One Solution for Emerging Water Quality Topics: Per- and Polyfluoroalkyl substances .

Ruth Marfil-Vega, PhD
Environmental Marketing Manager

Today's presentation

- Shimadzu Corporation
- General information
- Methods
- Results
- Questions

Before I start…

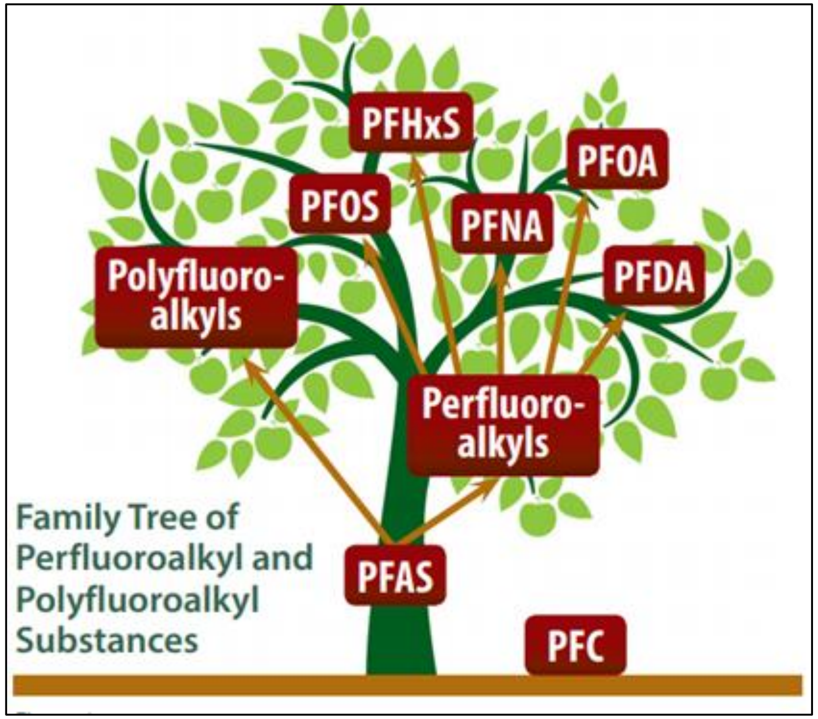
Thank you!

- 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.

Shimadzu Corporation & Shimadzu Scientific Instruments

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

What are PFAS?



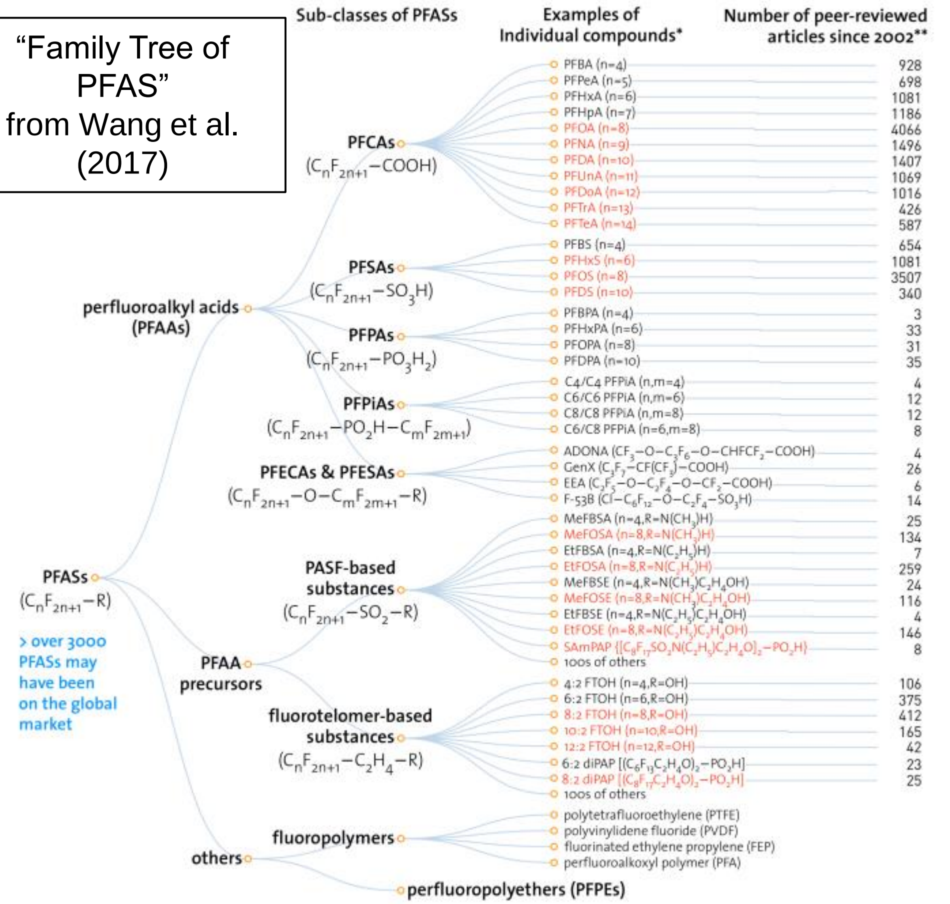
https://www.atsdr.cdc.gov/pfas/PFAS-health-effects.html

- ***Per- and polyfluoroalkyl substances* (PFAS)** are man-made chemicals that have been used in industry and consumer products worldwide since the 1950s.
- Previously, different organizations used the acronym **PFCs** (from ***perfluorinated chemicals***) to refer to a subset of PFAS, including PFOA and PFOS.
- PFCs also refers to perfluorocarbons, the most potent and long lasting anthropogenic green-house gases.

