



Modified EPA Method 533 for Analysis of PFAS in Drinking Water and Source Water

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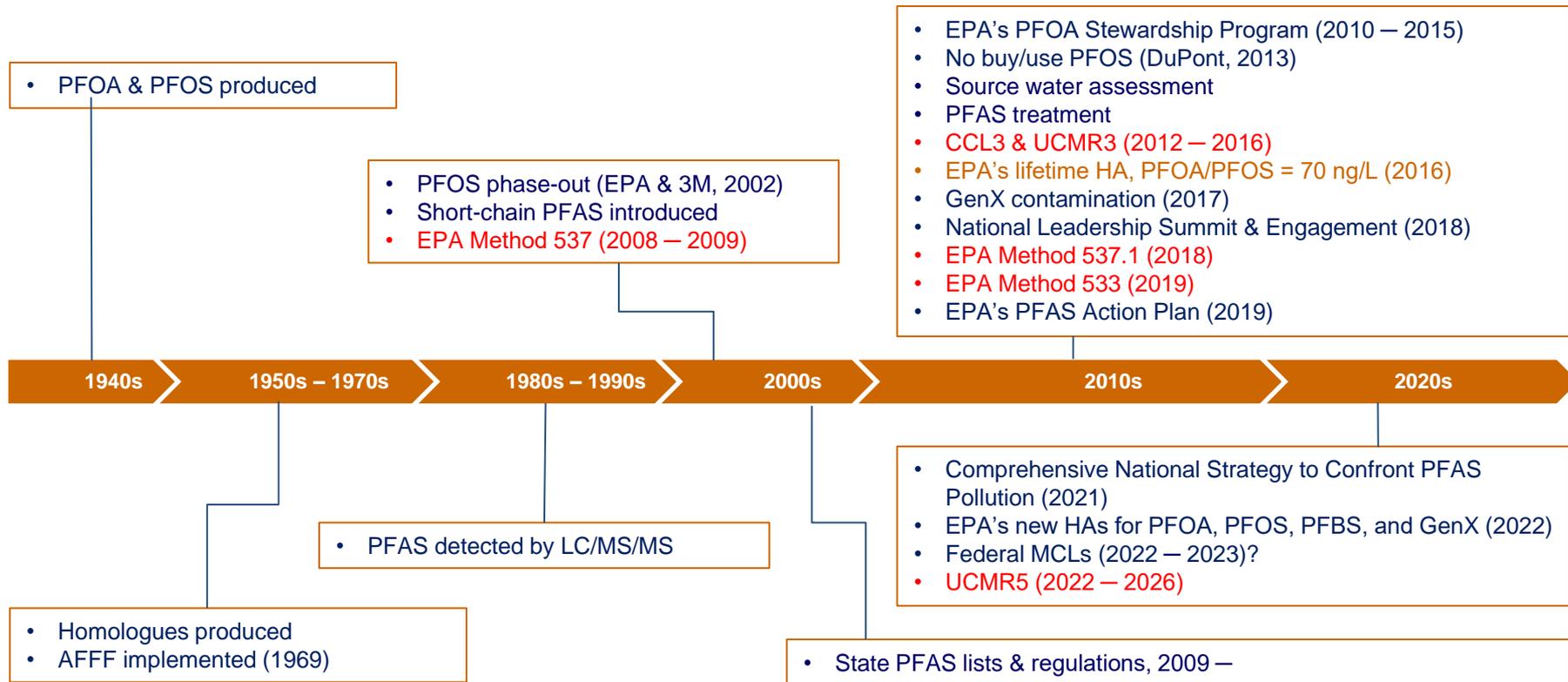


Presentation Outline



- PFAS and Regulations
- PFAS Analytics Review
- Modified EPA 533 Summary
- Modified EPA 533 Performance & Challenges
- Conclusions

PFAS Have Been around for a Long Time.



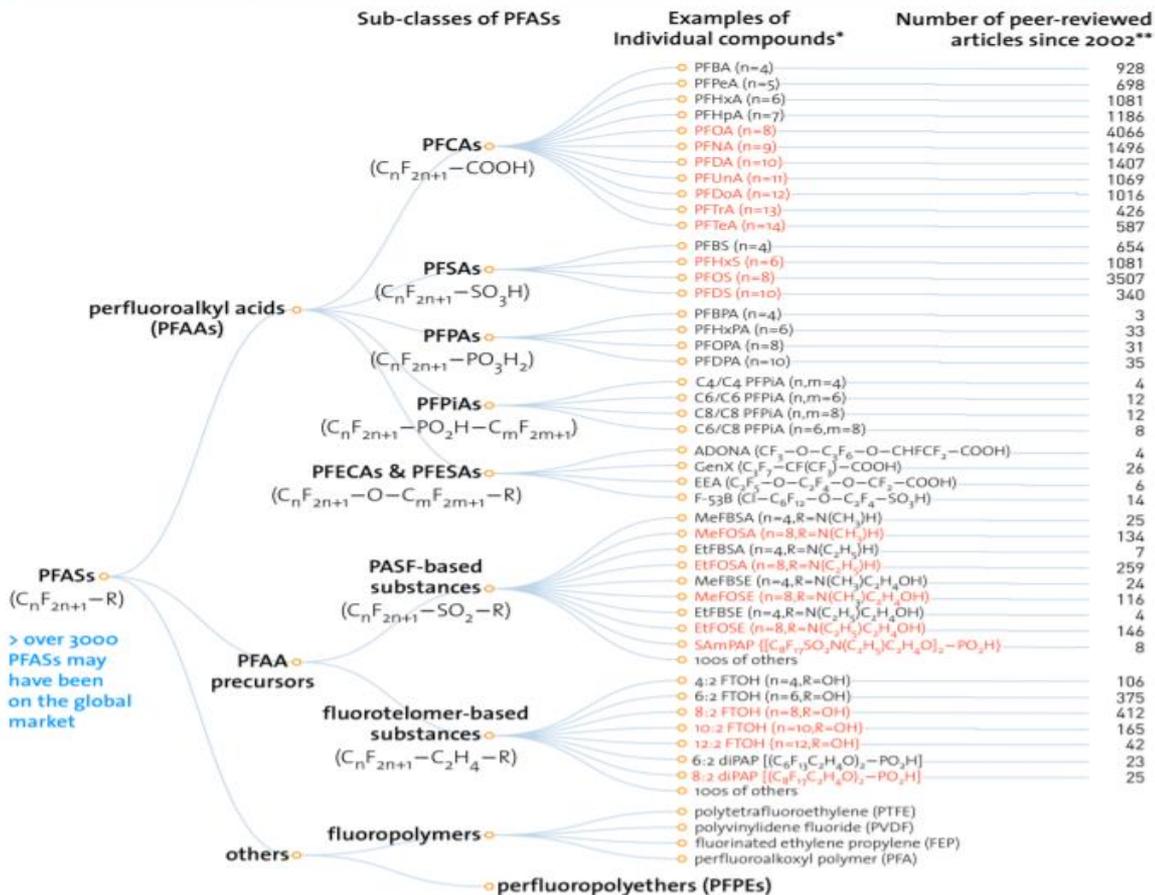
PFAS Drinking Water Regulations



- 22 states have had various regulations on 11 PFAS. Some regulations are more stringent than the others.
 - Individual PFAS (e.g., CA, DE, IL, MI, MN, NH, NJ, NY, OR, PA, WA)
 - Sum of PFAS (e.g., CT, MA, ME, RI, VT)
- EPA's new health advisories (June, 2022): 0.004 ng/L PFOA, 0.02 ng/L PFOS, 10 ng/L HFPO-DA/GenX, and 2000 ng/L PFBS.
- Unregulated Contaminant Monitoring Rule 5 (UCMR5, 2022 – 2026): 29 PFAS plus lithium.
- Federal MCLs are expected in late 2022 or 2023.

