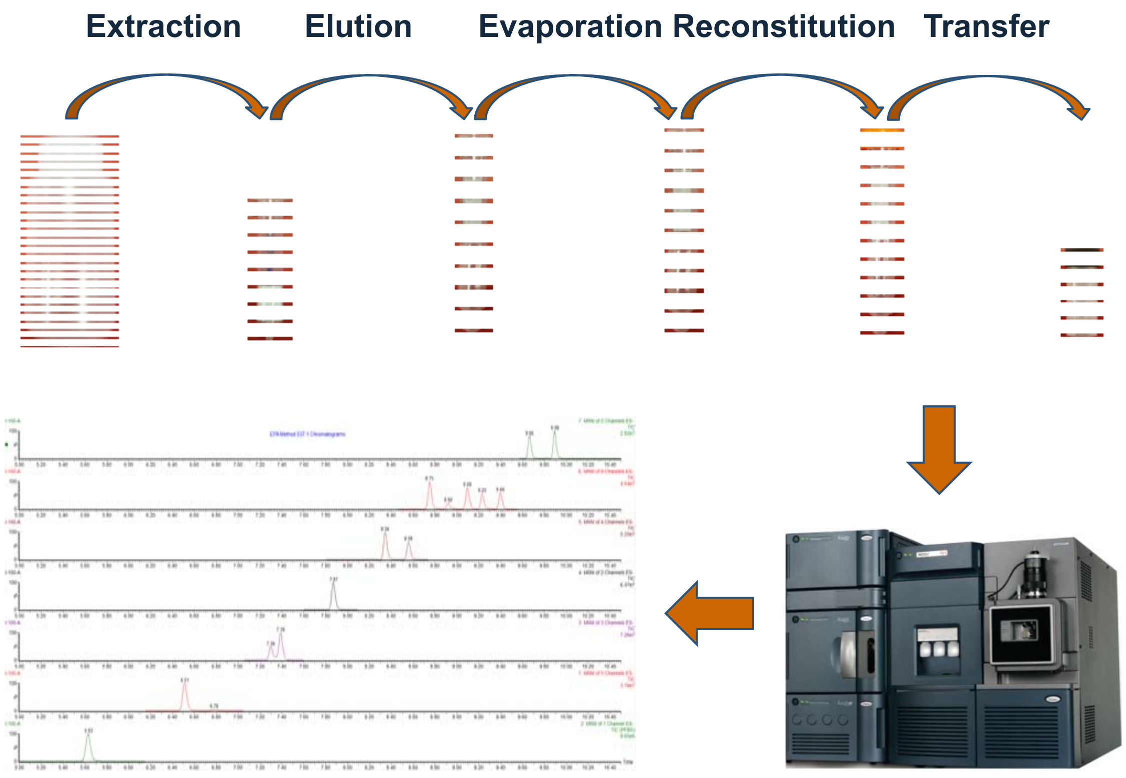
Courtesy to EPA UCMR5 shareholder meeting presentation, 04/06/2021.

Proposed UCMR5 29 PFAS (2023-2025)

EPA 533 (2-5 ng/L)	PFBA	PFPeA	PFHxA	PFHpA UCMR3, 10 ng/L	PFOA UCMR3, 20 ng/L
	PFNA UCMR3, 20 ng/L	PFDA	PFUnA	PPDoA	PFBS UCMR3, 90 ng/L
	PFPeS	PFHxS UCMR3, 30 ng/L	PFHpS	PFOS UCMR3, 40 ng/L	PFEESA
	4:2 FTS	6:2 FTS	8:2 FTS	HFPO-DA	ADONA
	9Cl-PF3ONS	11Cl-PF3OUdS	PFMBA	PFMPA	NFDHA
EPA 537.1 (5-8 ng/L)	MEtFOSAA	NMeFOSAA	PFTrDA	PFTeDA	

EPA 537.1 *vs.* EPA 533



Extraction **Elution** **Evaporation** **Reconstitution** **Transfer**

Method	EPA 537.1	EPA 533
250 mL samples	14 days Trizma pH 6.5 - 7.5	28 days ammonium acetate pH 6 - 8
1 mL extracts	28 days 96% MeOH/water,	28 days 80% MeOH/water
IS / IPS	Internal standards unextracted	Isotope performance standards unextracted
SS / IDA	Surrogate standards extracted	Isotope dilution analogues extracted
Calibration	Internal standard calibration	Isotope dilution calibration
QC	Typical	Typical

EPA 537.1 and 533 Applications

- Drinking water utilities are often involved in two types of analyses.
  - Finished drinking water quality compliance
  - Source water assessments

- EPA Methods 537.1 (evolving from 537) and 533 were developed and validated as drinking water methods.
  - What are the main challenges for drinking water analyses?
    - Relatively low EPA 537.1 surrogate NEtFOSAA-d5 recoveries
    - Field sample (FS) and field reagent blank (FRB) bottles switched

  - Are these methods applicable for source water assessments?
    - What are the main challenges for non-potable water analyses?
    - How to resolve these challenges?

