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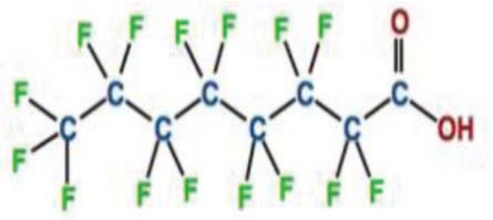
Validation of Automated SPE EPA Methods 537.1 and 533 for PFAS Analyses

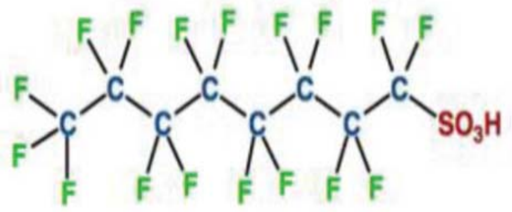
Yongtao Li and Joshua Whitaker
Eurofins Eaton Analytical, LLC

What are PFAS Compounds?

- A class of synthetic compounds with polar C-F covalent bonds, one of the strongest single bonds in organic chemistry.
- Most are chemically and thermally unreactive organic compounds produced for commercial and industrial uses over 60 years.
  - Resistant to degradation.
  - Environmentally persistent.
- Occur in soil, sludge, wastewater, environmental water, and drinking water.
- PFOA and PFOS are fully fluorinated and the most common PFAS.

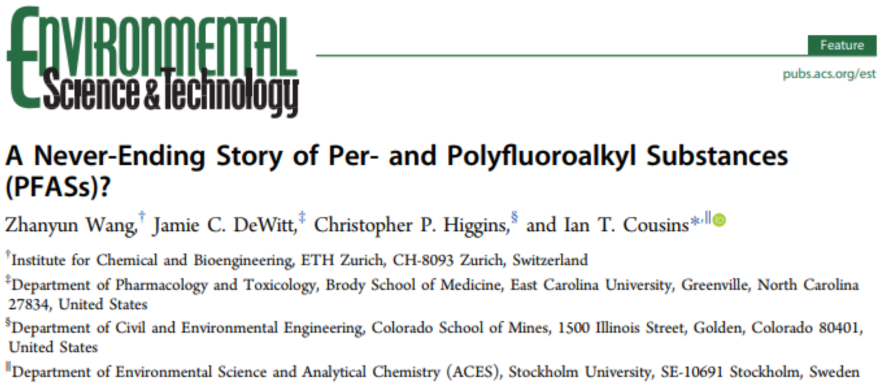


PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

PFAS is a Growing & Never-Ending Issue.



ENVIRONMENTAL Science & Technology

Feature

pubs.acs.org/est

A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?

Zhanyun Wang,[†] Jamie C. DeWitt,[‡] Christopher P. Higgins,[§] and Ian T. Cousins*[,∥]

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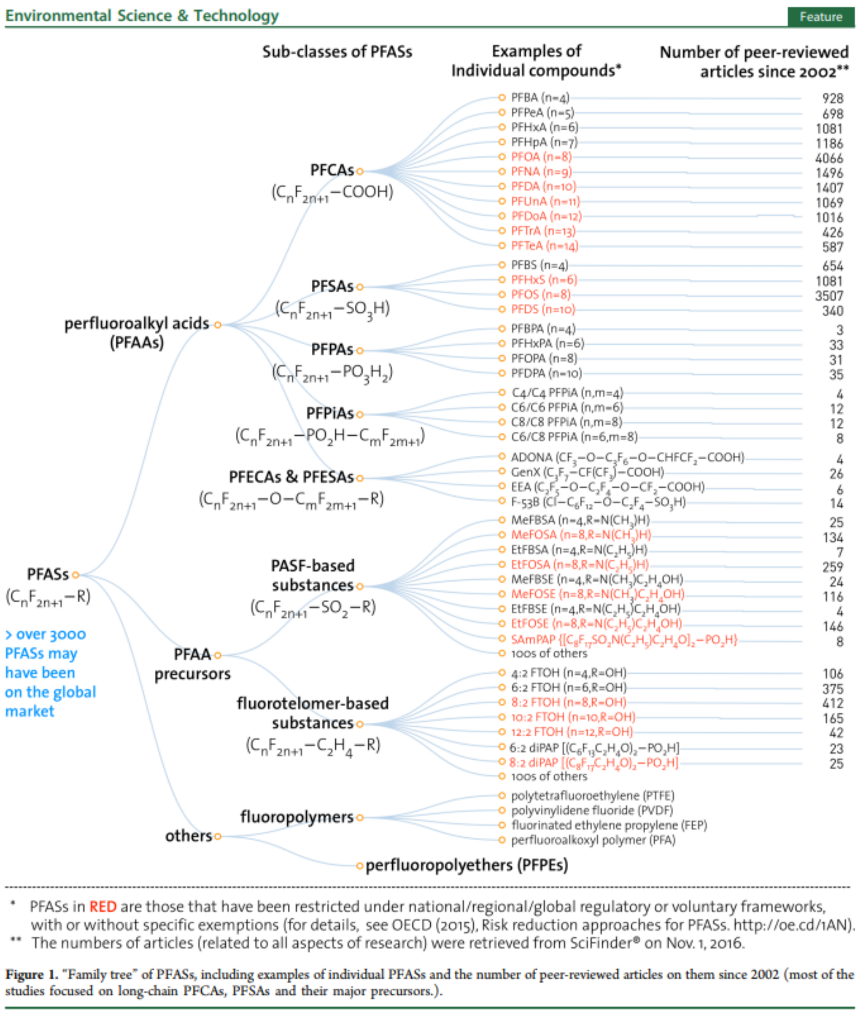
Wang et al. (2017). ES&T, 51(5), 2508-2518.

More than 3000 PFAS are or have been on the global market.



Environmental Science & Technology

Feature

* 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.).

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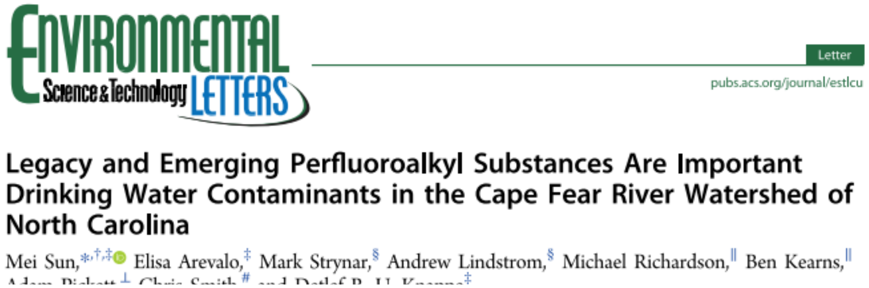
The More We Look, The More PFAS We Find.