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.



* 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/iAN>).

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

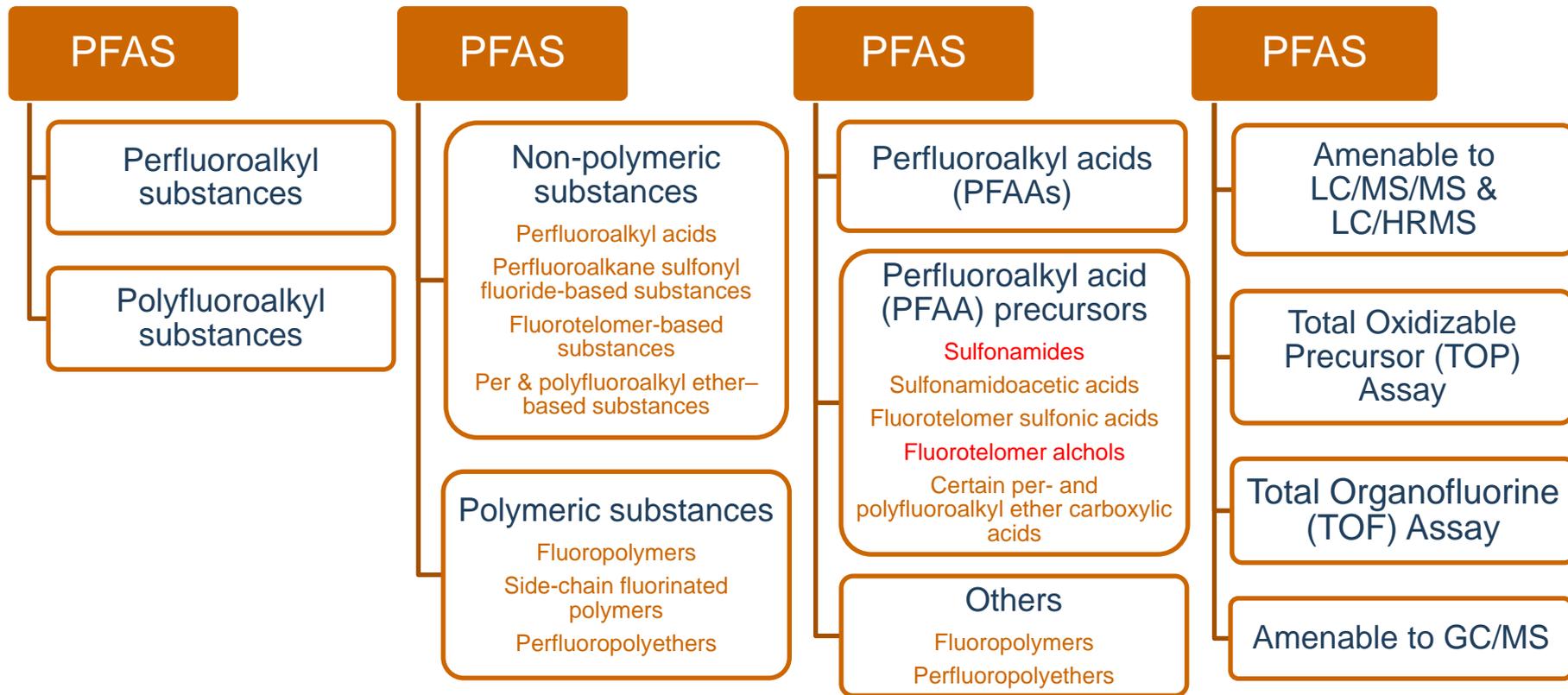
Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors).

Over 9000 PFAS?

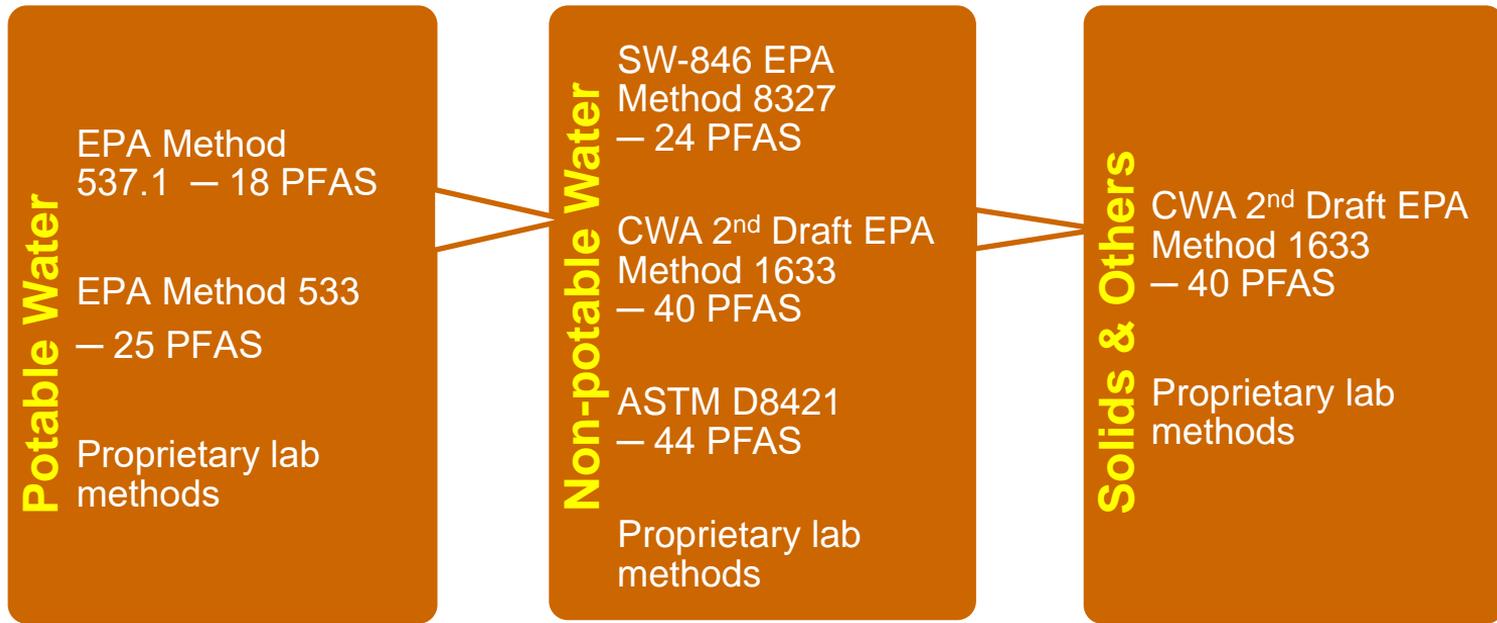


- EPA's Comptox Chemicals Dashboard PFAS Master List of PFAS Substances, <https://comptox.epa.gov/dashboard/chemical-lists/pfasmaster>
 - Use systematic review methods to identify and summarize over 9000 PFAS substances and structures.
- Cited as a group/family/class of over 9,000 man-made/synthetic chemicals/compounds identified/known.....
 - CDC/The National Institute for Occupational Safety and Health (NIOSH)
 - NIH/National Institute of Environmental Health Sciences
 - CT Department of Public Health

Types of PFAS



Primary PFAS LC/MS/MS Analytics



Is it possible to analyze more PFAS in drinking water and source water by using one single method?