Inter-Laboratory Study Water Matrices

RW1	Native (n = 1)	2 ng/L (n = 4)	RW2	Native (n = 1)	50 ng/L (n = 4)
DW1	Native (n = 2)	10 ng/L (n = 4)	DW2	Native (n = 2)	10 ng/L (n = 4)
GW1	Native (n = 2)	10 ng/L (n = 4)	GW2	Native (n = 2)	10 ng/L (n = 4)
SW1	Native (n = 2)	10 ng/L (n = 4)	SW2	Native (n = 2)	10 ng/L (n = 4)
WW1	Native (n = 2)	50 ng/L (n = 4)	WW2	Native (n = 2)	50 ng/L (n = 4)

Inter-Laboratory Study Water Matrices (Cont’d)

Matrix	DW1	DW2	GW1	GW2	SW1	SW2	WW1	WW2
pH	6.8	7.2	7.3	7.4	7.3	6.7	7.3	7.2
Free chlorine (mg/L)	0.86	0.86	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
TOC (mg/L)	0.52	0.52	0.86	0.43	3.1	5.8	2.4	3.7
Total hardness as $CaCO_3$ (mg/L)	401	563	257	256	278	122	412	324
Total alkalinity as $CaCO_3$ (mg/L)	276	275	208	320	214	109	276	213
Chloride (mg/L)	147	289	38	37	33	13	239	182
Sulfate (mg/L)	60	60	28	27	39	4.6	94	54
Nitrate as nitrogen (mg/L)	< 1.0	< 1.0	1.7	2.1	1.8	< 1.0	11	13
HPC (MPN/mL)	NA	NA	311	372	650	1000	440	623

Mean Native Concentrations ± SD (ng/L)

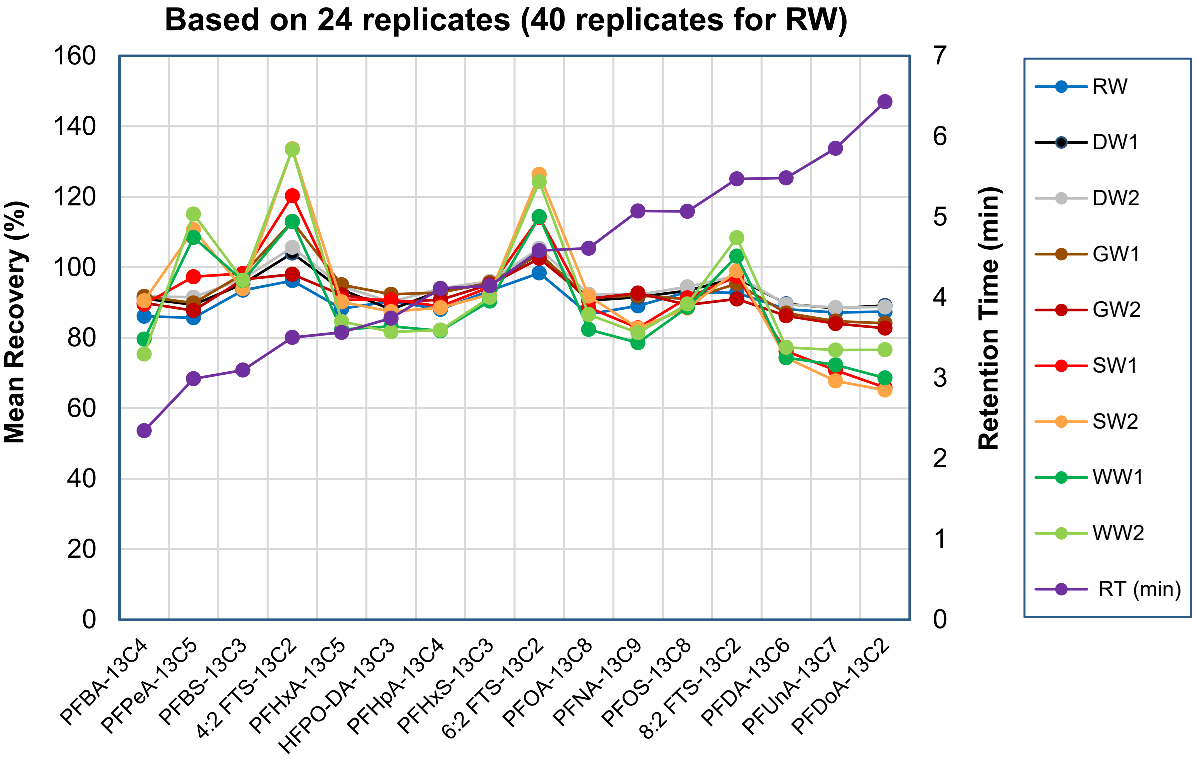
Analyte	Method	DW1	DW2	GW1	GW2	SW1	SW2	WW1	WW2
PFBA	533	3.2 ± 0.3	3.2 ± 0.3	4.5 ± 0.3	4.6 ± 0.5	2.0 ± 0.3	2.8 ± 0.5	6.9 ± 1.8	7.8 ± 2.9
PFPeA	533	1.7 ± 0.1	1.7 ± 0.2	0.9 ± 0.1	0.8 ± 0.1	1.4 ± 0.3	1.4 ± 0.3	20.3 ± 1.7	15.4 ± 1.2
PFBS	533	2.4 ± 0.1	2.4 ± 0.2	5.4 ± 0.4	5.2 ± 0.4	1.3 ± 0.7	0.9 ± 0.5	3.5 ± 0.3	4.0 ± 0.6
	537.1	2.5 ± 0.2	2.5 ± 0.2	5.5 ± 0.2	5.5 ± 0.4	1.4 ± 0.8	0.9 ± 0.5	3.5 ± 0.7	4.0 ± 1.5
PFHxA	533	2.0 ± 0.1	2.0 ± 0.2	1.0 ± 0.1	0.9 ± 0.1	0.9 ± 0.6	1.0 ± 0.6	14.9 ± 1.7	15.9 ± 1.7
	537.1	1.6 ± 0.9	2.1 ± 0.2	0.7 ± 0.4	0.8 ± 0.5	1.0 ± 0.6	1.1 ± 0.7	14.7 ± 0.8	15.5 ± 1.1
PFHpA	533	1.8 ± 0.2	1.9 ± 0.2	1.0 ± 0.1	0.8 ± 0.1	ND	1.1 ± 0.2	1.8 ± 0.2	1.5 ± 0.3
	537.1	1.5 ± 0.9	1.5 ± 0.9	ND	ND	ND	1.1 ± 0.6	2.0 ± 0.2	1.5 ± 0.3

