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Are You Ready for Monitoring PFAS in Your Waters? Mass Spectrometry Solutions for Answering Your Questions.

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Environmental Marketing Manager

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Today's presentation

- Shimadzu Corporation
- General information
- Instrumentation
- Results
- Questions

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Before I start…

Thank you!

- Mark Maitret, Alicia Neiner and Katie Kohoutek for generating data at American Water – Central Lab, and the personnel at the treatment plants for collecting the samples.
- Brahm Prakash and Jerry Byrne for generating data at Shimadzu.
- William Lipps at Eurofins for sharing extracts for QTOF analysis.

Shimadzu Corporation & Shimadzu Scientific Instruments

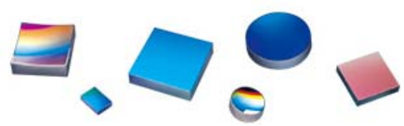
Established in March 1875
Consolidated Subsidiaries: 74
(23 in Japan, 51 overseas)

Analytical and Measuring Instruments

Medical Systems

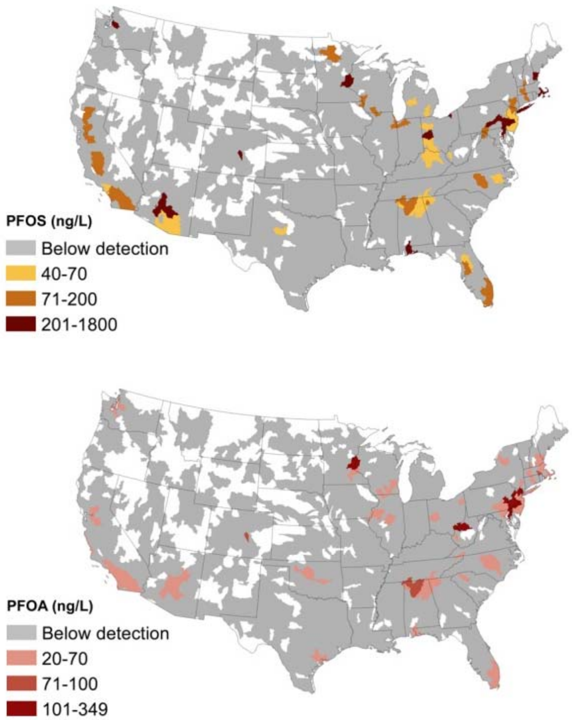
Aircraft Equipment

Industrial Machinery



Other Products

What has been done for monitoring PFAS in water in US?



Hu et al., Environ Sci Technol Lett. 2016 Oct 11; 3(10): 344–350.

- Data collection under Unregulated Chemical Monitoring Rule 3 (UCMR3) completed in 2015 with method EPA 537 (published in 2009).
- Localized hotspots for PFOA and PFOS, according to UCMR3 guidelines.

Unregulated Contaminant Monitoring Rule – EPA 537	
Compound	MRL, ng/L
PFBS	90
PFHpA	10
PFHxS	30
PFNA	20
PFOS	40
PFOA	20

- Drinking water Health Advisory issued in 2016: 70 ng/L PFOA+PFOS.

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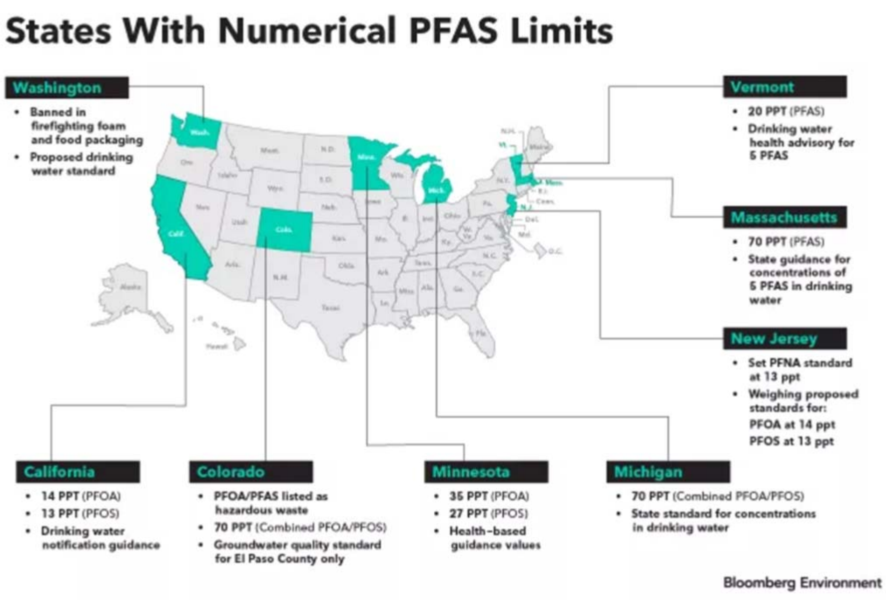
What has happened since 2016?



Map published in 2018; new limits were released by various States in 2019.

- Individual States are establishing specific limits in drinking water at ~10-15 ng/L.

  AWWA – document updated on a monthly basis with new limits

- Laboratories are working on providing results based on standardized or in-house developed methods, to answer specific questions from stakeholders.

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What's next?

- On 2/14/2019 EPA announced "the most comprehensive cross-agency plan to address an emerging chemical of concern ever undertaken by EPA", including:
  - Establishing a Maximum Contaminant Level and
  - Proposing a regulatory determination by the end of 2019
  - Monitoring of selected PFAS in next UCMR.