Drinking Water PFAS Analyses



- Drinking water compliance analysis
- Drinking water occurrence assessment
- Drinking water supply/source water evaluation
- Water reuse – DPR and IPR
- PFAS removal & treatment
- PFAS identification

Purposes of This Research



- Develop a single LC/MS/MS method to meet the increasing needs for monitoring and assessing PFAS contamination to drinking water supplies.
 - Combine EPA Methods 537.1 and 533 into one.
 - Capable of analyzing more PFAS.
 - Meet the QC requirements of EPA 537.1 and 533.
 - Provide superior sensitivity, accuracy, and robustness.
 - Applicable to drinking water and source water analyses.

Modified EPA 533

All 29 EPA 533 & 537.1 PFAS Included



EPA 533		EPA 533 & 537.1			EPA 537.1
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFTrDA
PFPeS	PFHpS	PFNA	PFDA	PFUnA	PFTeDA
PFMBA	PFMPA	PPDoA	PFBS	PFHxS	NMeFOSAA
PFEESA	NFDHA	PFOS	HFPO-DA	ADONA	MEtFOSAA
4:2 FTS	6:2 FTS	9Cl-PF3ONS	11Cl-PF3OUdS		
8:2 FTS					

Modified EPA 533 (Cont'd)

25 Additional PFAS Included



PFHxDA	PFODA	PFIpOBA	PFPrS	PFNS
PFDS	PFDoS	Nafion BP1	Nafion BP2	PFBSA
PFHxSA	PFOSA	PFDSA	NMeFOSE	NEtFOSE
NMeFOSA	NEtFOSA	NMeFBSA	10:2 FTS	3:3 FTA
5:3 FTA	7:3 FTA	6:2 FTUA	8:2 FTUA	10:2 FTUA

Modified EPA 533 (Cont'd)

25 Additional PFAS Included



- 2 perfluoralkyl carboxylic acids: PFHxDA and PFODA
- 1 perfluoralkyl ether carboxylic acid: Perfluoro-4-isopropoxybutanoic acid (PFIpOBA)
- 6 perfluoralkyl sulfonic acids: PFPrS, PFNS, PFDS, PFDoS, Nafion BP1, and Nafion BP2
- 9 perfluoralkyl sulfonamides and sulfonamidoethanols: PFBSA, PFHxSA, PFOSA, PFDSA, NMeFOSE, NEtFOSE, NMeFOSA, NEtFOSA, and NMeFBSA
- 7 fluorotelomer acids: 10:2 FTS, 3:3 FTA, 5:3 FTA, 7:3 FTA, 6:2 FTUA, 8:2 FTUA, and 10:2 FTUA

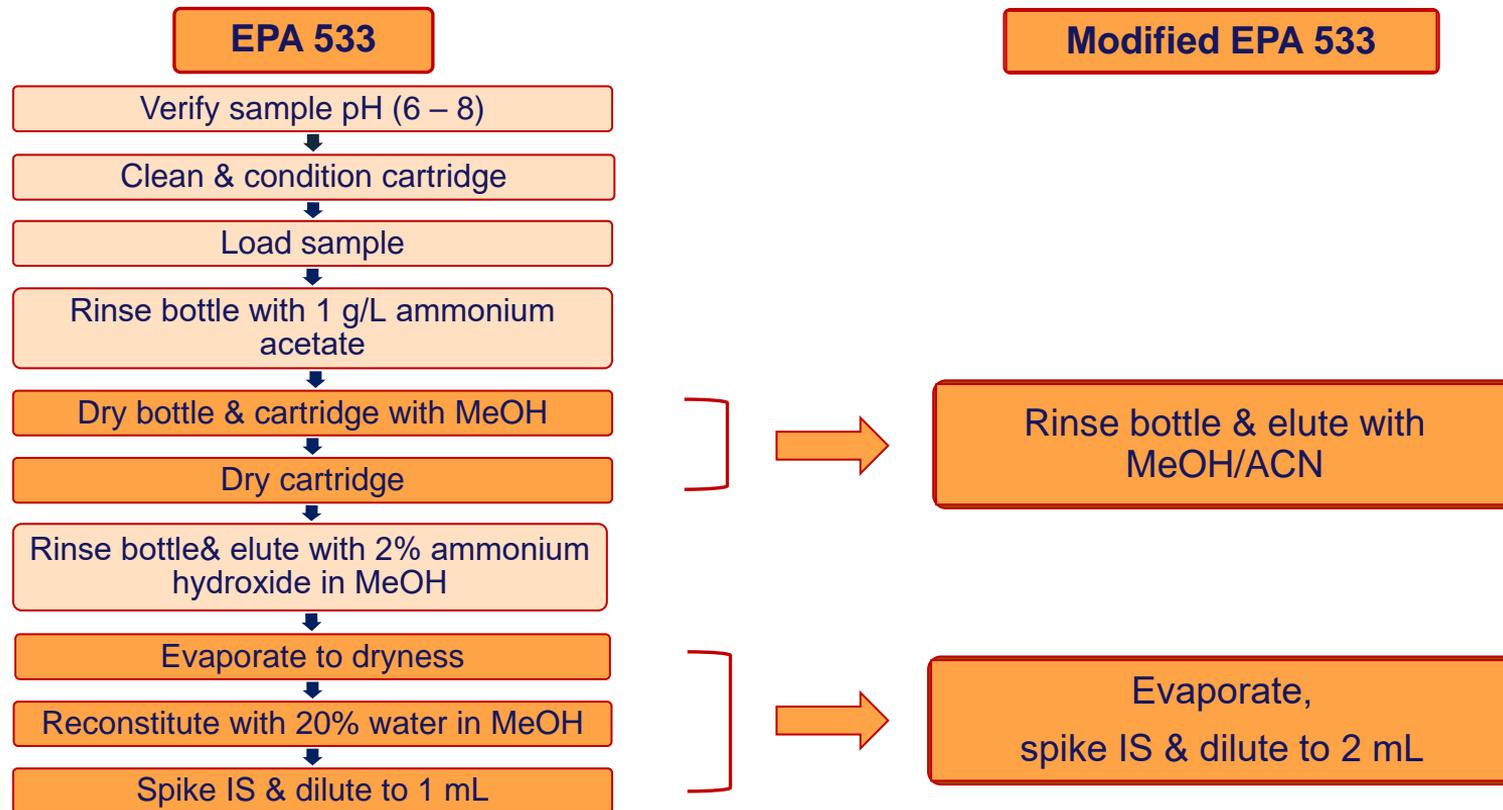
Modified EPA 533 (Cont'd)