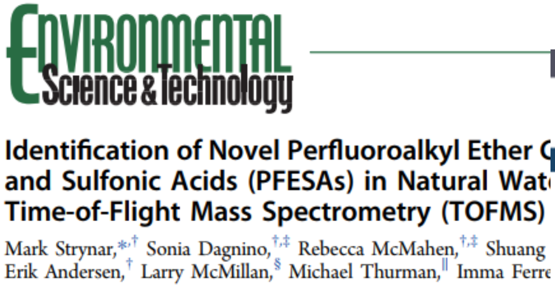


Letter

pubs.acs.org/journal/estlcu

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

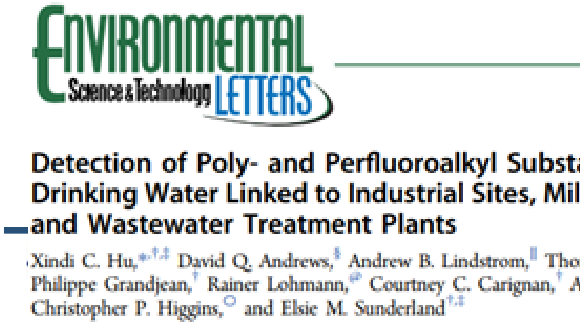
Mei Sun,[*,†,‡] Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,[||] Ben Kearns,[||] Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]



Article

Identification of Novel Perfluoroalkyl Ether and Sulfonic Acids (PFESAs) in Natural Wat Time-of-Flight Mass Spectrometry (TOFMS)

Mark Strynar,[*,†] Sonia Dagnino,[†,‡] Rebecca McMahen,[†,‡] Shuang Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,[||] Imma Ferre



Detection of Poly- and Perfluoroalkyl Subst Drinking Water Linked to Industrial Sites, Mil and Wastewater Treatment Plants

Xindi C. Hu,[*,†,‡] David Q. Andrews,[§] Andrew B. Lindstrom,[||] Tho Philippe Grandjean,[†] Rainer Lohmann,[#] Courtney C. Carignan,[†] A Christopher P. Higgins,[○] and Elsie M. Sunderland[†,‡]

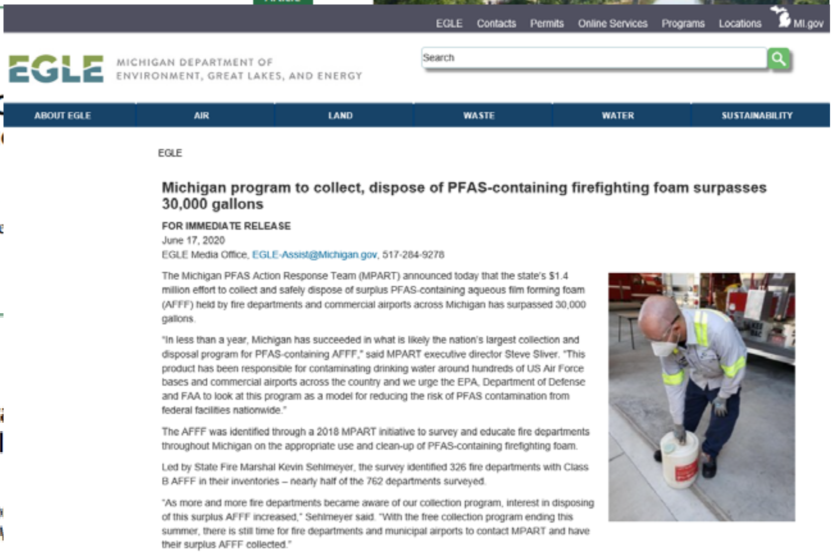
@NCCapitol

Timeline: Tracking GenX contamination in NC

Tags: Department of Environmental Quality, GenX

Posted August 17, 2017
Updated April 9

32 Reactions



EGLE

Michigan program to collect, dispose of PFAS-containing firefighting foam surpasses 30,000 gallons

FOR IMMEDIATE RELEASE
June 17, 2020
EGLE Media Office, EGLE-Assist@Michigan.gov, 517-284-9278

The Michigan PFAS Action Response Team (MPART) announced today that the state's $1.4 million effort to collect and safely dispose of surplus PFAS-containing aqueous film forming foam (AFFF) held by fire departments and commercial airports across Michigan has surpassed 30,000 gallons.

"In less than a year, Michigan has succeeded in what is likely the nation's largest collection and disposal program for PFAS-containing AFFF," said MPART executive director Steve Sliver. "This product has been responsible for contaminating drinking water around hundreds of US Air Force bases and commercial airports across the country and we urge the EPA, Department of Defense and FAA to look at this program as a model for reducing the risk of PFAS contamination from federal facilities nationwide."

The AFFF was identified through a 2018 MPART initiative to survey and educate fire departments throughout Michigan on the appropriate use and clean-up of PFAS-containing firefighting foam.

Led by State Fire Marshal Kevin Sehlmeyer, the survey identified 326 fire departments with Class B AFFF in their inventories – nearly half of the 762 departments surveyed.

"As more and more fire departments became aware of our collection program, interest in disposing of this surplus AFFF increased," Sehlmeyer said. "With the free collection program ending this summer, there is still time for fire departments and municipal airports to contact MPART and have their surplus AFFF collected."

In this 2004 file photo, workmen scurry over a H-53 Super Stallion at the Naval Air Depot facility at Cherry Point Marine Corps Air Station. Chuck Liddy - clidy@newsobserver.com

LOCAL

Contaminated drinking water found outside an NC military base. It could be just the start.

BY BRIAN MURPHY
bmurphy@mcclatchydc.com

March 15, 2018 06:01 PM

WASHINGTON — The tiny Eastern North Carolina community of Atlantic has joined a growing list of military areas across the country affected by contaminated drinking water.

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, 2013-2015

State Lists & Guidance Levels, 2009/2015 -

UCMR5?

MCLs?

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Do Reporting Limits Matter?