Mean Native Concentrations ± SD (ng/L)

Analyte	Method	DW1	DW2	GW1	GW2	SW1	SW2	WW1	WW2
PFHxS	533	1.2 ± 0.1	1.2 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.7 ± 0.4	ND	2.9 ± 0.4	5.5 ± 0.6
	537.1	ND	1.0 ± 0.6	0.8 ± 0.5	0.7 ± 0.5	0.9 ± 0.6	ND	3.2 ± 0.3	5.9 ± 0.7
PFOA	533	9.6 ± 0.8	9.4 ± 0.7	3.0 ± 0.3	2.8 ± 0.2	0.8 ± 0.5	1.9 ± 1.1	4.0 ± 0.5	3.8 ± 0.6
	537.1	9.7 ± 0.8	10.1 ± 0.6	2.8 ± 0.2	2.8 ± 0.2	1.0 ± 0.6	2.7 ± 0.2	4.6 ± 0.5	3.9 ± 0.3
PFOS	533	ND	ND	ND	ND	1.1 ± 0.7	1.0 ± 0.6	2.5 ± 0.3	9.6 ± 0.6
	537.1	ND	ND	0.7 ± 0.6	0.7 ± 0.6	1.2 ± 0.9	1.1 ± 0.8	3.1 ± 0.9	9.4 ± 1.1
PFNA	533	ND	ND	ND	ND	ND	0.7 ± 0.5	ND	ND
	537.1	ND	ND	ND	ND	ND	ND	0.7 ± 0.3	ND

EPA 533 IDA Recoveries

- All multi-lab IDA recoveries were within 50-200%.
- The SW and WW matrices resulted in slightly low recoveries for long-chain IDA.
  - PFDA-13C6
  - PFUnA-13C7
  - PFDoA-13C2
- The WW matrices significantly affected IPS-PFBA-13C3 and IDA-PFBA-13C4 peak areas.



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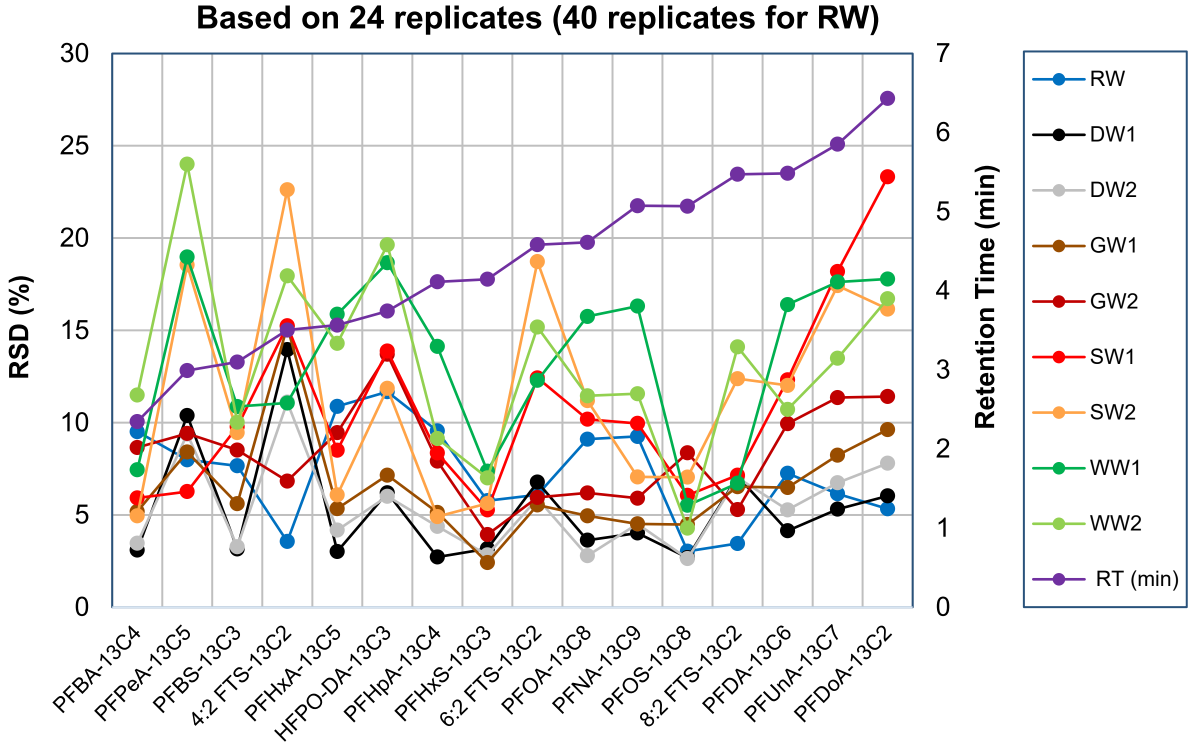
EPA 533 IDA %RSD