3 IPS and 28 IDA

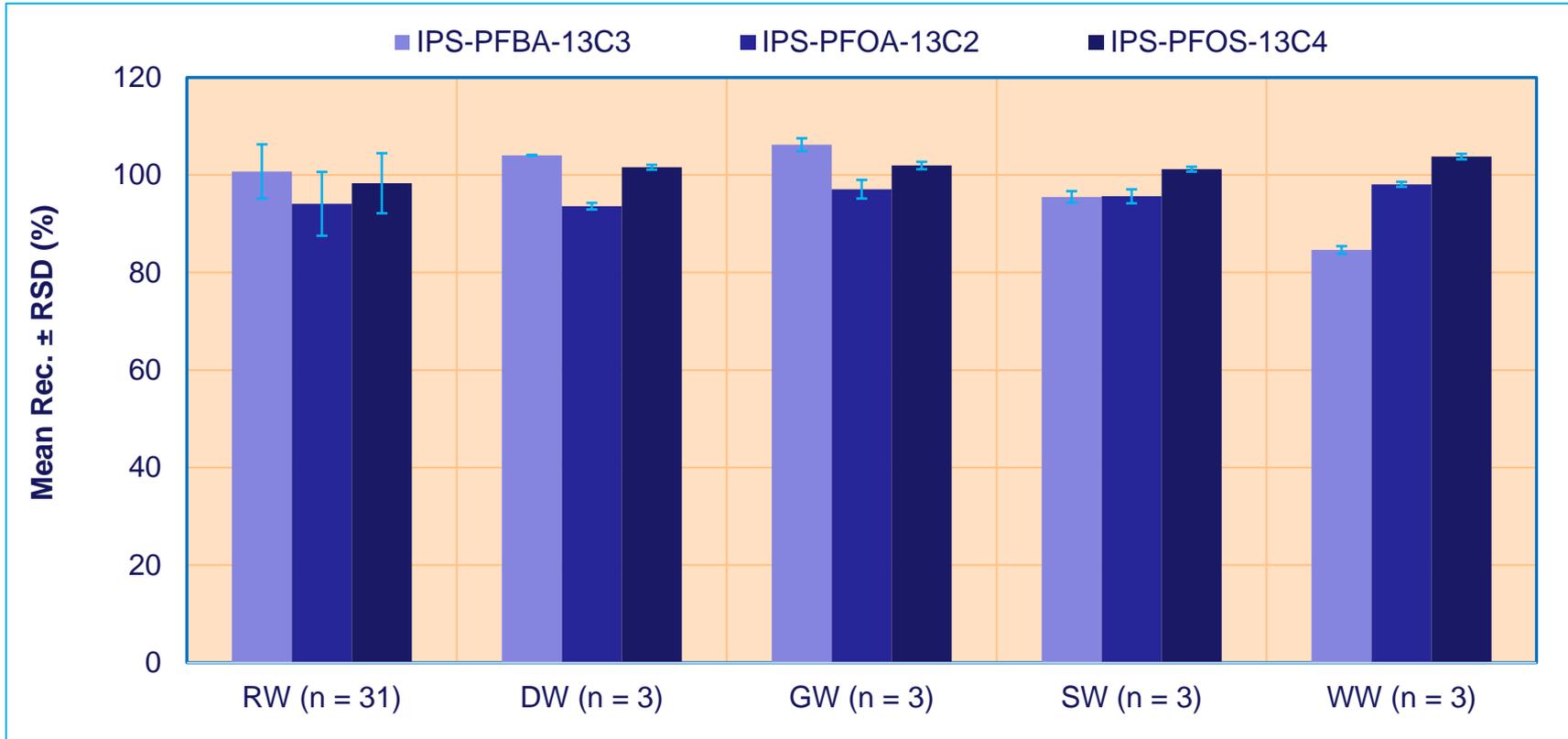


3 EPA 533 IPS	PFBA-13C3	PFOA-13C2	PFOS-13C4	10 Additional IDA	
18 EPA 533 IDA	PFBA-13C4	PFDA-13C6	PFOS-13C8	PFTeDA-13C2	NMeFOSE-d7
	PFPeA-13C5	PFUnA-13C7	4:2 FTS-13C2	PFHxDA-13C2	NEtFOSE-d9
	PFHxA-13C5	PFDoA-13C2	6:2 FTS-13C2	PFOSA-13C8	NMeFOSA-d3
	PFHpA-13C4	HFPO-DA-13C3	8:2 FTS-13C2	6:2 FTUA-13C2	NEtFOSA-d5
	PFOA-13C8	PFBS-13C3	NMEFOSAA-d3	8:2 FTUA-13C2	
	PFNA-13C9	PFHxS-13C3	NEtFOSAA-d5	10:2 FTUA-13C2	