PFAS	UCMR3 MRL (ng/L)	UCMR3 NCOD % of Results ≥ UCMR3 MRL (~ 4920 PWS)	CA SWB % of Results ≥ 5 ng/L (> 600 PWS Sites)	CA SWB % of Results ≥ 2 ng/L (> 600 PWS Sites)
PFHxA	NA	NA	18.8	30.2
PFHpA	10	1.7	8.2	19.5
PFOA	20	2.4	25.8	35.6
PFNA	20	0.3	1.9	10.2
PFBS	90	0.2	20.9	31.6
PFHxS	30	1.1	26.9	41.0
PFOS	40	1.9	33.6	41.7

NCOD = National Contaminant Occurrence Database
SWB = State Water Board

PFAS Regulation Updates

State	Action	Level (ng/L)	Published Date	Promulgation
USEPA	HA	PFOA +/or PFOS = 70	05/2006	
CA	NL	PFOA = 5.1, PFOS = 6.5	08/2019	08/2019
	RL	PFOA = 10, PFOS = 40	02/2020	02/2020
NJ	MCL	PFNA = 13, PFOA = 14, PFOS = 13	09/2018	01/2019
NH	MCL	PFOA = 12, PFNA = 11, PFOS = 15, PFHxS = 18	09/2019	09/2019
VT	MCL	PFHpA + PFOA + PFNA + PFHxS + PFOS = 20	05/2019	02/2020
MA	Proposed MCL	PFHpA + PFOA + PFNA + PFDA + PFHxS + PFOS = 20	12/2019	Spring, 2020
NY	Proposed MCL	PFOA = 10, PFOS = 10	12/2018	Spring, 2020
PA	MCL Development	PFHpA, PFOA, PFNA, PFBS, PFHxS, and PFOS	09/2018	02/2019
WI	MCL Development	PFOA + PFOS = 20	08/2019	
MI	Proposed HBV	PFHxA = 400,000, PFOA = 8, PFNA = 6, PFBS = 420, PFHxS = 51, PFOS = 16, GenX = 370	07/2019	Spring, 2020

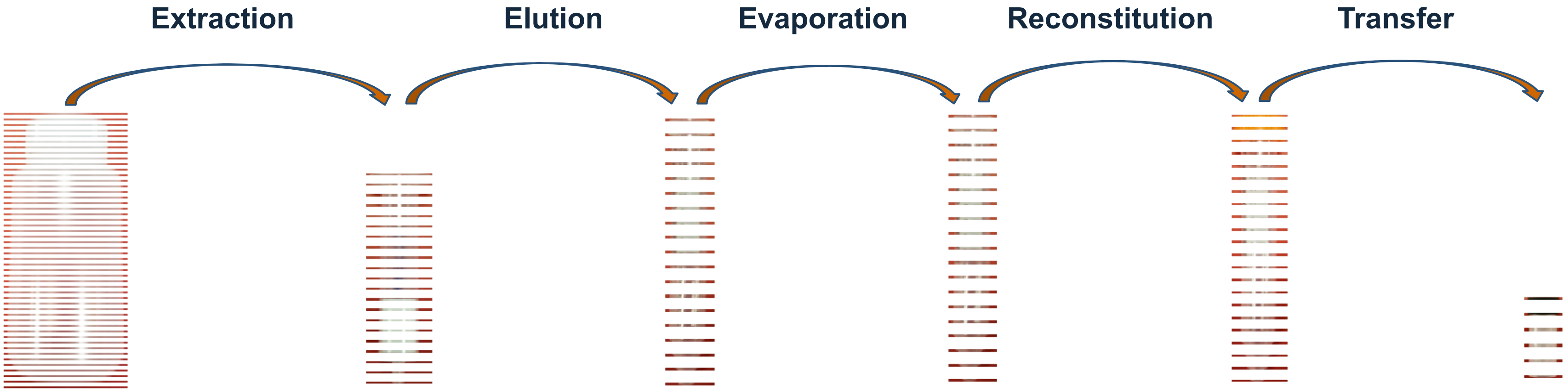
PFAS Regulation Updates (cont'd)

State	Action	Level (ng/L)	Published Date	Promulgation
OH	AL Development	PFOA +/or PFOS = 70, PFNA = 21, PFBS = 140,000, PFHxS = 140, GenX = 700	12/2019	12/2019
NC	HG	PFOA +/or PFOS = 70, GenX = 140	07/2017	07/2017
RI	Interim SL	PFHpA + PFOA + PFNA + PFHxS + PFOS = 20	03/2019	
OR	Proposed TL	PFHpA = 10,000, PFOA = 500, PFNA = 40, PFOS = 20,000, PFOSA = 0.7	12/2009	
ME		Governor's Executive Order, PFAS Task Force	03/2019	03/2019
CO		Developed statewide action plans	09/2019	
AL		Developed statewide action plan		
CT		Developed statewide action plan including future recommendation of MCLs.	11/2019	11/2019
WA		Revised the action plan to establish ALs	05/2019	
MN	Recommended HBV	PFBA = 7000, PFOA = 35, PFBS = 2,000, PFOS = 15	04/2017	

Which Method Should I Choose?

Method	SPE	Calibration	Analyte	Application
537/537.1	Polymeric single-phase sorbent (SDVB)	Internal Standards	14/18	Potable water
533	Polymeric mixed mode sorbent (WAX)	Isotope Dilution	25	Potable water
ASTM D7979-17	No extraction	External Standards	21	Water, wastewater, sludge, etc.
8327	No extraction	External Standards	24	Non-potable water
8328	?	Isotope Dilution	24	Non-potable water
In-house (537M)	Polymeric single-phase sorbent (WAX)	Isotope Dilution	36	Potable and non-potable water
In-house (L402)	Polymeric single-phase sorbent (WAX)	Isotope Dilution	39 + 6 NTA	Potable and non-potable water

537/537.1/533 SPE Procedures



Extraction

Elution

Evaporation

Reconstitution

Transfer

Method	Preservative	Sorbent	Calibration	PFAS	Application
537/537.1	Trizma, pH =7	Polymeric Single-Phase (SDVB)	Internal Standard	14/18	Potable Water
533	Ammonium Acetate, pH = 7	Polymeric Mixed Mode (WAX)	Isotope Dilution	25	Potable Water

Manual *vs.* AutoTrace SPE

Step	Manual SPE (40 FS)	AutoTrace (40 FS)
Preparation	**~ 3 hrs**	**~ 3 hrs**
Extraction & Elution	**~ 9 hrs**	**~ 2 hrs**
Evaporation & Reconstitution	**~ 3 hrs**	**~ 3 hrs**
Spiking IS & Transfer	**~ 1 hrs**	**~ 1 hrs**
Total	**~ 16 hrs**	**~ 9 hrs**

1) Reduce hand touch time.
2) Reduce human errors.
3) Reduce blank levels.
4) Avoid massive lab contamination.
5) Improve accuracy and precision.