PFAS Method Scope

Draft Method 533	Both Methods	Method 537.1
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)[1]	N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)
1H, 1H, 2H, 2H- perfluorohexane sulfonic acid (4:2 FTS)	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)[2]	N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)	4,8-dioxa-3H-perfluorononanoic acid (ADONA)[3]	Perfluorotetradecanoic acid (PFTA)
Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)	Hexafluoropropylene oxide dimer acid (HFPO-DA)*	Perfluorotridecanoic acid (PFTrDA)
Perfluoro (2-ethoxyethane) sulfonic acid (PFEESA)	Perfluorodecanoic acid (PFDA)	
Perfluoro-3-methoxypropanoic acid (PFMPA)	Perfluorododecanoic acid (PFDoA)	
Perfluoro-4-methoxybutanoic acid (PFMBA)	Perfluorohexanoic acid (PFHxA)	
Perfluorobutanoic acid (PFBA)	Perfluoroundecanoic acid (PFUnA)	
Perfluoroheptanesulfonic acid (PFHpS)	**Perfluorobutanesulfonic acid (PFBS)**	
Perfluoropentanesulfonic acid (PFPeS)	**Perfluoroheptanoic acid (PFHpA)**	
Perfluoropentanoic acid (PFPeA)	**Perfluorohexanesulfonic acid (PFHxS)**	
	Perfluorononanoic acid (PFNA)	
	Perfluorooctanoic acid (PFOA)	
	Perfluorooctanesulfonic acid (PFOS)	

[1] 11Cl-PF3OUdS is also available as potassium salt
[2] 9Cl-PF3ONS is also available as potassium salt
[3] ADONA is also available as sodium salt and ammonium salt

Bold= monitored under UCMR 3
* GenX chemical

Presented at the UCMR5 Stakeholders Meeting on 7/16/2019

Standardized Analytical Methods

Safeguard Our Water from PFAS: Analytical Methods at a Glance

Method	EPA 537 & 537.1	ASTM D7979-17	ASTM D7968-17	EPA 8327 (TO BE PUBLISHED)	EPA 8328 (TO BE PUBLISHED) Meets DOD QSM	EPA 8329 (TO BE PUBLISHED)	EPA "Short Chain" (TO BE PUBLISHED)
Sample	Drinking Water	Ground/ Surface/ Waste Water Effluent	Soil Sediment Sludge	Ground/ Surface/ Waste Water Effluent	EPA 8327 + Soil, Sediment, Sludge	Soil Sediment Sludge	Water
Sample Preparation	Solid phase extraction (polymeric sorbent)	Direct injection	Solvent extraction + direct injection	Direct injection	Solid phase extraction	Direct injection	Solid phase extraction
Quantitation	Internal standard calibration (1 MRM)	External calibration (2 MRMs + ion ratio)	External calibration (2 MRMs + ion ratio)	External calibration	Isotopic dilution	External calibration	Internal standard calibration
Targets	EPA 537 – 14 EPA 537.1 – 18	21	21	24 (EPA 537 + 10)	25 (EPA 8327 + GenX)	24 (EPA 537 + 10)	25 (Mostly outside EPA 537.1)
Shimadzu's Platform	Triple Quad LCMS-8045 or LCMS-8050	Triple Quad LCMS-8050 or LCMS-8060	Triple Quad LCMS-8050 or LCMS-8060	Triple Quad LCMS-8050 or LCMS-8060	Triple Quad LCMS-8045 or LCMS-8050	Triple Quad LCMS-8050 or LCMS-8060	Triple Quad LCMS-8045 or LCMS-8050

www.OneLabOneEarth.com

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www.ssi.shimadzu.com

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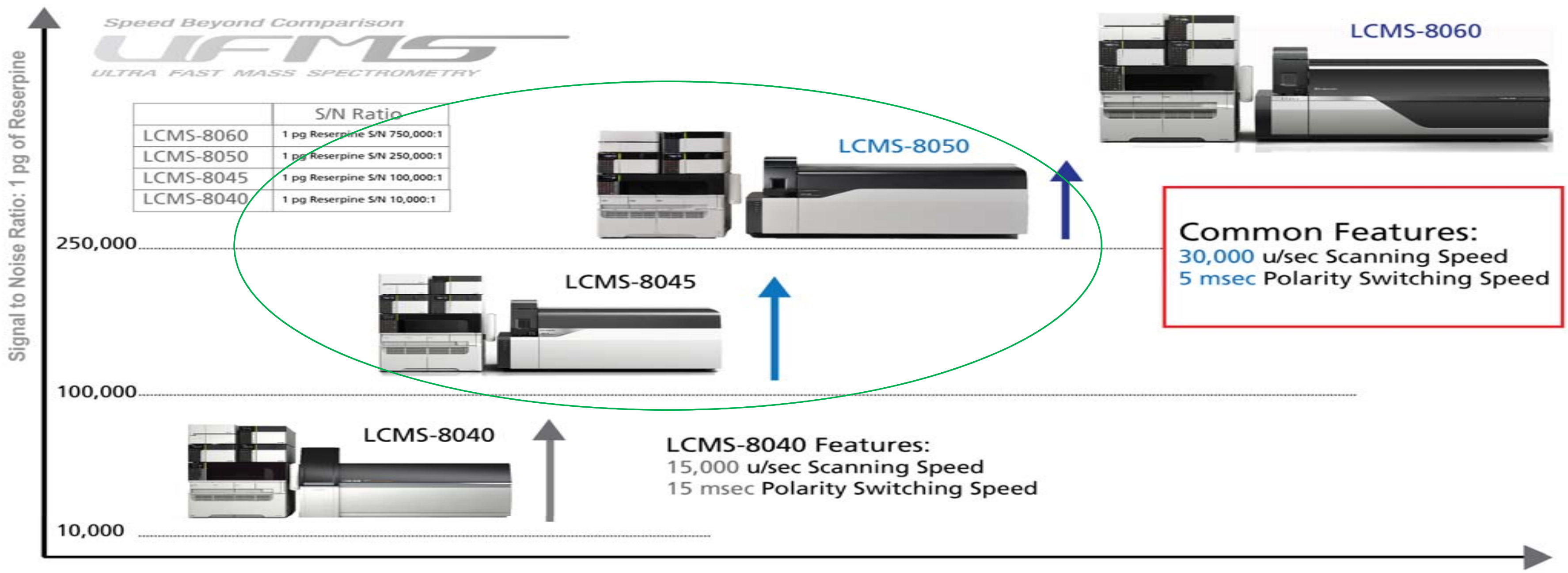
EPA 533