- Single lab RSD were ≤20%.
- The multi-lab IDA RSD were generally ≤20%.
- The SW and WW matrices resulted in relatively higher RSD.
  - PFDoA-13C2 = 23% for SW1
  - 4:2 FTS-13C2 = 23% for SW2
  - PFPeA-13C5 = 24% for WW2



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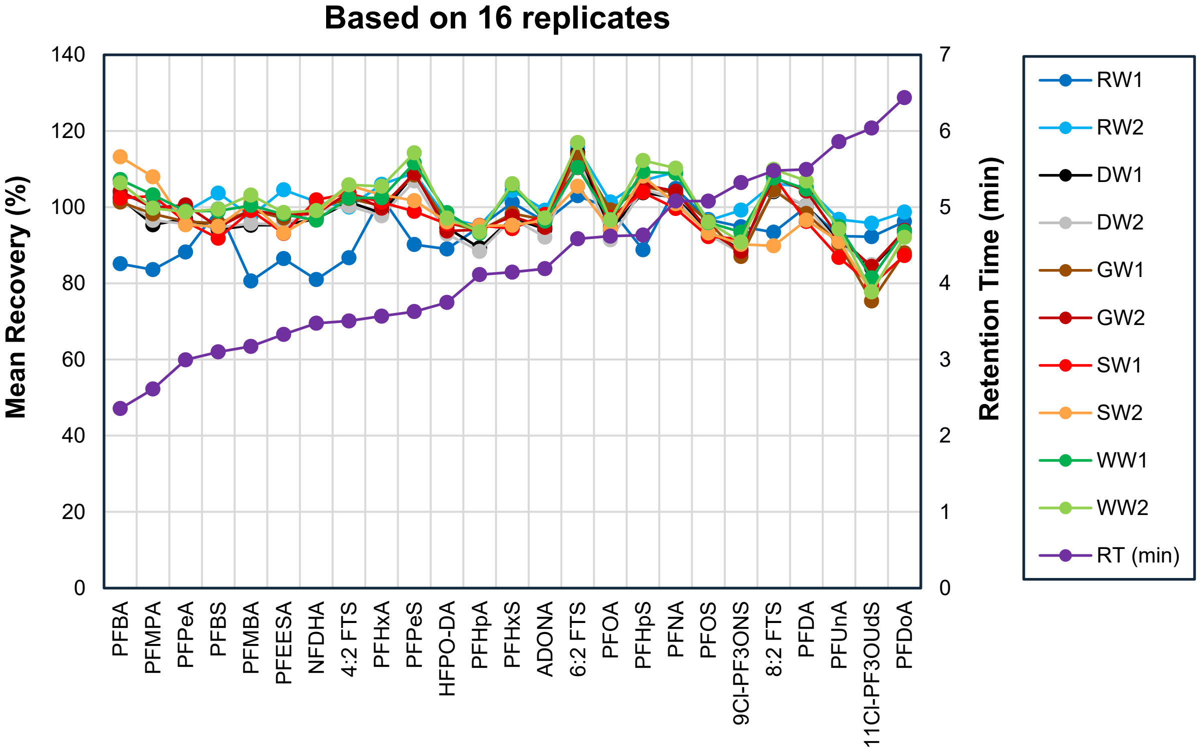
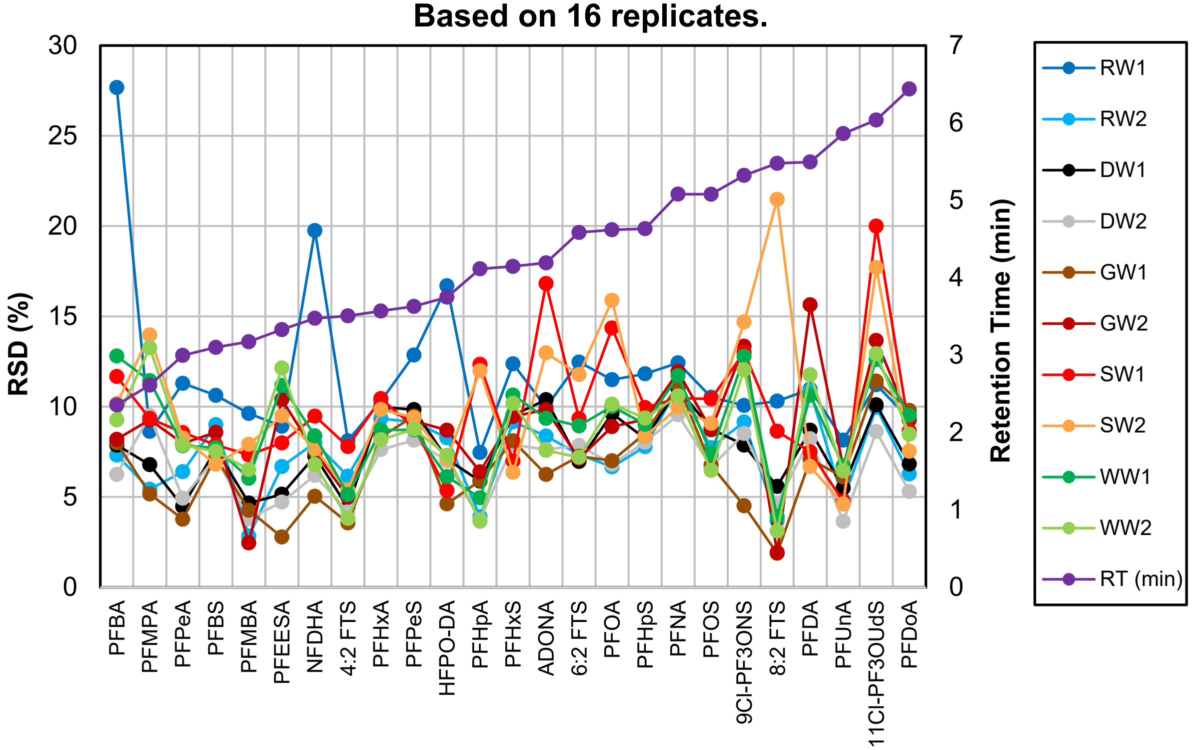
EPA 533 Analyte Recoveries