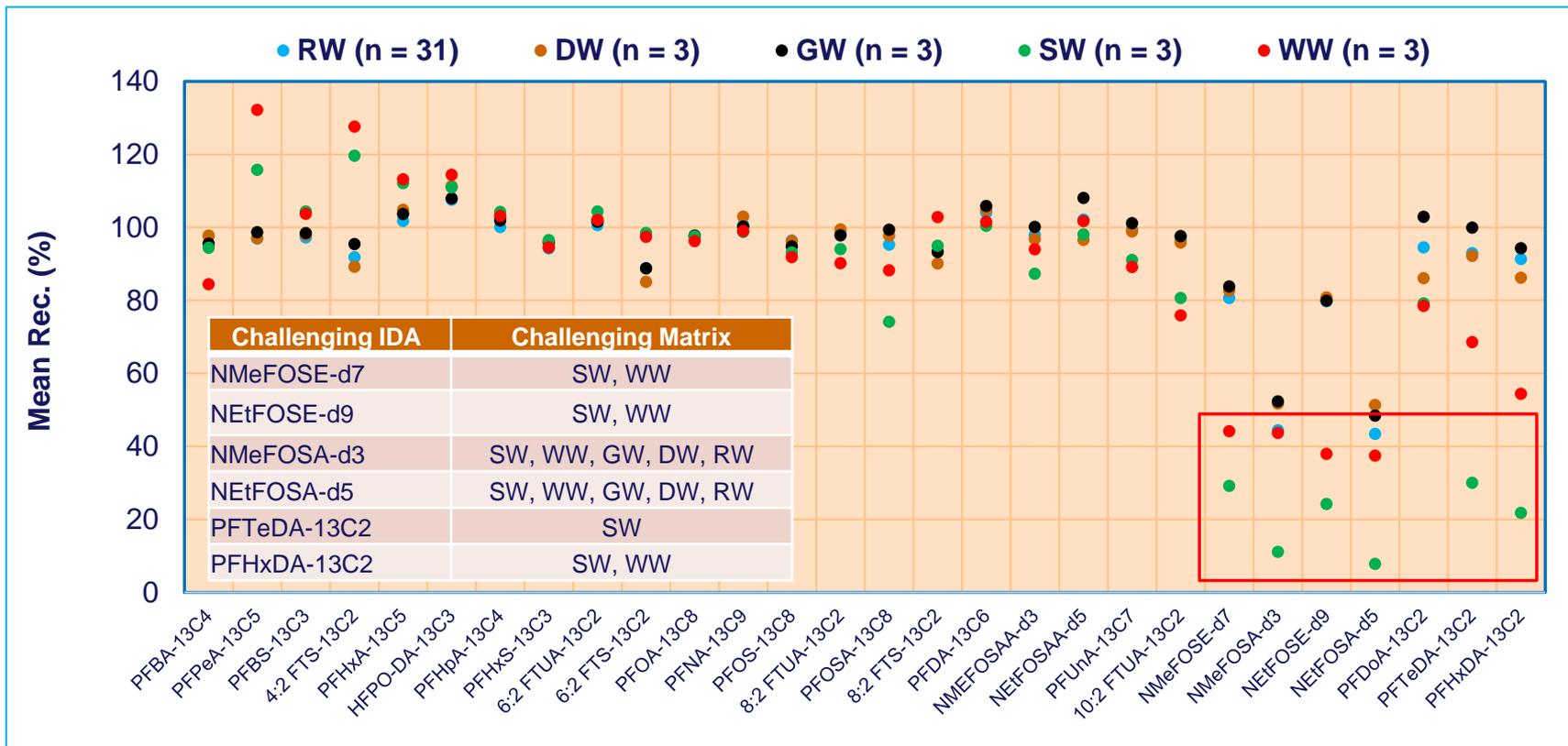
EPA 533 vs. Modified EPA 533



Modified EPA 533 IPS Performance



Modified EPA 533 IDA Performance



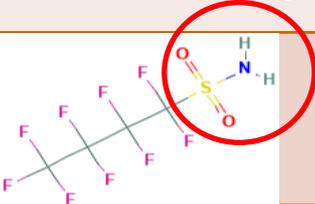
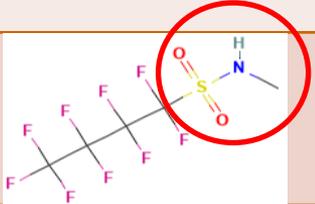
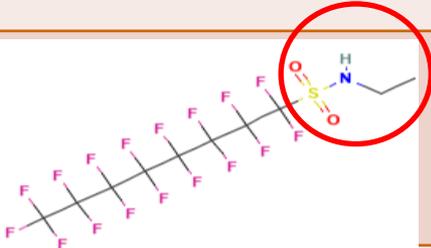
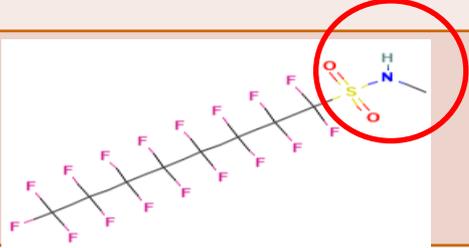
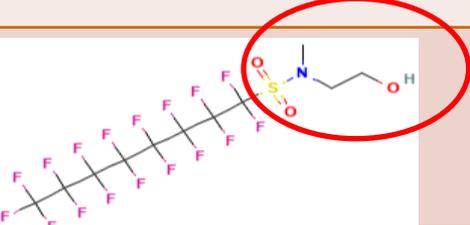
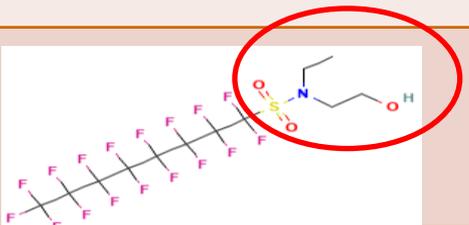
Modified EPA 533 Challenging IDA



NMeFOSA-d3	SW > WW > GW, DW, RW	Passing NMeFOSA DOC	Failing NMeFOSA PIR Passing NMeFOSA MDL
NEtFOSA-d5	SW > WW > GW, DW, RW	Passing NEtFOSA DOC	Failing NEtFOSA PIR Passing NEtFOSA MDL
NMeFOSE-d7	SW > WW	Passing NMeFOSE DOC	Passing NMeFOSE PIR
NEtFOSE-d9	SW > WW	Passing NEtFOSE DOC	Passing NEtFOSE PIR
PFTeDA-13C2	SW	Passing FTrDA DOC Passing PFTeDA DOC	Passing PFTeDA PIR Passing PFTeDA PIR
PFHxDA-13C2	SW > WW	Passing PFHxDA DOC Passing PFOA DOC	Passing PFHxDA PIR Passing PFOA PIR

Modified EPA 533 Challenging PFAS

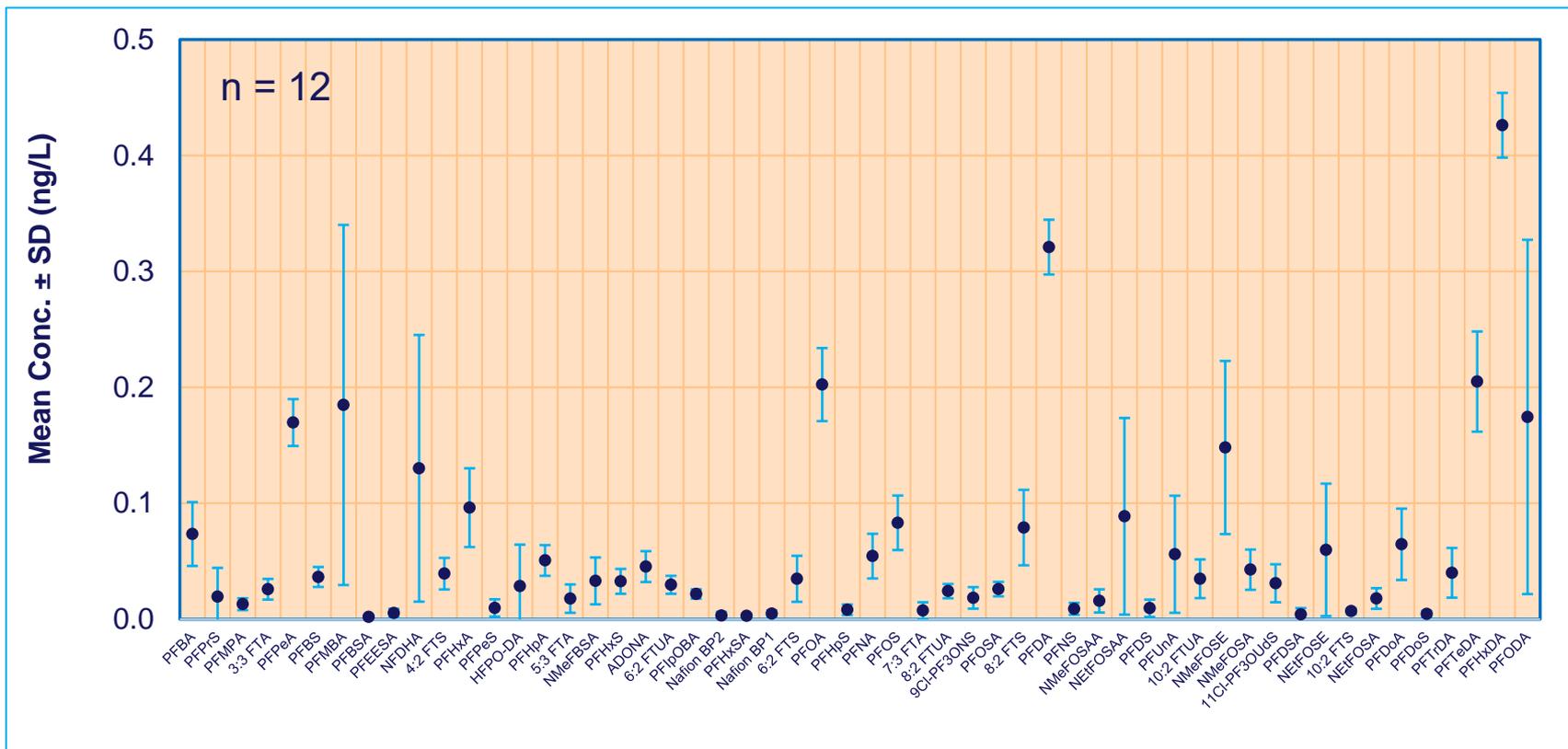


<p>Perfluoro-1-butane sulfonamide (PFBSA)</p>	<p>N-Methylperfluoro-1-butane sulfonamide (NMeFBSA)</p>
	
<p>N-methylperfluoro-1-octanesulfonamide (NMeFOSA)</p>	<p>N-ethylperfluoro-1-octanesulfonamide (NEtFOSA)</p>
	
<p>N-methylperfluorooctane sulfonamidoethanol (NMeFOSE)</p>	<p>N-ethylperfluorooctane sulfonamidoethanol (NEtFOSE)</p>
	