Method published for public comment (until 8/22/2019).

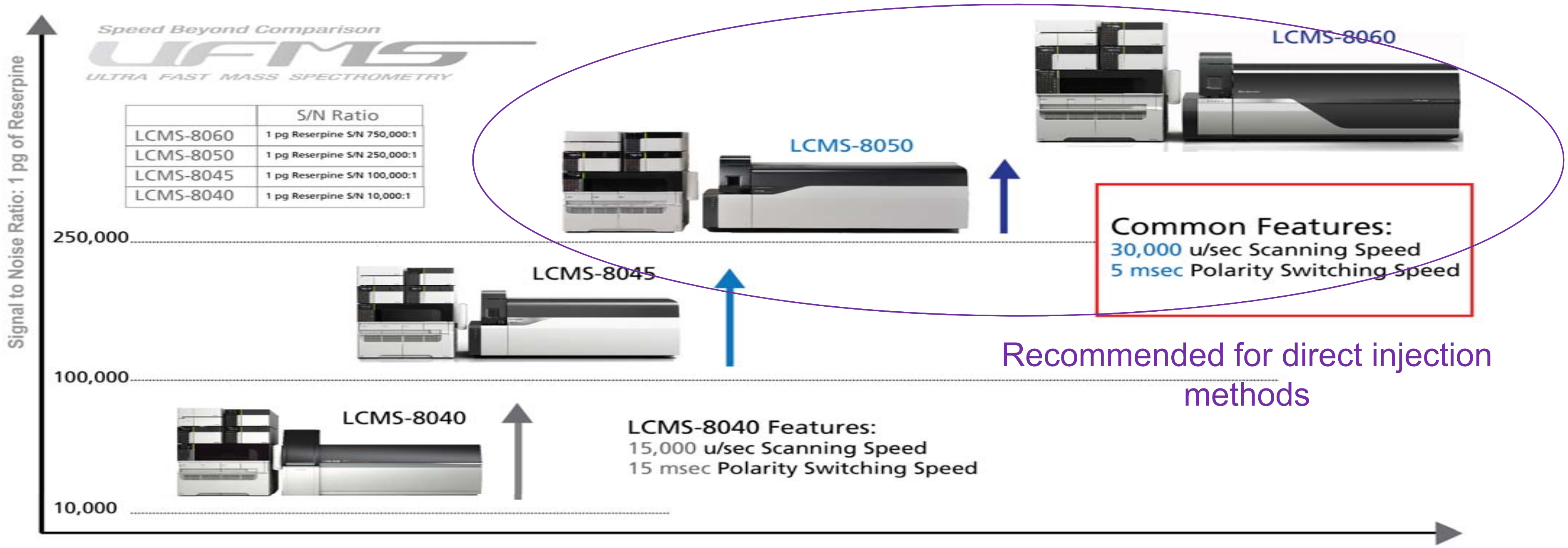
Shimadzu’s Solutions for PFAS quantitation