- **All multi-lab PFAS recoveries were within 70-130%.**
- **The SW and WW matrices resulted in slightly low recoveries for long-chain PFAS.**
  - **PFUnA**
  - **11Cl-PF3OUdS**
  - **PFDoA**
- **PFMPA recoveries depended on the selected IDA.**



EPA 533 Analyte %RSD

- **Single lab RSD were ≤20%.**
- **The multi-lab PFAS RSD were generally ≤20%.**
- **8:2 FTS = 22% for SW2**
- **PFBA spiked at 2 ng/L = 28% for RW1**
  - **Lab D MRL = 5 ng/L**



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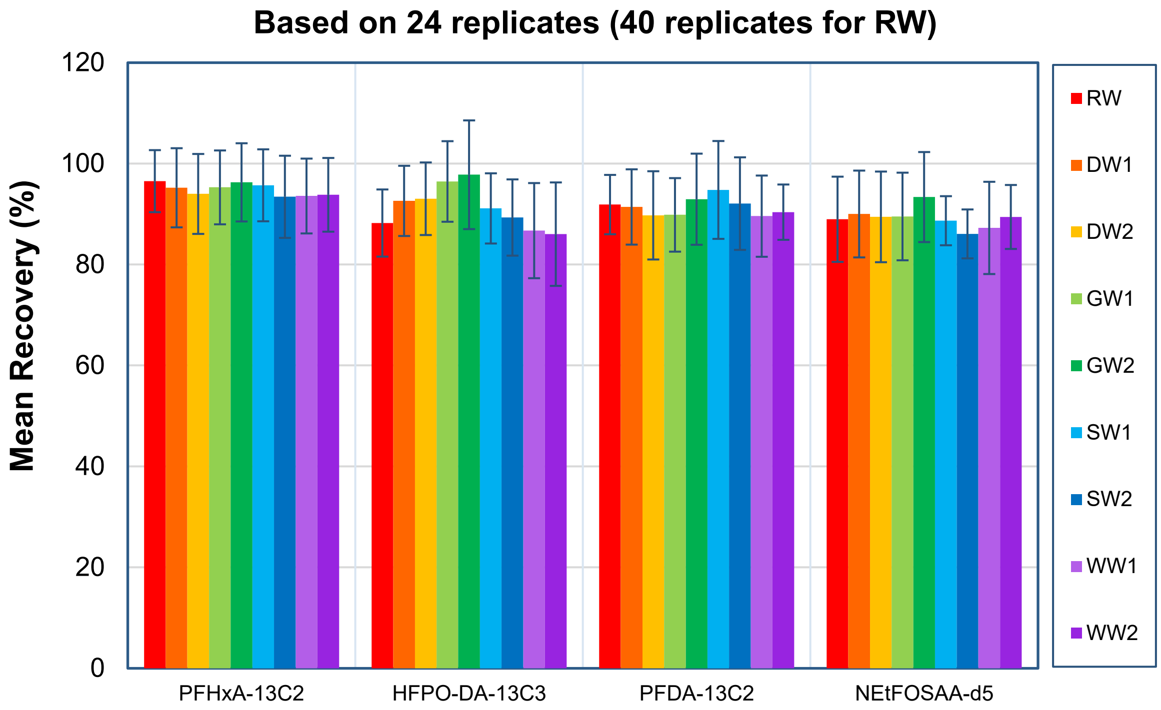
EPA 537.1 Surrogate Recoveries and %RSD

- The multi-lab SS recoveries were within 70-130%.
- The SS recoveries slightly trended lower from PFHxS-13C2 to NETFOSAA-d5.
- The multi-lab RSD were within 10%.