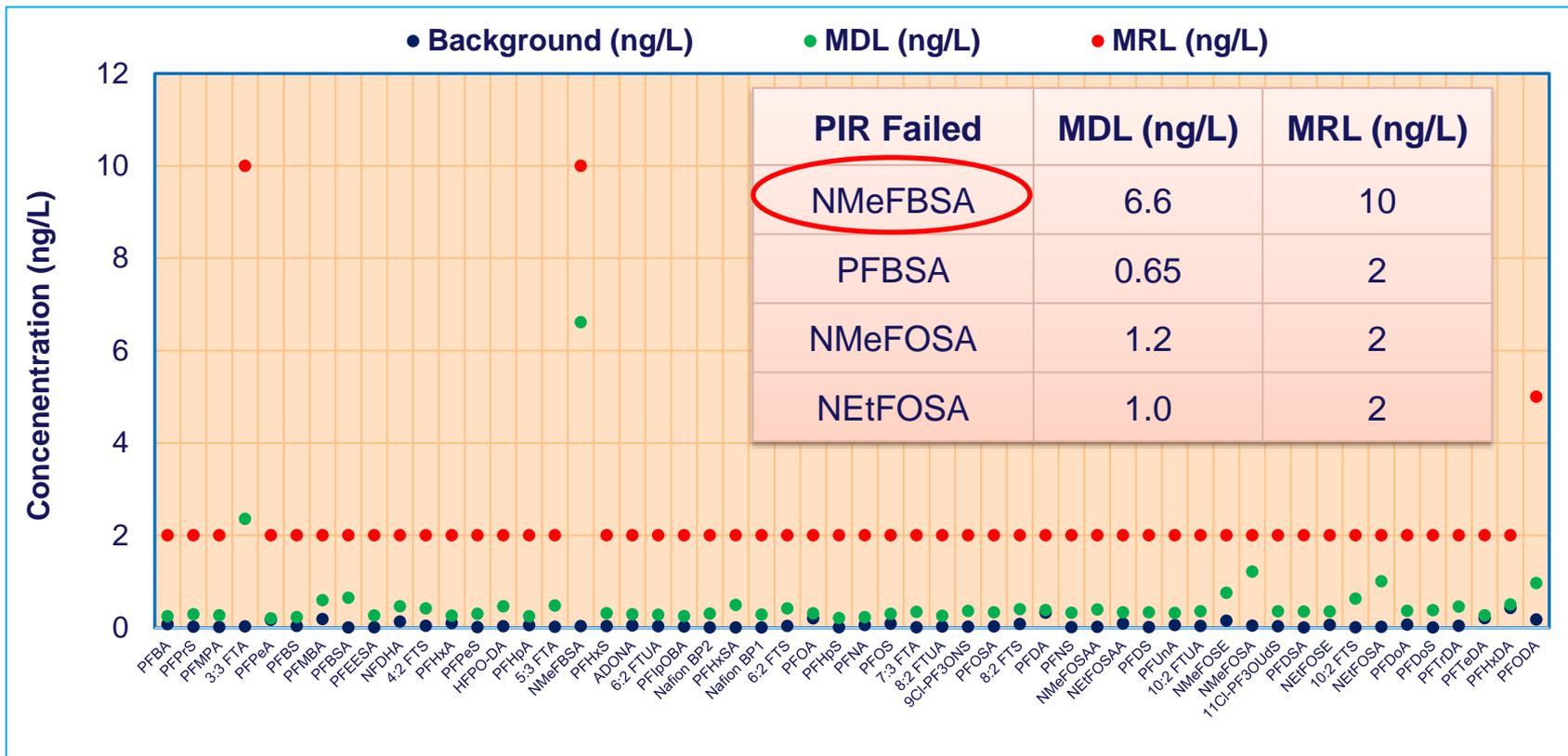


Modified EPA 533 Background Levels

Autotrace 280 SPE

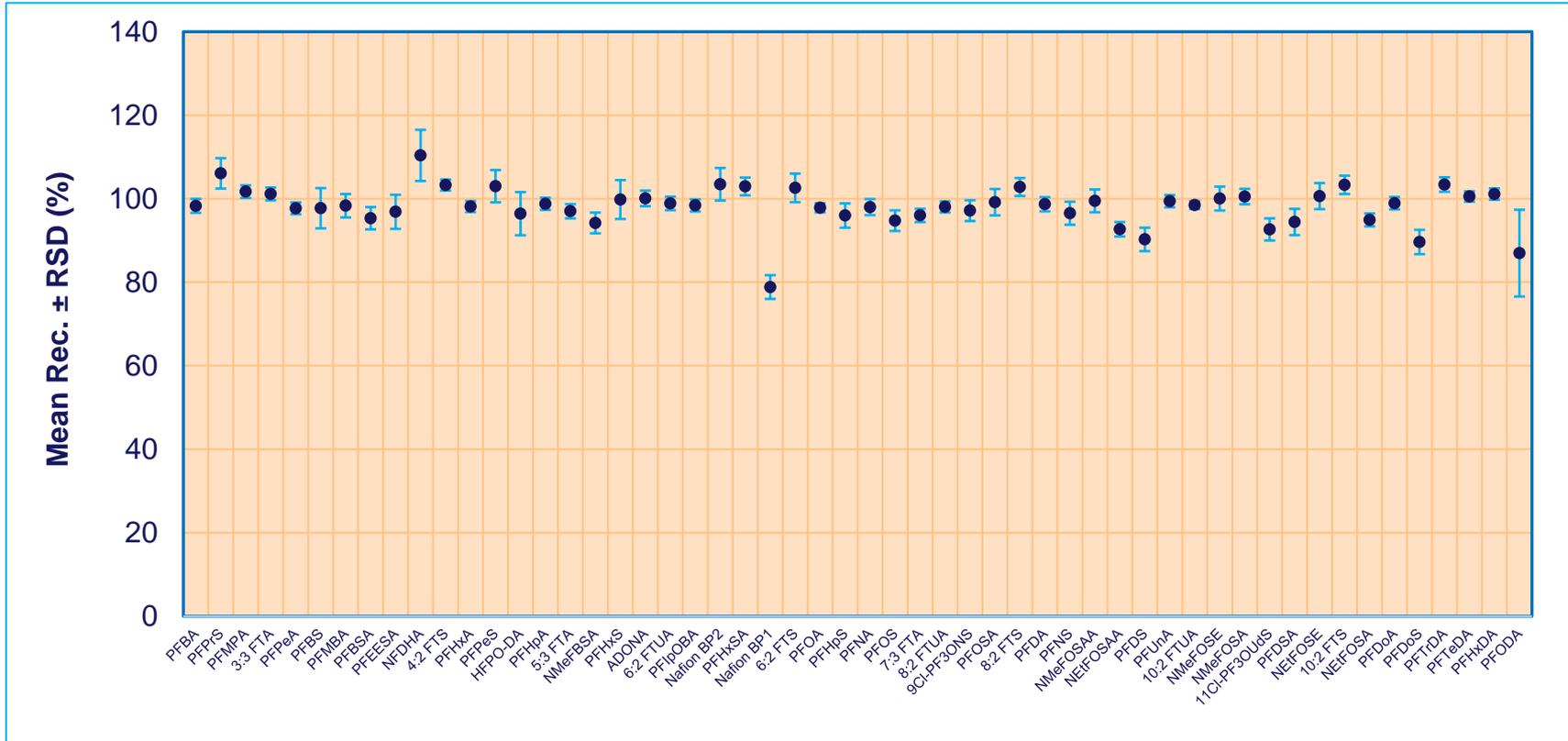


Modified EPA 533 MRLs & MDLs



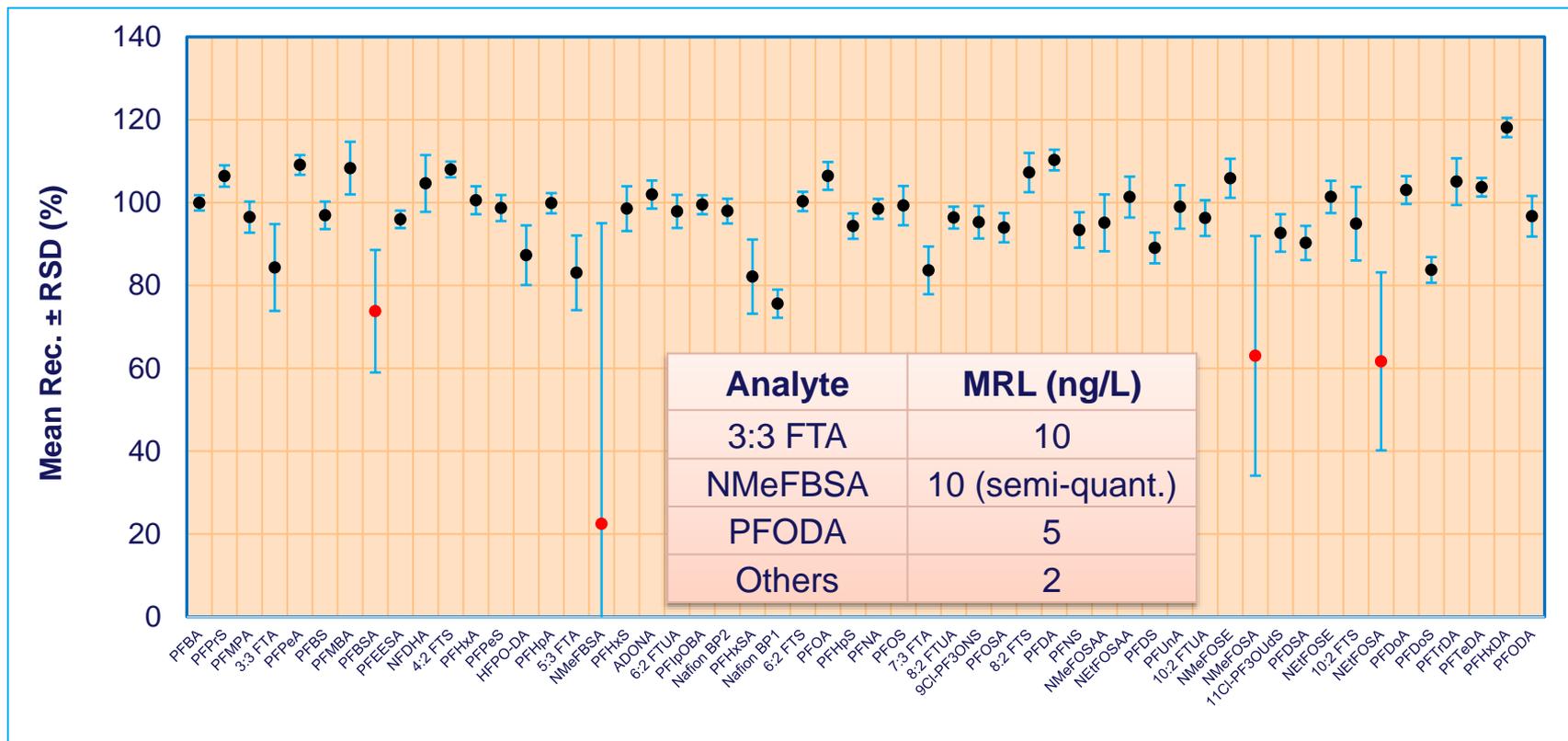
Modified EPA 533 Accuracy & Precision

Recoveries \pm RSDs at Mid Calibration Levels

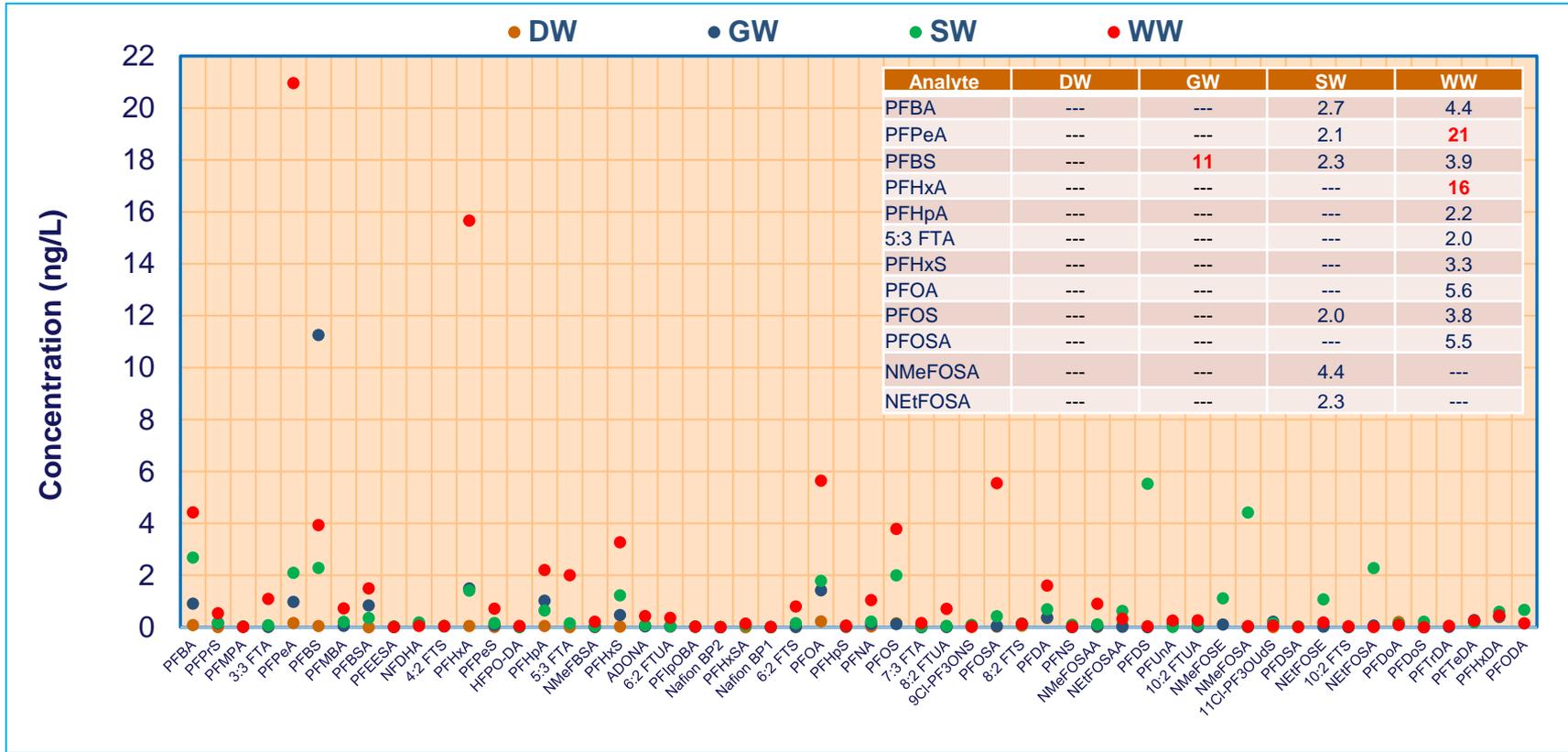


Modified EPA 533 Accuracy & Precision

Recoveries \pm RSDs at MRLs



Modified EPA 533 Sample Results

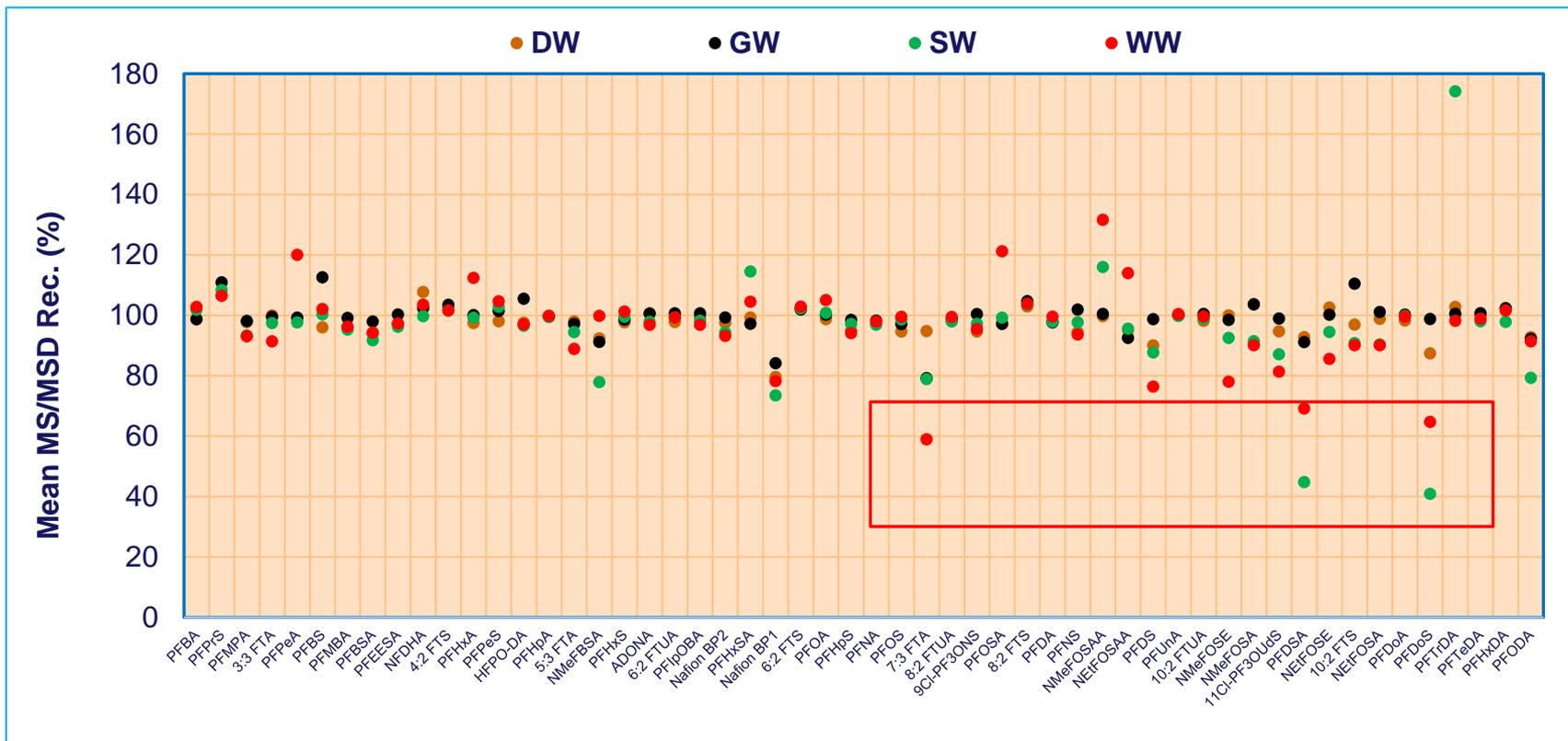