Recommended for methods requiring Solid Phase Extraction

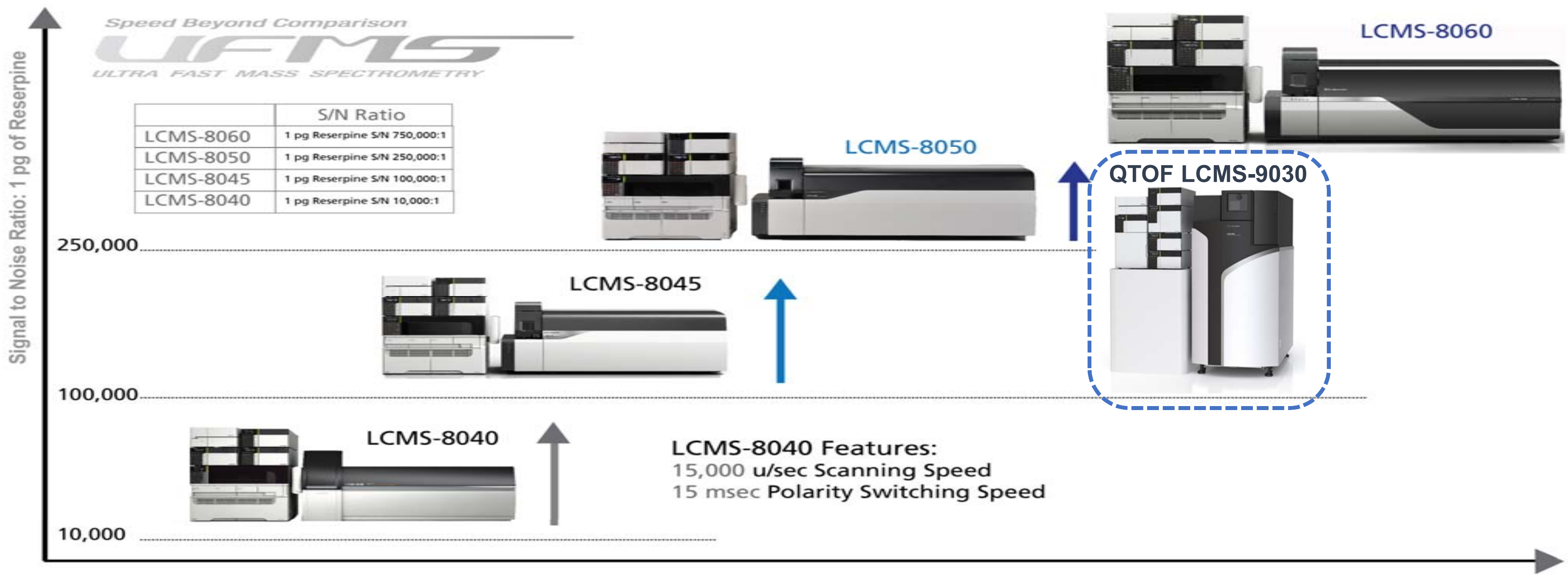


	S/N Ratio
LCMS-8060	1 pg Reserpine S/N 750,000:1
LCMS-8050	1 pg Reserpine S/N 250,000:1
LCMS-8045	1 pg Reserpine S/N 100,000:1
LCMS-8040	1 pg Reserpine S/N 10,000:1

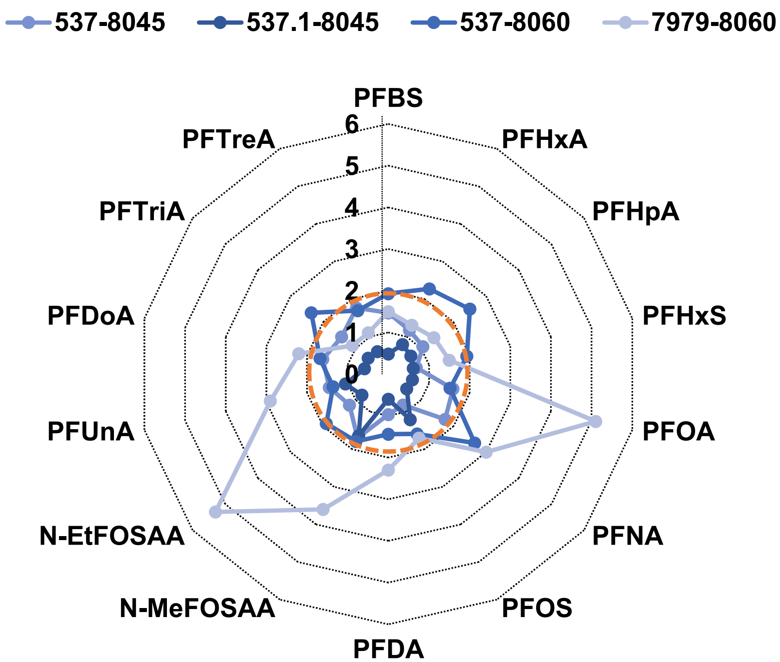
Shimadzu's Solutions for PFAS quantitation



Shimadzu's Solutions for PFAS quantitation



Performance comparison – Method Detection Limits in ng/L



METHOD/MODEL	SAMPLE VOLUME, ml	INJECTION VOLUME, µL
537-8045	250	1
537.1-8045	250	5
537-8060	250	1
7979-8060	na	10

537.1 – 9030 (QTOF):
Lowest standard analyzed: 2 ng/L
Injection volume: 5 µL

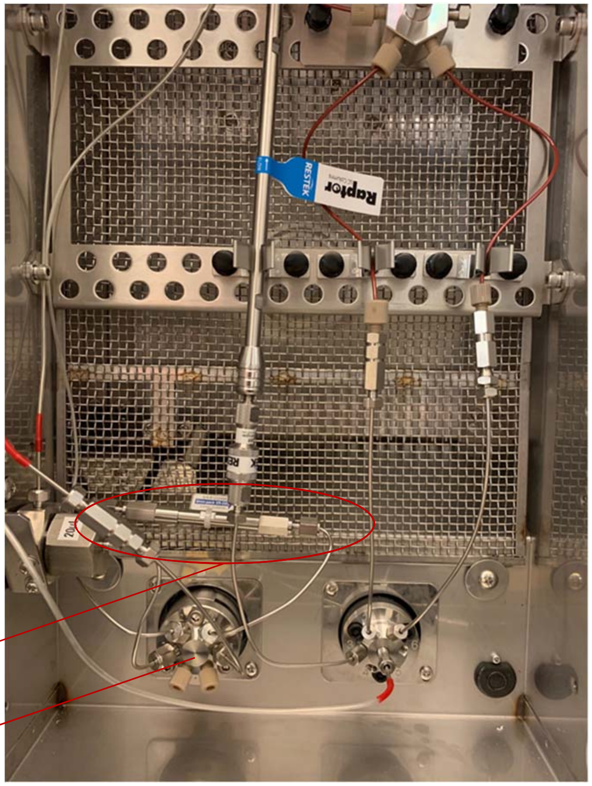
MDLs between <1 to <6 ng/L;
most compounds: <2 ng/L

MORE INFORMATION AND RESULTS IN POSTER
"Analysis and Quantitation of PFAS in EPA Method 537.1 Using High Resolution Accurate Mass Spectrometry
(Brahm Prakash)

Addressing monitoring requirements

AMERICAN WATER

- Compliance monitoring for the largest publicly traded water utility in the US.
- Participated in UCMR3 and continued to monitor PFAS for utilities in 16 States and external customers.
- LCMS 8050 set-up for the automatic switching between methods: EPA 537, EPA 544 and EPA 545 (selected cyanotoxins).