EPA 537/537.1/533 PFAS

PFAS	537	537.1	533
Perfluoroalkyl Carboxylic Acids	9	9	9
Perfluoroalkyl Sulfonic Acids	3	3	5
Perfluoroalkyl Sulfonamidoacetic Acids	2	2	0
Poly- & Perfluoroalkyl Ether Carboxylic Acids	0	4	7
Fluorotelomer Sulfonic Acids	0	0	3
Poly- & Perfluoroalkyl Ether Sulfonic Acids	0	0	1
Total	14	18	25

29 EPA 537.1 & 533 PFAS: 2-250 ng/L & 2-500 ng/L

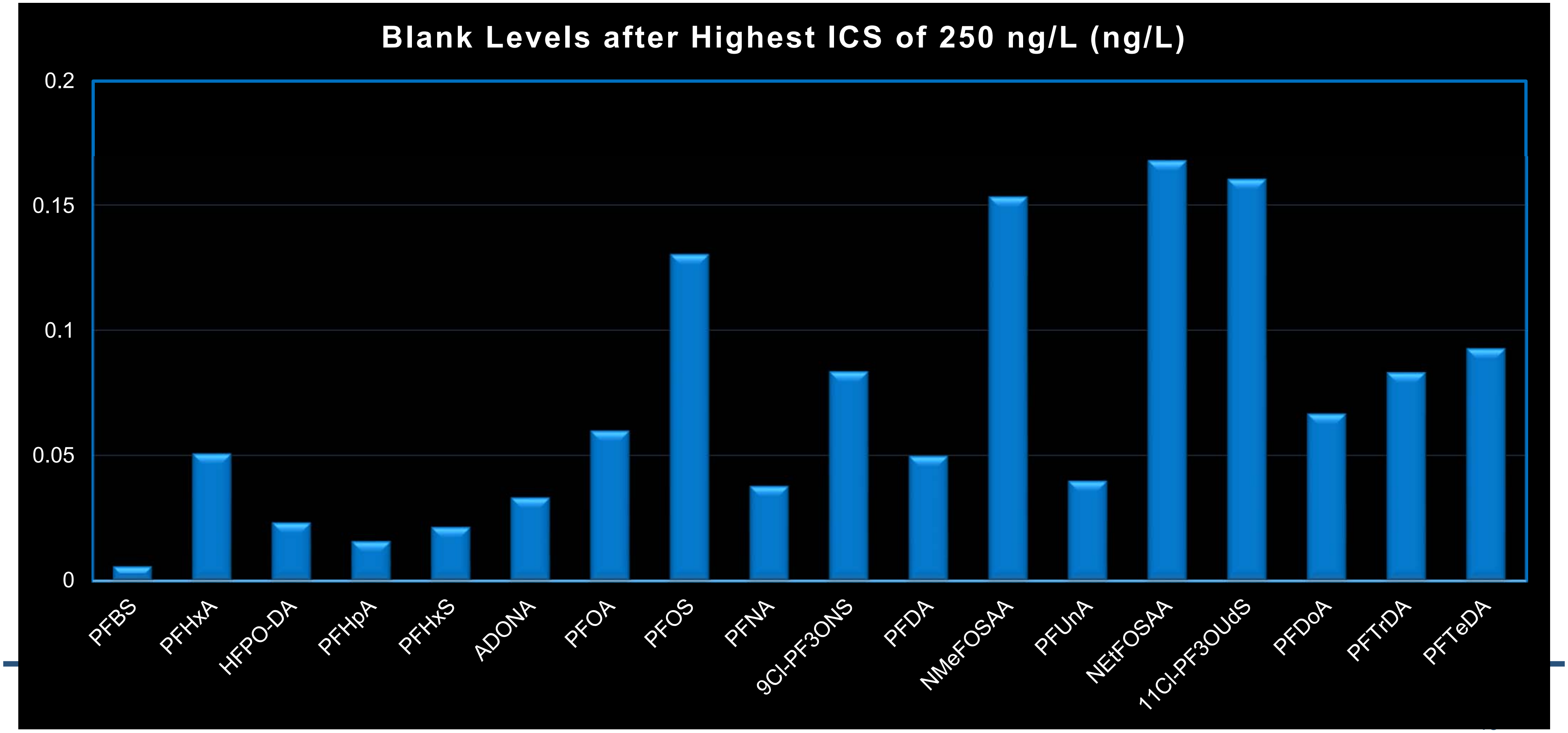
PFAS	C No.	537.1	533	PFAS	C No.	537.1	533
PFBA	C4		X	PFOS	C8	X	X
PFPeA	C5		X	HFPO-DA	C6	X	X
PFHxA	C6	X	X	ADONA	C7	X	X
PFHpA	C7	X	X	9Cl-PF3ONS	C9	X	X
PFOA	C8	X	X	11Cl-PF3OUdS	C11	X	X
PFNA	C9	X	X	PFMBA	C5		X
PFDA	C10	X	X	PFMPA	C4		X
PFUnA	C11	X	X	NFDHA	C5		X
PFDoA	C12	X	X	NMeFOSAA	C10	X	
PFTrDA	C13	X		NEtFOSAA	C11	X	
PFTeDA	C14	X		4-2-FTS	C6		X
PFBS	C4	X	X	6-2-FTS	C8		X
PFPeS	C5		X	8-2-FTS	C10		X
PFHxS	C6	X	X	PFEESA	C4		X
PFHpS	C7		X				