Modified EPA 533 Sample Results

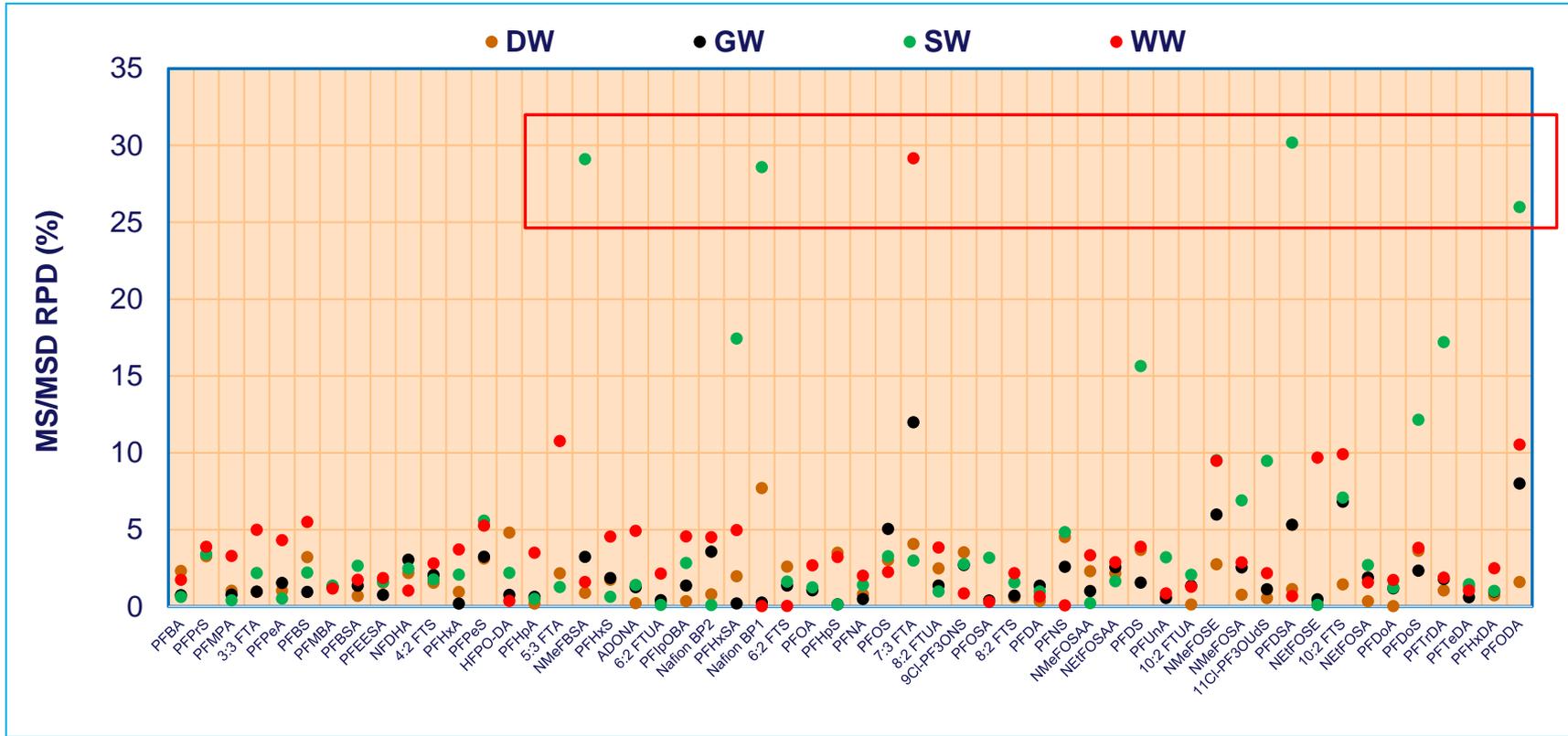


Analyte	DW	GW	SW	WW
PFBA	---	---	2.7	4.4
PFPeA	---	---	2.1	21
PFBS	---	11	2.3	3.9
PFHxA	---	---	---	16
PFHpA	---	---	---	2.2
5:3 FTA	---	---	---	2.0
PFHxS	---	---	---	3.3
PFOA	---	---	---	5.6
PFOS	---	---	2.0	3.8
PFOSA	---	---	---	5.5
NMeFOSA	---	---	4.4	---
NEtFOSA	---	---	2.3	---

Modified EPA 533 MS/MSD Recoveries



Modified EPA 533 MS/MSD RPD



Conclusions



- Presented a sensitive and robust single SPE-LC/MS/MS method for analysis of 54 PFAS in drinking water and source water.
 - All 29 EPA 537.1 and 533 PFAS plus 25 additional PFAS
- Achieved satisfactory MRLs.
 - All 51 PFAS = 2 ng/L, 3:3 FTA = 10 ng/L, NMeFBSA = 10 ng/L (semi-quantitative), PFODA = 5 ng/L.
- Met EPA 537.1 and 533 QC acceptance criteria with exceptions,
 - 6 additional IDAs and MRL confirmation of 4 additional PFAS
- The modified EPA 533 can be used for potable and pristine non-potable water analyses.



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