Delay column for PFAS background minimization

Optional switching valve

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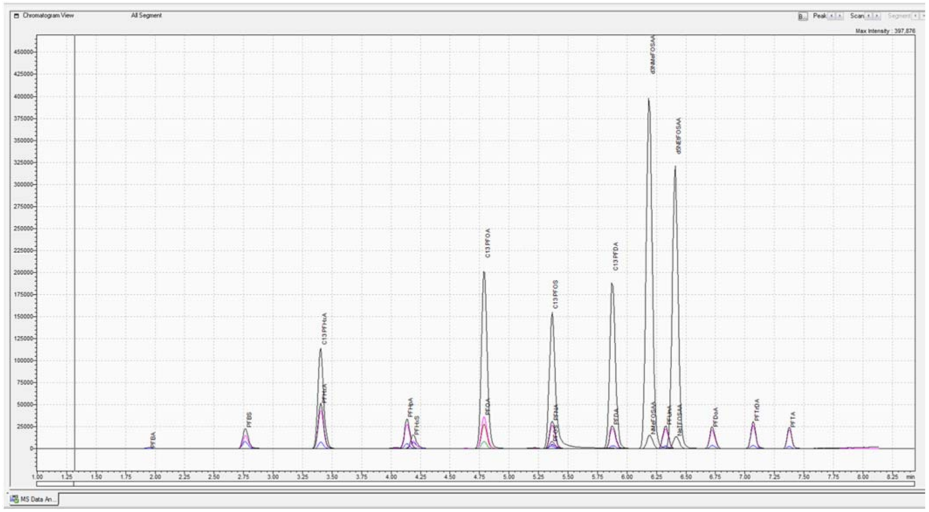
Addressing monitoring requirements

- Reporting limits suitable for current limits for PFAS in potable water.
  Injection volume: 3 μL.

- High throughput running an 8.5 min gradient.



Acronym	Reporting Limit	Method Detection Limit
PFOS	5 ng/L	0.88 ng/L
PFOA	5 ng/L	1.2 ng/L
PFHxS	5 ng/L	1.42 ng/L
PFHpA	5 ng/L	1.16 ng/L
PFNA	5 ng/L	1.15 ng/L
PFBS	5 ng/L	1.67 ng/L
PFHxA	5 ng/L	1.25 ng/L
PFDA	5 ng/L	1.14 ng/L
NMeFOSAA	5 ng/L	1.08 ng/L
PFUnA	5 ng/L	1.24 ng/L
NEtFOSAA	5 ng/L	1.14 ng/L
PFDoA	5 ng/L	1.31 ng/L
PFTrDA	5 ng/L	1.1 ng/L
PFTA	5 ng/L	1.08 ng/L

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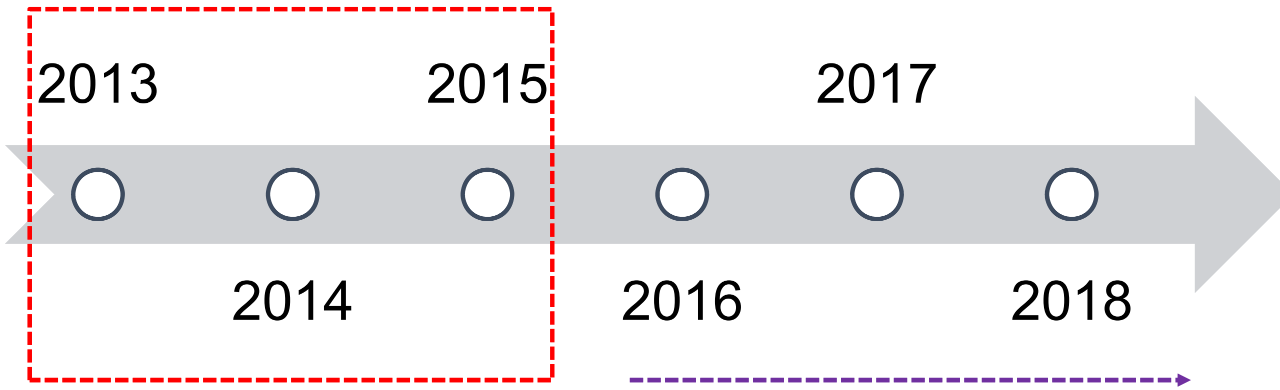
Some results



Unregulated Contaminant Monitoring Rule – EPA 537	
Compound	MRL, ng/L
PFBS	90
PFHpA	10
PFHxS	30
PFNA	20
PFOS	40
PFOA	20

EPA 537	
Compound	PQL, ng/L
PFBS	5.0
PFHxS	5.0
PFHxA	5.0
PFHpA	5.0
PFOS	5.0
PFOA	5.0
PFNA	5.0
PFDA	5.0
PFUnA	5.0
PFDoA	5.0
PFTrDA	5.0
PFTA	5.0