EPA 537.1 Linear Calibration: IS & SS

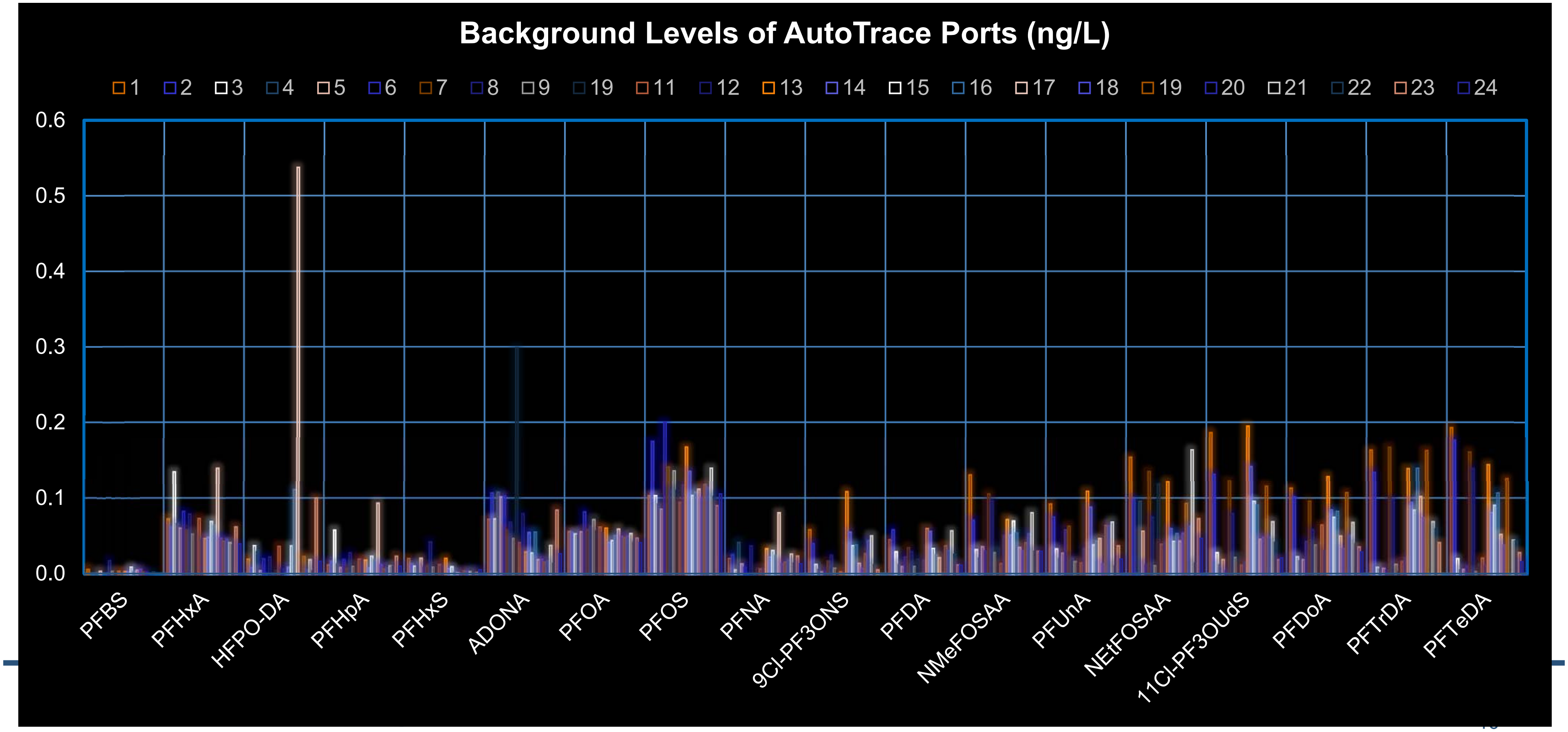
IS	Conc. (ng/L)	SS	Conc. (ng/L)
IS-PFOA-$^{13}C_2$	40	SS-PFHxA-$^{13}C_2$	40
IS-PFOS-$^{13}C_4$	120	SS-PFDA-$^{13}C_2$	40
IS-NMeFOSAA-d_3	160	SS-NEtFOSAA-d_5	160
		SS-HFPO-DA-$^{13}C_3$	40

EPA 537.1 Instrumental Carryover





EPA 537.1 AutoTrace Background Levels



Background Levels of AutoTrace Ports (ng/L)

EPA 537.1 Sensitivity

Target = 2.0 ng/L, MDL < 0.4 ng/L, MRL = 2.0 ng/L

PFAS	Lower & Upper PIR (%)	MDL (ng/L)	PFAS	Lower & Upper PIR (%)	MDL (ng/L)
PFBS	87 - 97	0.17	9Cl-PF3ONS	83 - 99	0.20
PFHxA	90 - 103	0.15	PFDA	88 -103	0.20
HFPO-DA	84 - 100	0.14	NMeFOSAA	82 - 95	0.15
PFHpA	89 - 101	0.15	PFUnA	89 - 96	0.24
PFHxS	86 - 101	0.21	NEtFOSAA	82 - 99	0.28
ADONA	88 - 105	0.18	11Cl-PF3OUdS	80 - 95	0.22
PFOA	82 - 115	0.31	PFDoA	85 - 96	0.25
PFOS	90 - 103	0.13	PFTrDA	85 - 94	0.28
PFNA	94 - 104	0.18	PFTeDA	85 - 97	0.31

EPA 537.1 Accuracy and Precision

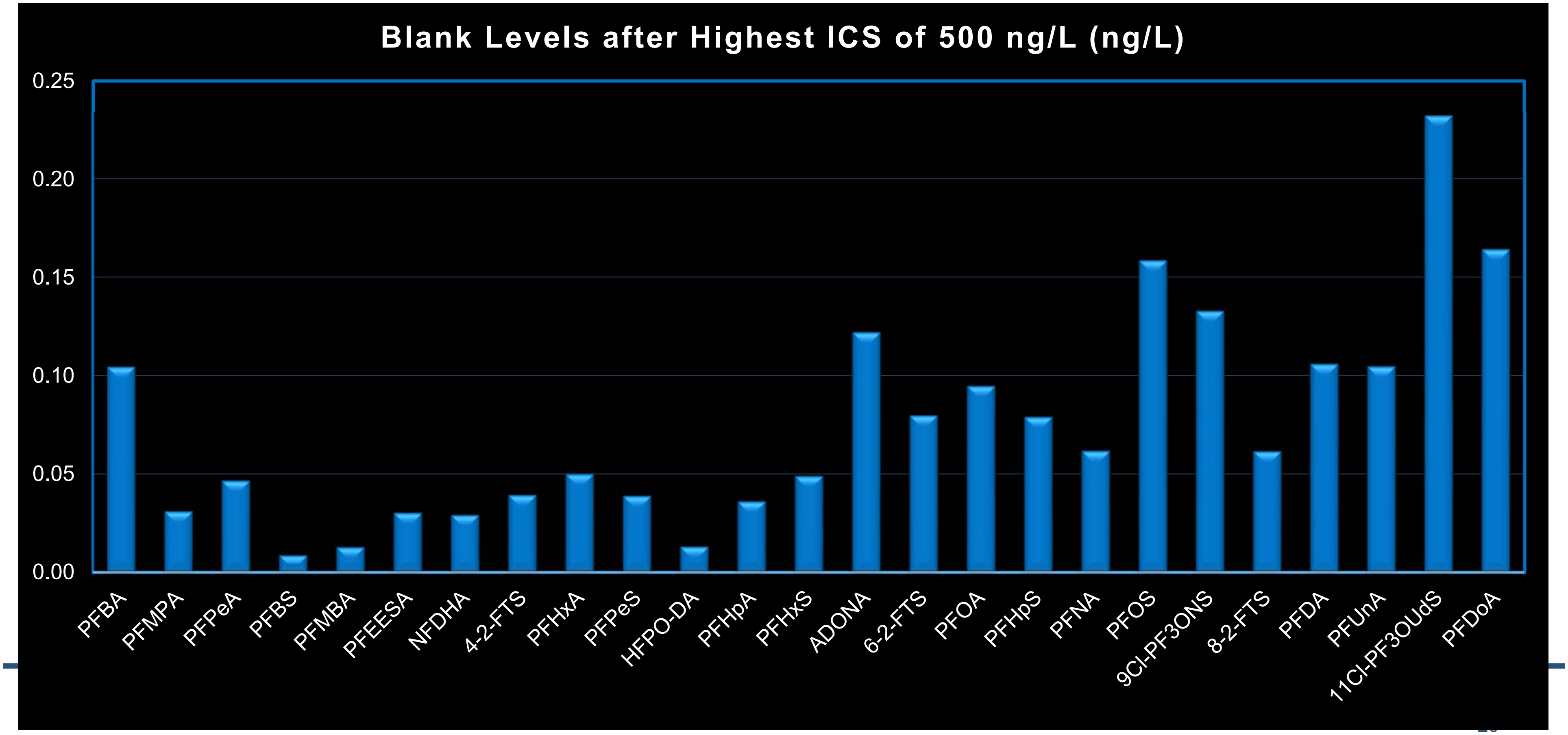
Target = 100 ng/L, Mean Recovery = 89-105%, RSD = 0.3-3.2%