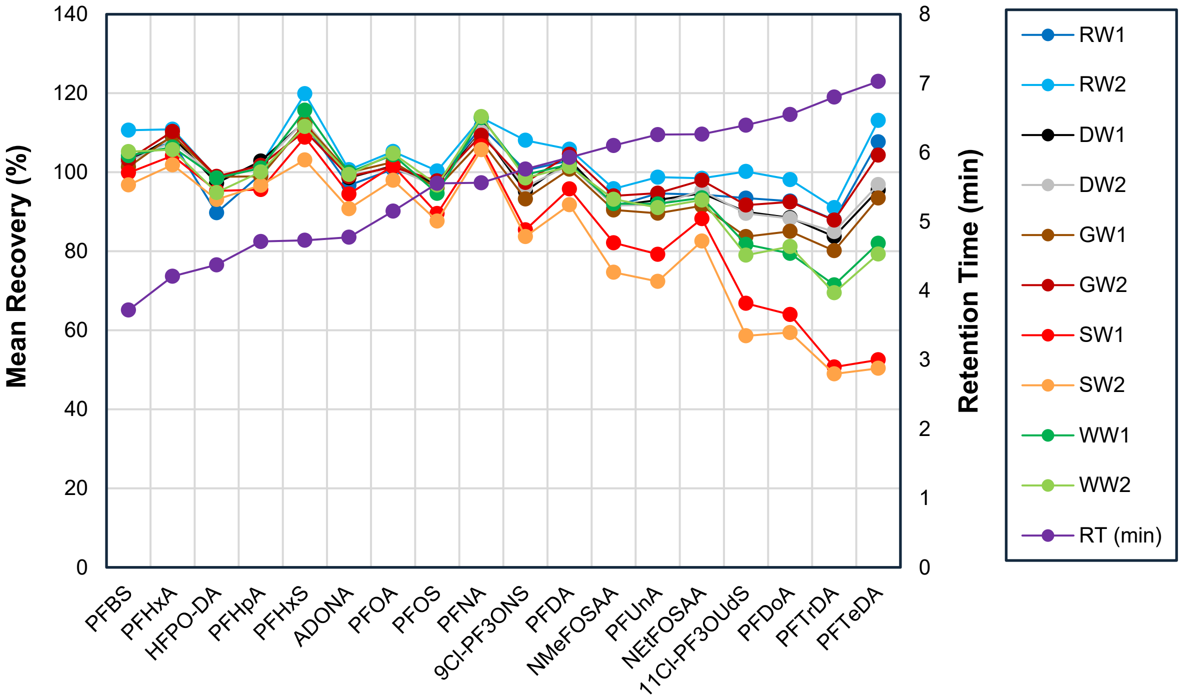


EPA 537.1 Analyte Recoveries

- The multi-lab PFAS recoveries were within 70-130% except
  - 11Cl-PF3OUdS
  - PFDoA
  - PFTrDA
  - PFTeDA

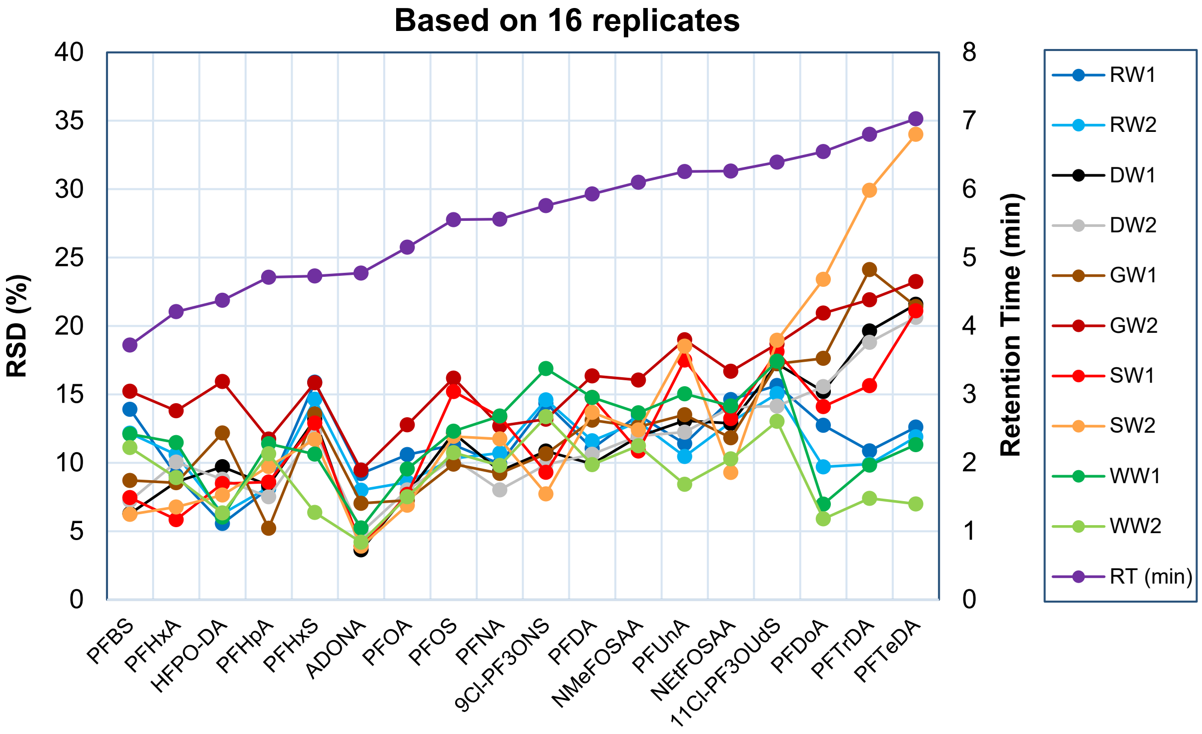
- SW1 and SW2 resulted in lower recoveries for these long-chain PFAS.