12,581 data reported, from 6 States and commercial customers

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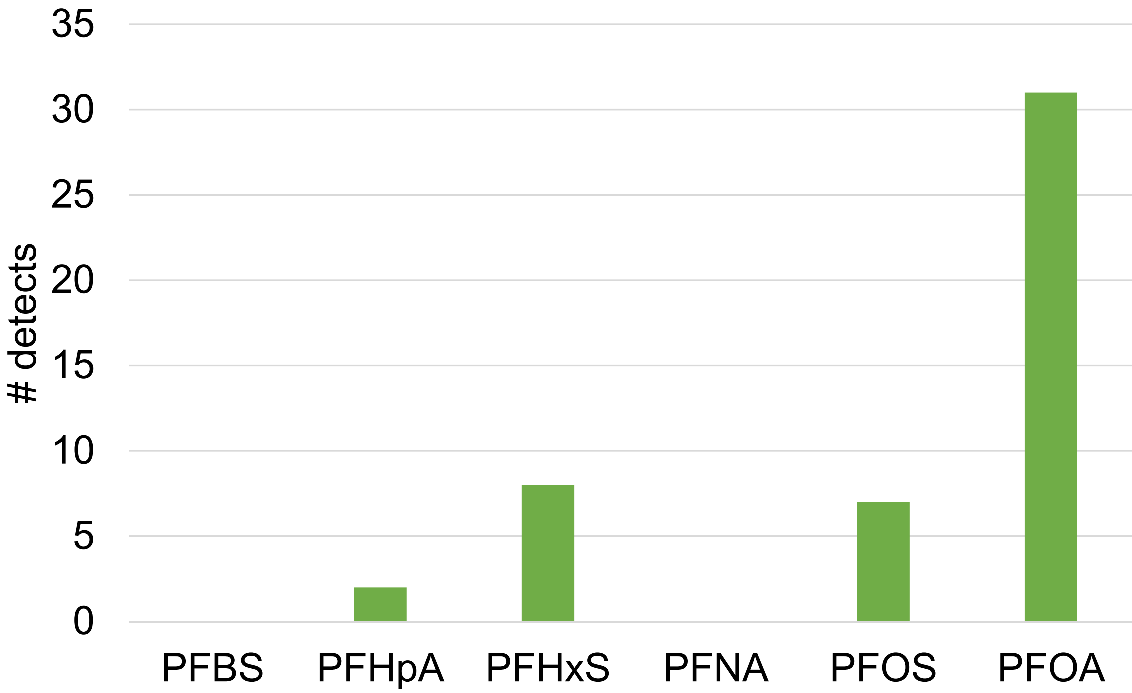
Some results – UCMR3

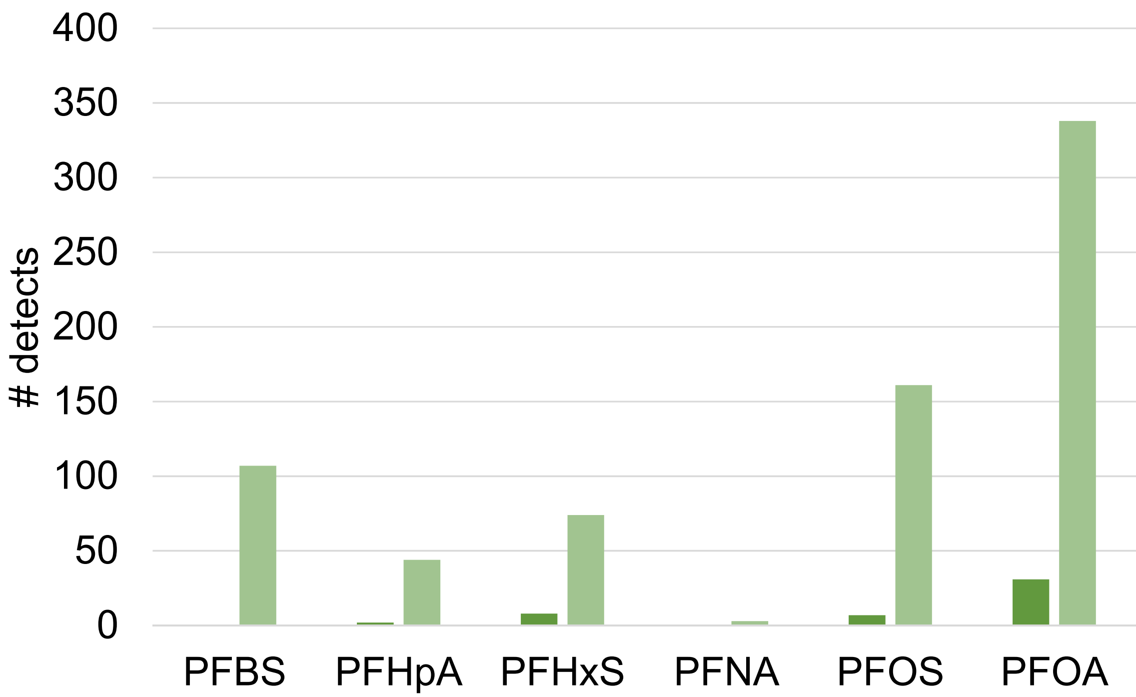


Total # of detects >MRL: 48

from 6 States and commercial customers

Unregulated Contaminant Monitoring Rule – EPA 537	
Compound	MRL, ng/L
PFBS	90
PFHpA	10
PFHxS	30
PFNA	20
PFOS	40
PFOA	20

Some results – UCMR3



Total # of detects
>MRL: 48
">5 ng/L": 727

from 6 States and commercial customers

Unregulated Contaminant Monitoring Rule – EPA 537	
Compound	MRL, ng/L
PFBS	90
PFHpA	10
PFHxS	30
PFNA	20
PFOS	40
PFOA	20