PFAS	Mean Rec (%)	RSD (%)	PFAS	Mean Rec (%)	RSD (%)
PFBS	98 - 104	0.3 - 1.5	9Cl-PF3ONS	96 - 101	1.0 - 1.9
PFHxA	95 - 101	0.1 - 2.1	PFDA	96 - 101	1.1 - 3.2
HFPO-DA	91 - 98	1.6 - 2.9	NMeFOSAA	93 - 96	1.8 - 2.1
PFHpA	94 - 103	0.3 - 1.7	PFUnA	95 - 98	1.3 - 1.8
PFHxS	99 - 105	0.6 - 1.3	NEtFOSAA	92 - 96	1.3 - 2.4
ADONA	94 - 100	0.3 - 2.4	11Cl-PF3OUdS	91 - 95	0.9 - 1.5
PFOA	98 - 102	0.8 - 1.3	PFDoA	90 - 96	1.4 - 2.1
PFOS	98 - 99	0.6 - 1.3	PFTrDA	89 - 96	1.6 - 2.1
PFNA	97 - 102	0.7 - 1.1	PFTeDA	89 - 97	1.8 - 3.2

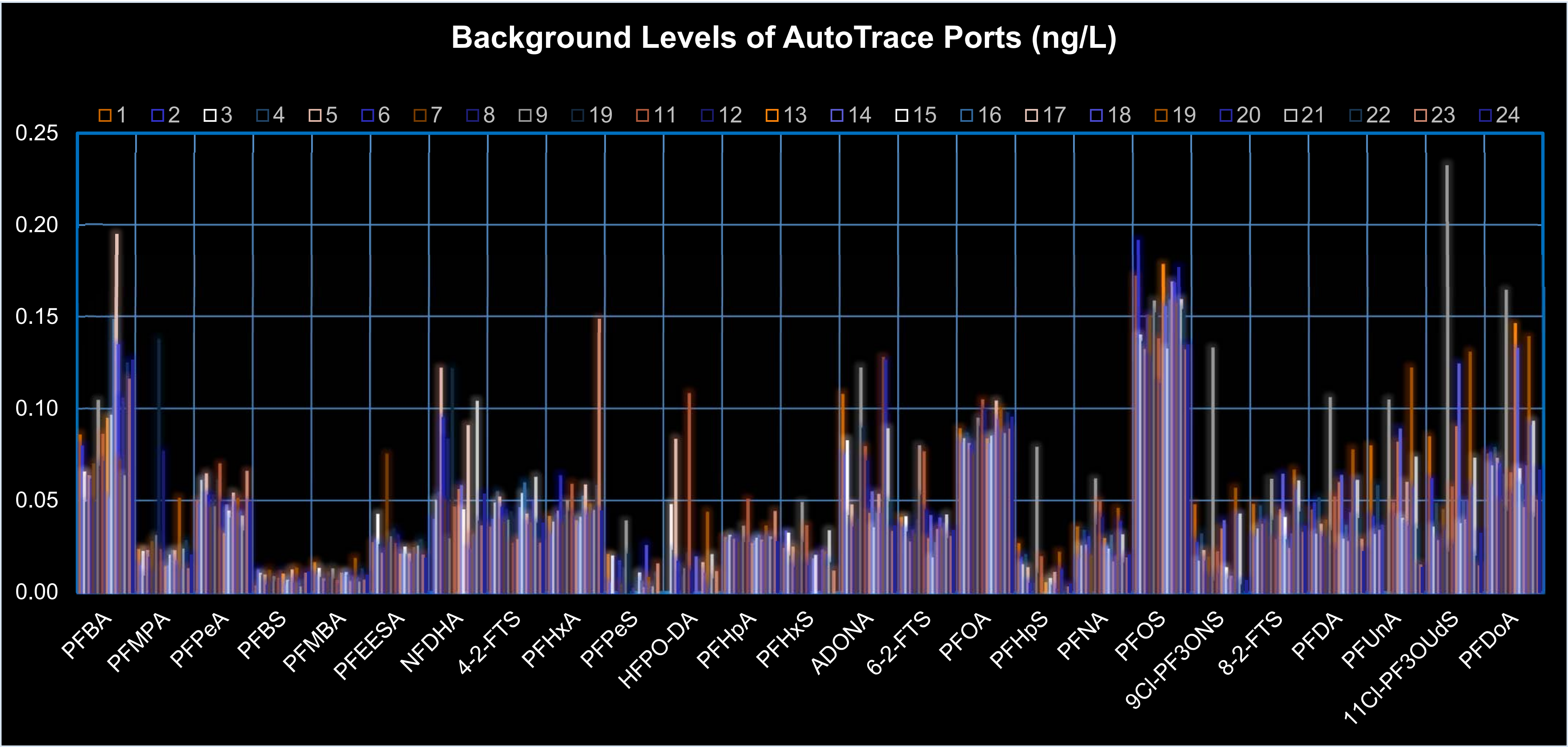
EPA 533 Linear Calibration: IPS & IDA

IPS/IDA	Conc. (ng/L)	IPS/IDA	Conc. (ng/L)
IPS-PFBA-$^{13}C_3$	40	IDA-PFDA-$^{13}C_6$	40
IPS-PFOA-$^{13}C_2$	40	IDA-PFUnA-$^{13}C_7$	40
IPS-PFOS-$^{13}C_4$	120	IDA-PFDoA-$^{13}C_2$	40
		IDA-HFPO-DA-$^{13}C_3$	40
IDA-PFBA-$^{13}C_4$	40	IDA-PFBS-$^{13}C_3$	40
IDA-PFPeA-$^{13}C_5$	40	IDA-PFHxS-$^{13}C_3$	40
IDA-PFHxA-$^{13}C_5$	40	IDA-PFOS-$^{13}C_8$	40
IDA-PFHpA-$^{13}C_4$	40	IDA-4:2-FTS-$^{13}C_2$	160
IDA-PFOA-$^{13}C_8$	40	IDA-6:2-FTS-$^{13}C_2$	160
IDA-PFNA-$^{13}C_9$	40	IDA-8:2-FTS-$^{13}C_2$	160

EPA 533 Instrumental Carryover



EPA 533 AutoTrace Background Levels



Background Levels of AutoTrace Ports (ng/L)

EPA 533 Sensitivity

Target = 2.0 ng/L, MDL < 0.5 ng/L, MRL = 2.0 ng/L

PFAS	Lower & Upper PIR (%)	MDL (ng/L)	PFAS	Lower & Upper PIR (%)	MDL (ng/L)
PFBA	85 - 102	0.11	ADONA	84 - 98	0.094
PFMPA	75 - 101	0.17	6-2-FTS	95 - 107	0.087
PFPeA	84 - 98	0.12	PFOA	90 - 97	0.075
PFBS	78 - 94	0.14	PFHpS	84 - 100	0.14
PFMBA	87 - 104	0.15	PFNA	89 - 96	0.073
PFEESA	89 - 98	0.16	PFOS	88 - 105	0.11
NFDHA	60 - 105	0.29	9Cl-PF3ONS	80 - 89	0.059
4-2-FTS	96 - 108	0.13	8-2-FTS	95 - 108	0.083
PFHxA	84 - 97	0.10	PFDA	87 - 95	0.13
PFPeS	96 - 109	0.12	PFUnA	84 - 96	0.095
HFPO-DA	57 - 119	0.46	11Cl-PF3OUdS	67 - 113	0.32
PFHpA	86 - 96	0.082	PFDoA	87 - 98	0.11
PFHxS	80 - 99	0.12			