Based on 16 replicates



EPA 537.1 Analyte %RSD

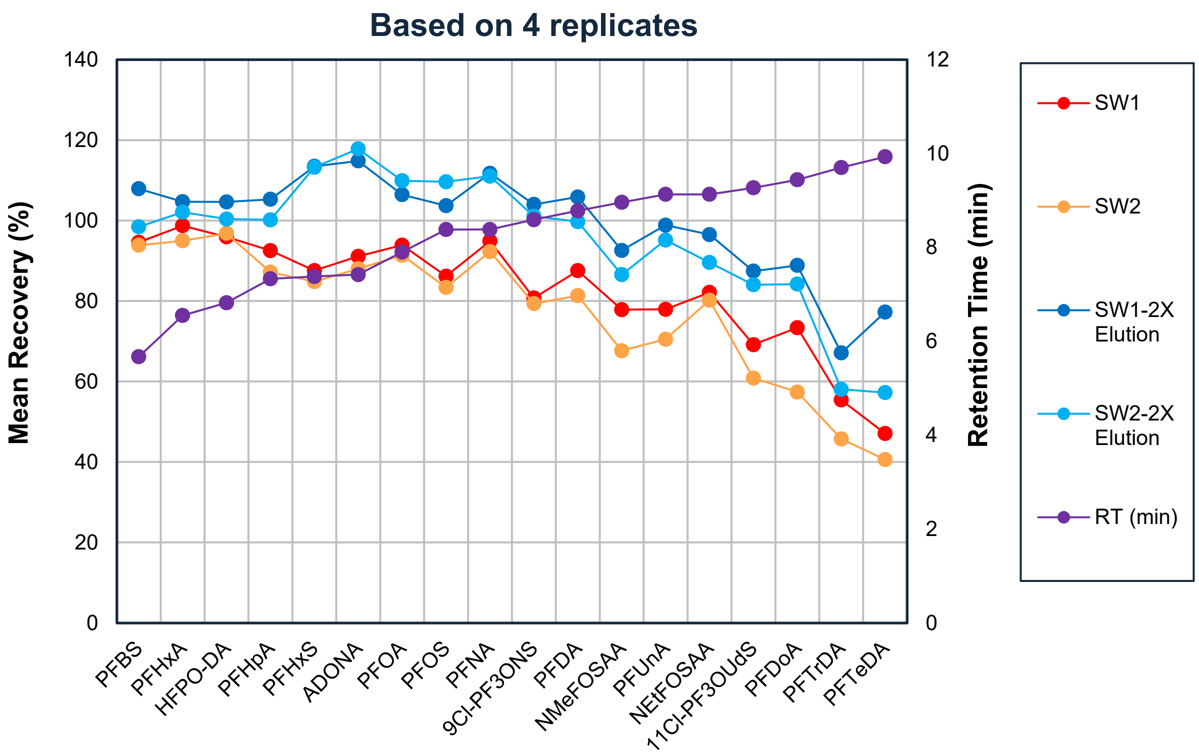
- **Single lab RSD were <20%.**
- **The multi-lab PFAS RSD were generally <20% except**
  - **PFDoA**
  - **PFTrDA**
  - **PFTeDA**
- **SW2 resulted in higher RSD for these long-chain PFAS.**
  - **SW2 contained the highest TOC and HPC contents.**



EPA 537.1 Experience

- ➢ **Low recoveries (50-69%) of SS NEtFOSAA-d5 were often observed for a small fraction of field samples.**
  - ▪ **Reanalysis**
  - ▪ **Re-extraction**
  - ▪ **Re-collection**

- ➢ **Long-chain PFAS recoveries could be improved by enhancing elution.**


Based on 4 replicates

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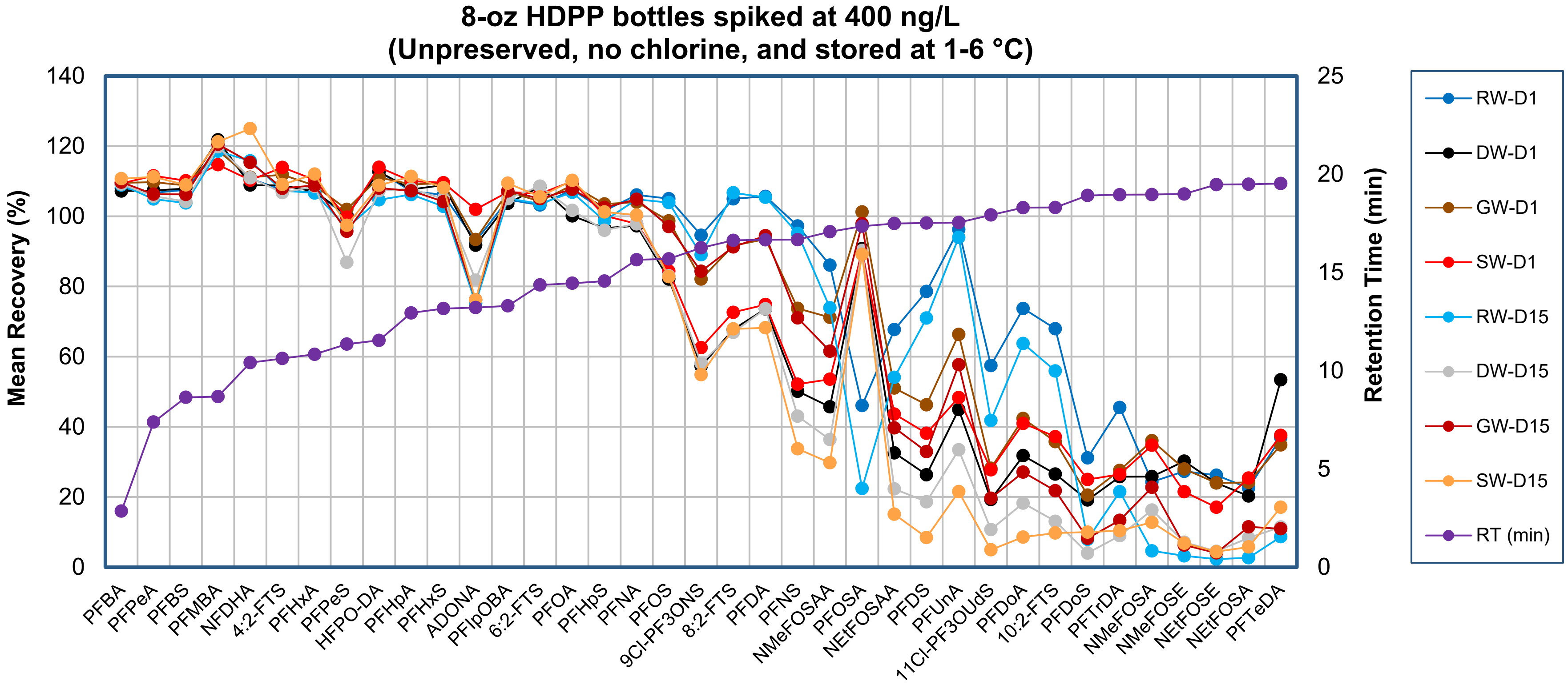
Bottle Surface Adsorption Losses