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Some results – after UCMR3

	PFBS	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFDA	PFUnA	PFDoA	PFTrD
# data reported	954	954	497	954	954	954	954	497	497	497	497
# >MRL	47	207	197	244	25	447	278	0	0	0	0
Min conc, ng/L	**PFBS**	**PFHpA**	**PFHxA**	**PFHxS**	**PFNA**	**PFOA**	**PFOS**	**PFDA**	**PFUnA**	**PFDoA**	**PFTrD**
2016	31.1	6.4		5.1		12.1	5.5				
2017	5.1	5	5	5.1	5.1	5.1	5				
2018	5	5.5	5	5	5	5.3	5.2				
Max conc, ng/L	**PFBS**	**PFHpA**	**PFHxA**	**PFHxS**	**PFNA**	**PFOA**	**PFOS**	**PFDA**	**PFUnA**	**PFDoA**	**PFTrD**
2016	336	54		1304		66	584				
2017	35.9	21.6	60.4	60.8	57.1	57.1	118.5				
2018	16.1	36.2	67.2	60.1	52.9	64.1	90.2				
Average conc, ng/L	**PFBS**	**PFHpA**	**PFHxA**	**PFHxS**	**PFNA**	**PFOA**	**PFOS**	**PFDA**	**PFUnA**	**PFDoA**	**PFTrD**
2016	183.5	11.3		119.8		35.8	55.8				
2017	8.4	7.7	9.9	10.9	12.7	23.4	13.1				
2018	9.7	14.9	20.4	19.8	16.2	22.1	26.5				
Overall	16.2	9.6	13.8	22.7	13.8	25.0	19.3				

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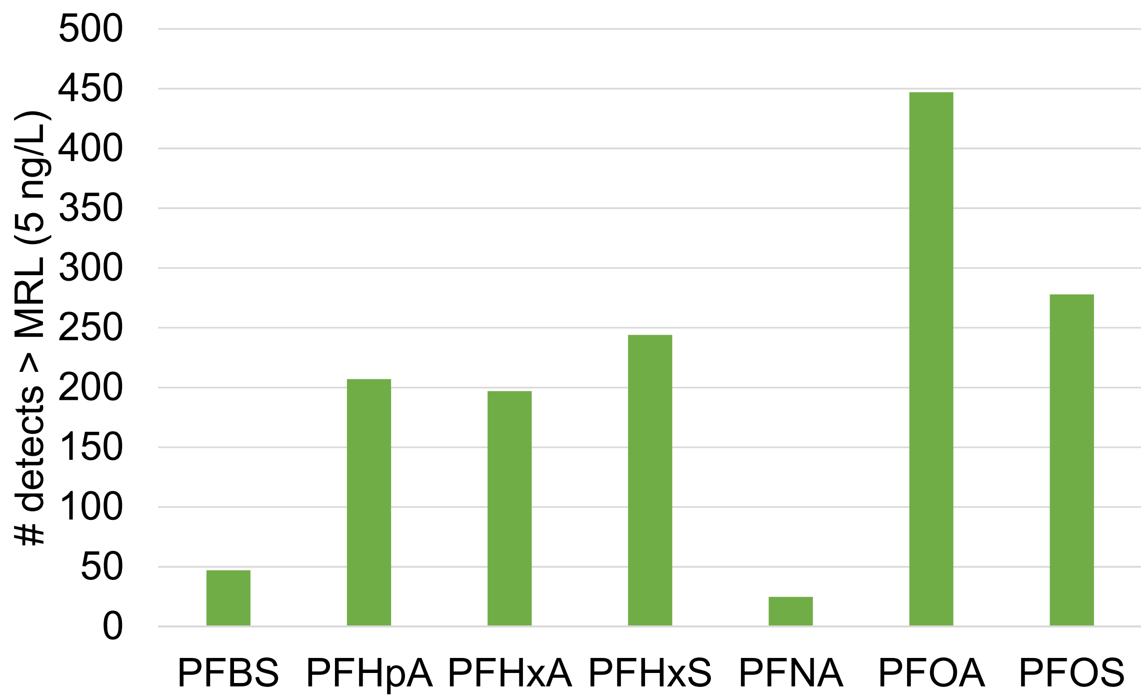
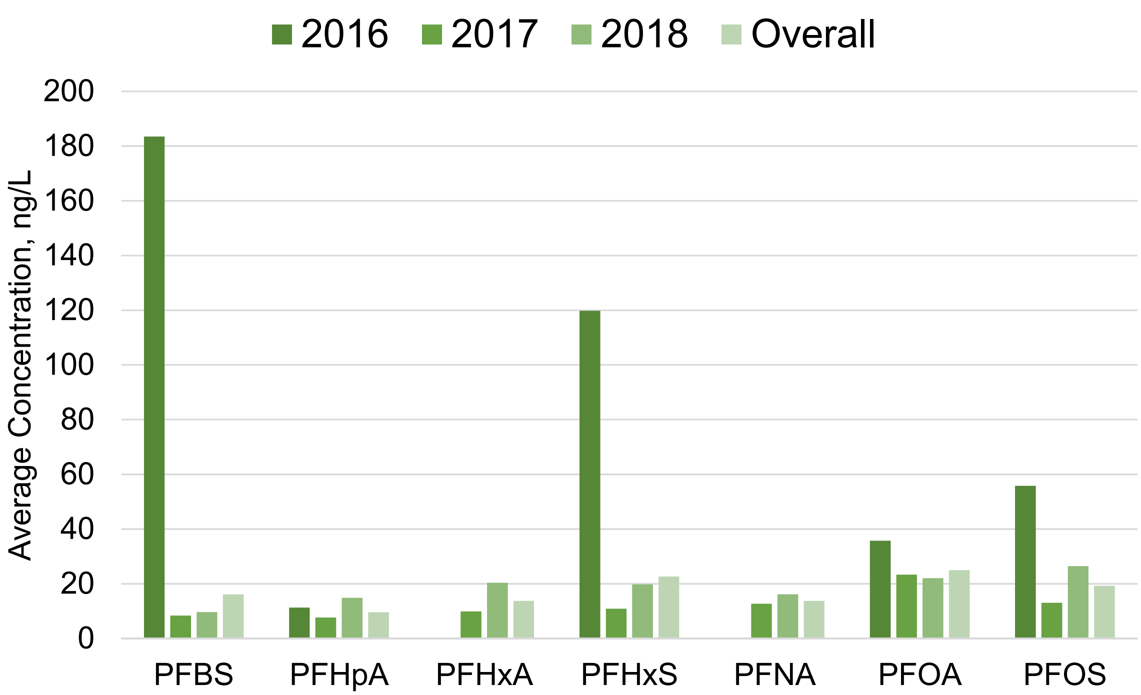
Some results – after UCMR3