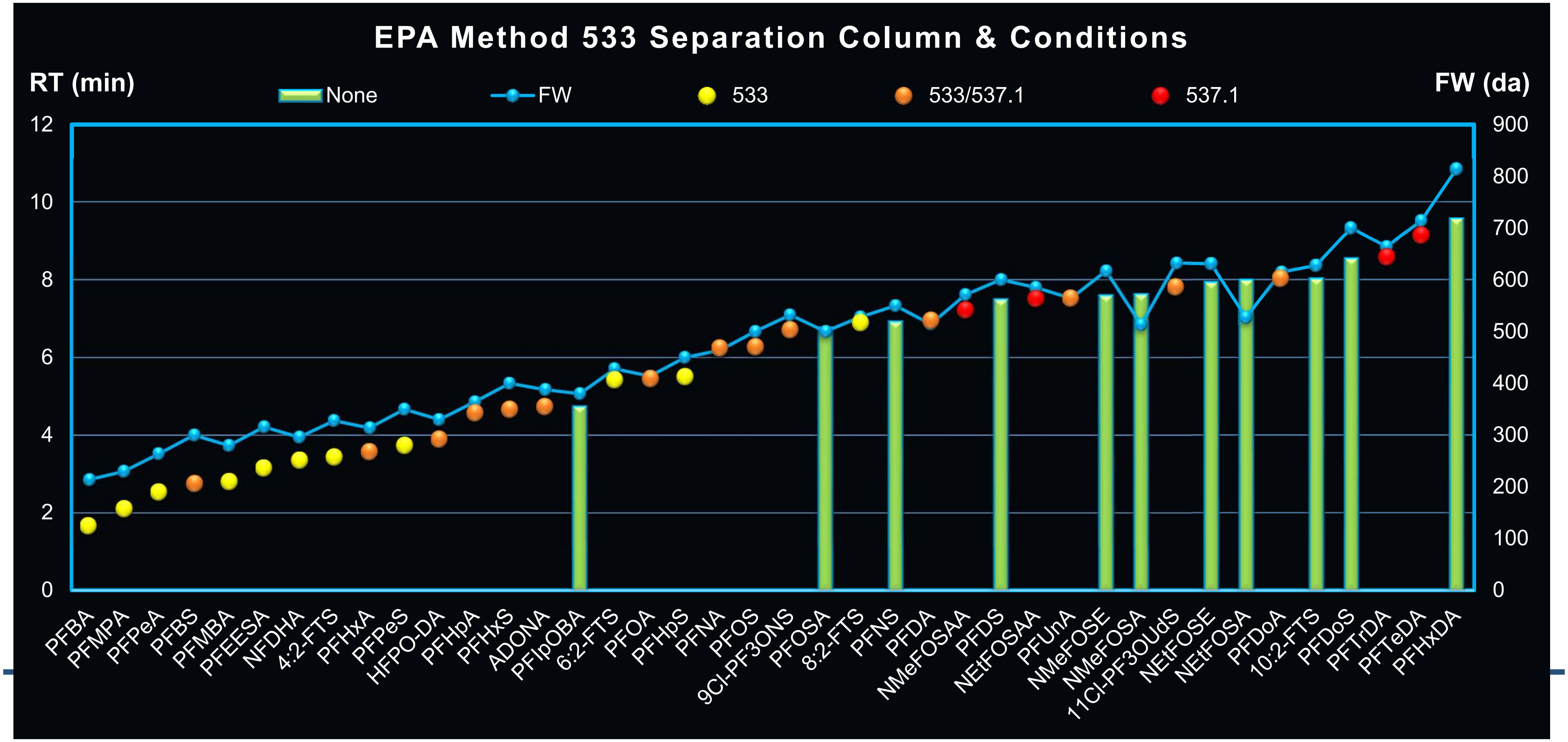
EPA 533 Accuracy and Precision

Target = 100 ng/L, Mean Recovery = 91-106%, RSD = 0.6-6.1%

PFAS	Mean Rec (%)	RSD (%)	PFAS	Mean Rec (%)	RSD (%)
PFBA	97 - 102	1.2 - 2.7	ADONA	95 - 101	1.1 - 2.3
PFMPA	93 - 101	2.3 - 2.5	6-2-FTS	104 - 104	1.0 - 2.5
PFPeA	97 - 101	1.2 - 2.0	PFOA	96 - 102	1.3 - 2.3
PFBS	93 - 101	1.8- 2.2	PFHpS	99 - 102	1.4
PFMBA	101 - 103	1.1 - 2.4	PFNA	98 - 102	1.2 - 2.0
PFEESA	98 - 101	2.3 - 2.8	PFOS	97 - 100	0.9 - 2.4
NFDHA	93 - 101	3.8 - 6.1	9Cl-PF3ONS	91 - 99	1.3 - 2.0
4-2-FTS	103 - 105	1.8 - 3.4	8-2-FTS	105 - 106	0.9 - 2.2
PFHxA	96 - 102	1.0 - 2.5	PFDA	97 - 102	0.6 - 2.7
PFPeS	106 - 107	2.2 - 2.4	PFUnA	95 - 101	0.6 - 2.1
HFPO-DA	100 - 104	3.8 - 4.3	11Cl-PF3OUdS	97 - 101	2.0 - 2.5
PFHpA	96 - 101	1.1 - 2.1	PFDoA	96 - 101	0.9 - 2.5
PFHxS	96 - 101	1.4 - 2.1			

Applications & Challenges: 29 + 11 PFAS

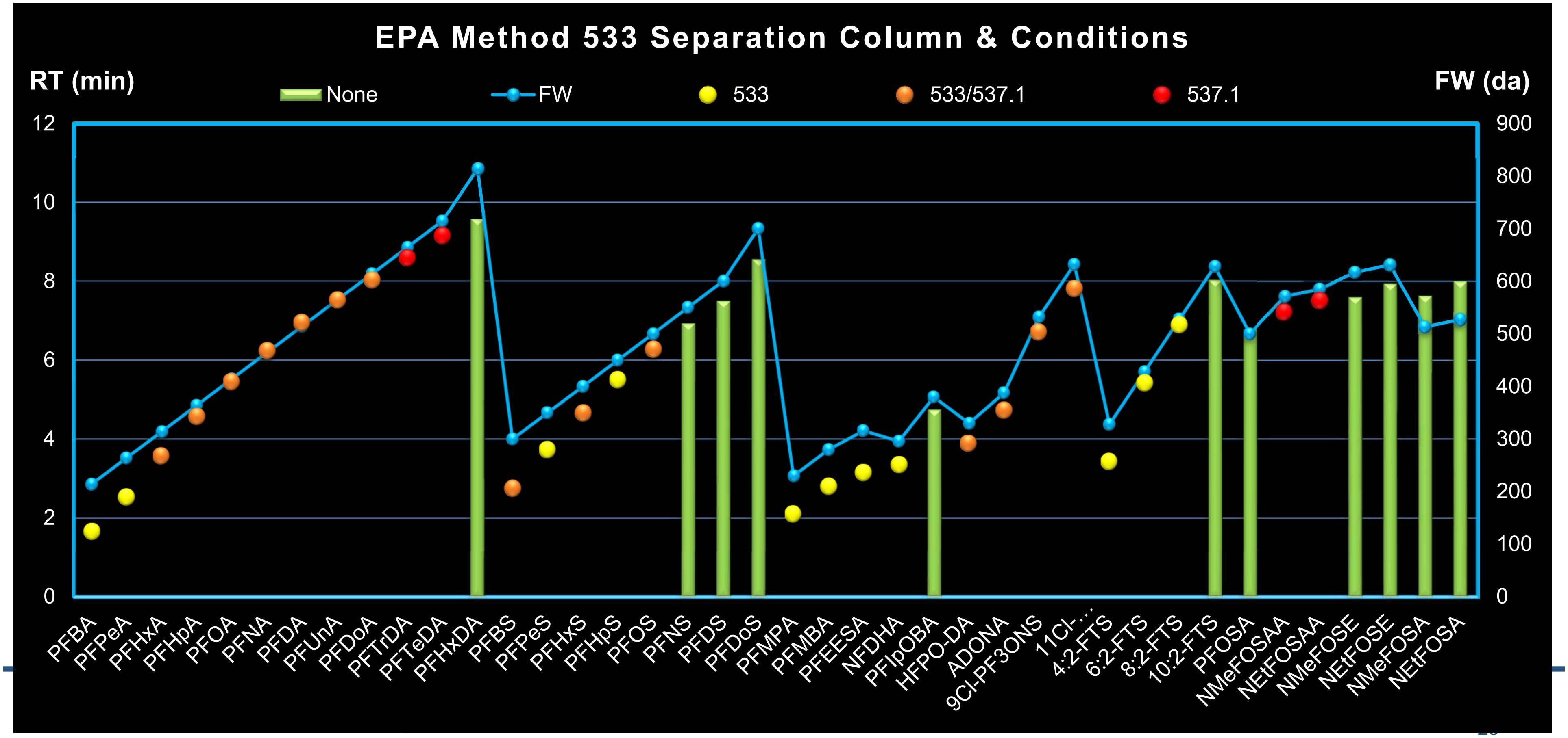
RP SPE *vs.* WAX SPE



EPA Method 533 Separation Column & Conditions

Applications & Challenges: 29 + 11 PFAS

RP SPE *vs.* WAX SPE



EPA Method 533 Separation Column & Conditions

Conclusions

- PFAS contaminants are a moving target.
  - There is no federal MCL established.
  - May need more national occurrence assessment at reasonably low reporting limits.
  - May be included in the next round UCMR5.
- States act on PFAS issues individually.
  - Some proposed regulatory levels may have changed.
  - Test for a reasonable list of compounds.
  - Choose appropriate MRLs.

Conclusions (cont'd)

- **UCMR3 PFAS list is a generally good indicator.**
  - A few other PFAS frequently detected may include:
    - PFBA, PFPeA, PFHxA, PFDA, and PFPeS
    - HFPO-DA/GenX.
- **Choose appropriate methods.**
  - EPA 537.1 meets the need for most drinking water regulations.
  - EPA 533 expands to several shorter chain PFAS.
  - Automated SPE can reduce operational costs, improve data quality, and minimize errors and contamination.
  - Direct injection LC/MS/MS may become a good choice.

Any Questions?

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