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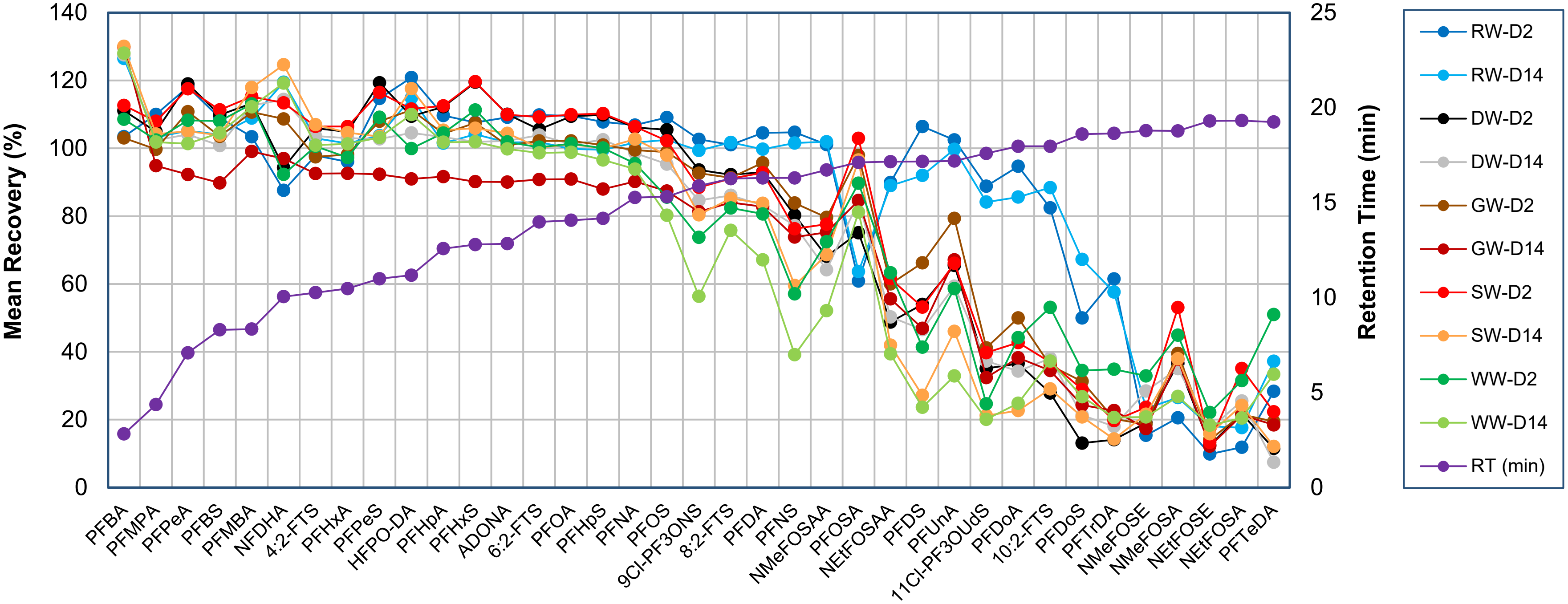
Bottle Surface Adsorption Losses (Cont’d)

8-oz HDPE bottles spiked at 400 ng/L
(Unpreserved, no chlorine, stored at 1-6 °C)



Conclusions

- EPA 537.1 and 533 are sensitive and robust drinking water methods.
  - Batch QC failures are rare.
  - 2 ng/L or lower MRLs can be achieved for most PFAS of interest. Slightly higher MRLs (PFBA, PFHpA, 6:2 FTS, etc.) may be applicable for some labs.
  - Field reagent blank (FRB) contamination was rarely observed. Most FRB failures were related to switching bottles.
  - Carryover contamination from very high PFAS concentration samples was occasionally observed.
  - The most common EPA 537.1 QC failure was relatively low SS-NEtFOSAA-d5 recoveries, < 70%.

Conclusions (Cont’d)

- EPA 537.1 and 533 are generally applicable for source water assessments – Pristine GW, SW, and treated WW matrices.
- EPA 533 is more robust in tolerating matrix interferences.
  - ESI suppression to PFBA and its IPS and IDA can be caused by high concentration common inorganic anions and/or polar organic compounds extracted particularly from WWTP effluents.
  - Sufficient rinsing of sample bottles and SPE cartridges with reagent water may be necessary.
  - It may be critical to choose appropriate IDA for those PFAS without their own labeled analogues available (e.g., PFMPA).

Conclusions (Cont'd)

- EPA 537.1 is less robust in extracting long-chain PFAS (C10 and above) from difficult SW and WW matrices.
    - Adsorption losses of long-chain PFAS are a primary challenge, which can be enhanced by high concentration TOC and biological contents in SW and WW matrices.
    - Enhanced rinsing of sample bottles and SPE cartridge elution may be necessary.
    - Improved recoveries of long-chain PFAS was observed by increasing the elution solvent volumes.
- Most contents will be published in AWWA Water Science.

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