PFUnA, PFDoA, PFTrDA, PFTA not detected
detects (1,445) represents 13% of total data

Some results – after UCMR3



		PFBS	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS
2016	Min	31.1	6.4		5.1		12.1	5.5
	Max	336	54		1304		66	584
2017	Min	5.1	5	5	5.1	5.1	5.1	5
	Max	35.9	21.6	60.4	60.8	57.1	57.1	118.5
2018	Min	5	5.5	5	5	5	5.3	5.2
	Max	16.1	36.2	67.2	60.1	52.9	64.1	90.2

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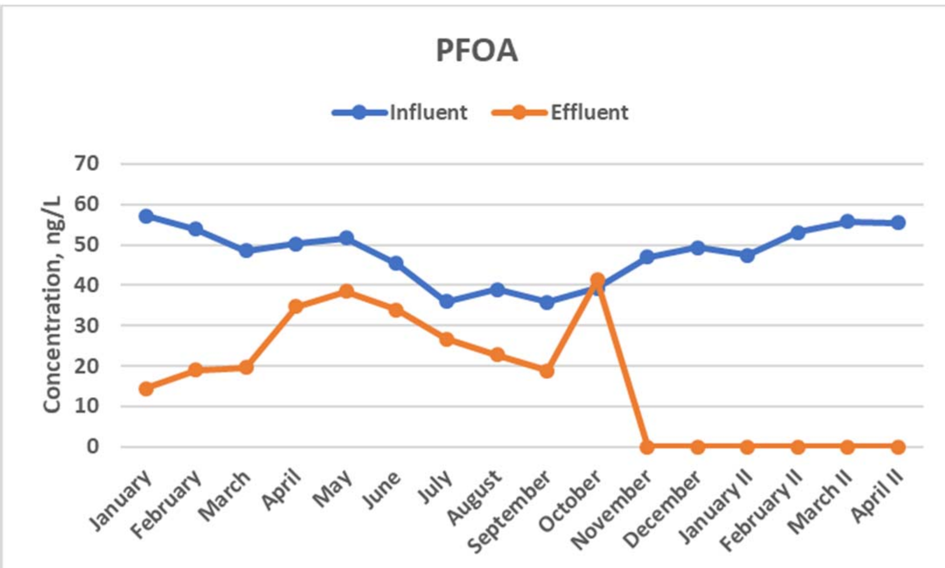
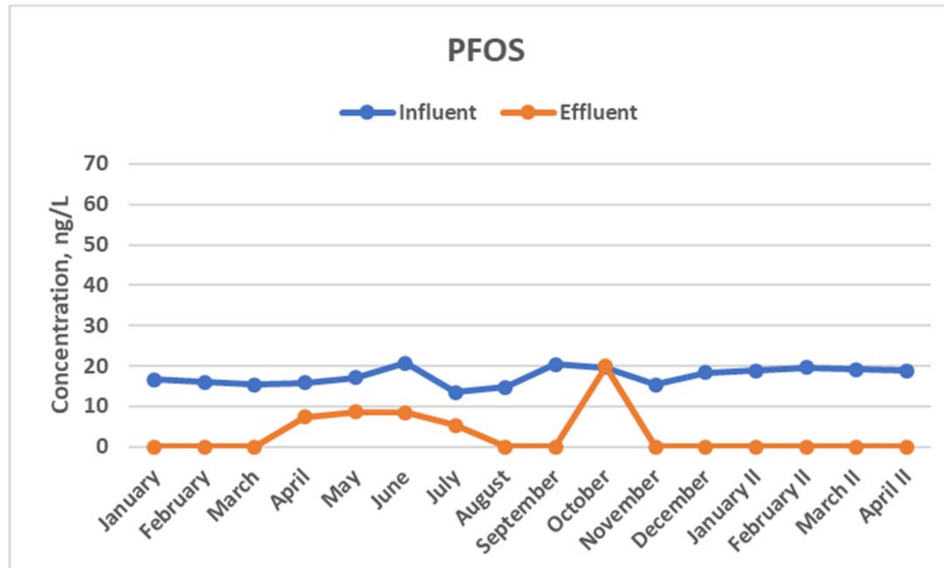
Some results: what do the numbers mean?





Location in violation of potential regulatory limit for PFOA and PFOS before implementing treatment via adsorption onto Granular Activated Carbon

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Take home messages

- Scientific community has been working on PFAS for more than 10 years. And there is information and robust solutions for monitoring available.
- It is important to understand the specific needs and questions from your laboratory and stakeholders.
- To succeed in monitoring PFAS in your waters, engage early in conversations with teams outside your lab!

Solutions for your environmental analysis

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