PFAS… only PFOA and PFOS?

PFOA and PFOS are the most studied (and known) PFAS.

“Family Tree of PFAS”
from Wang et al. (2017)



* 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.).

Replacement compounds for PFAS

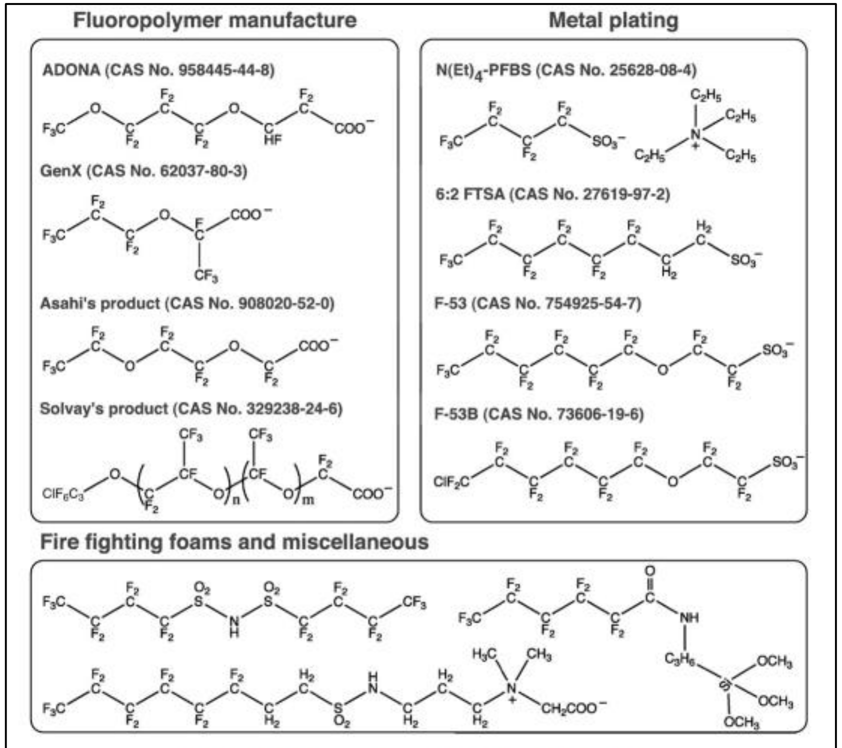


Fig. 1. Examples of fluorinated alternatives identified in different industry branches.

Replacement PFAS
from Wang et al. (2013)

- Replacement for long-chain PFAS (≥C8) and their precursors.
- Chemistries include shorter-chain homologues and other (non-) fluorinated chemicals.
- In response to concerns about impact of PFAS on the environment and human health and restrictions of production and use under the Stockholm Convention, the European Union[(1)] and US Environmental Protection Agency (EPA) [(2)].

[(1)] REACH, [(2)] PFOA Stewardship Program

The emergence of GenX

Outcomes from publication by Sun et al. were reported in the news in Mid-June 2017.

Environ. Sci. Technol. Lett., **2016**, *3* (12), pp 415–419

Environmental Science & Technology Letters

Letter

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[‡]

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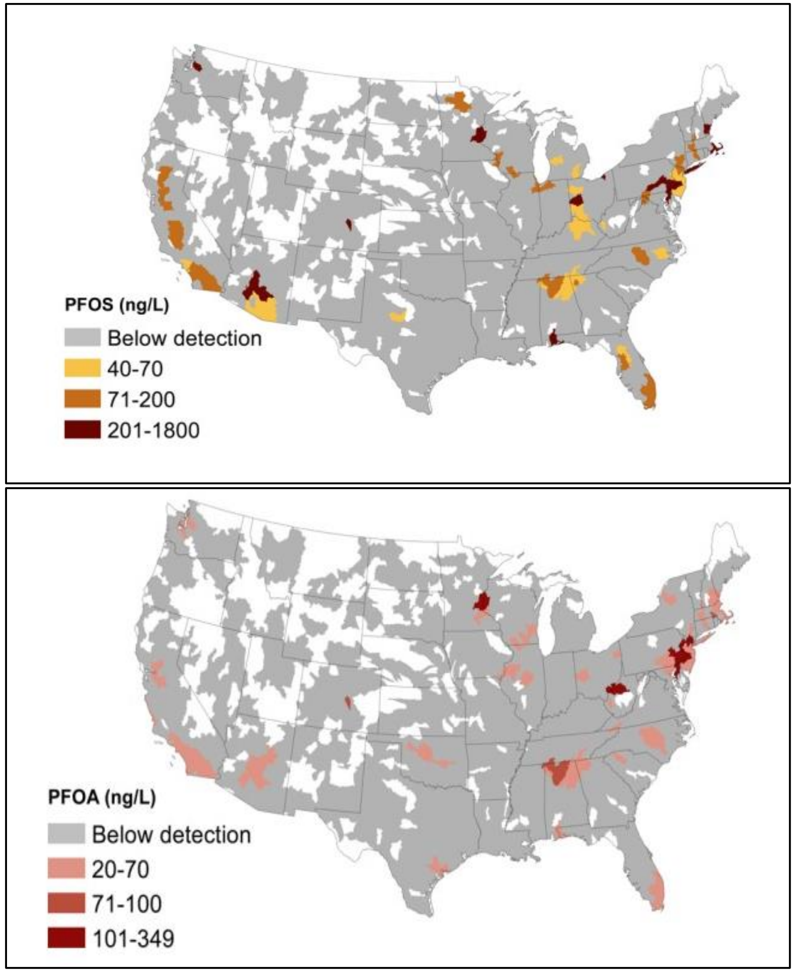
What has been done for monitoring PFAS in water in US?



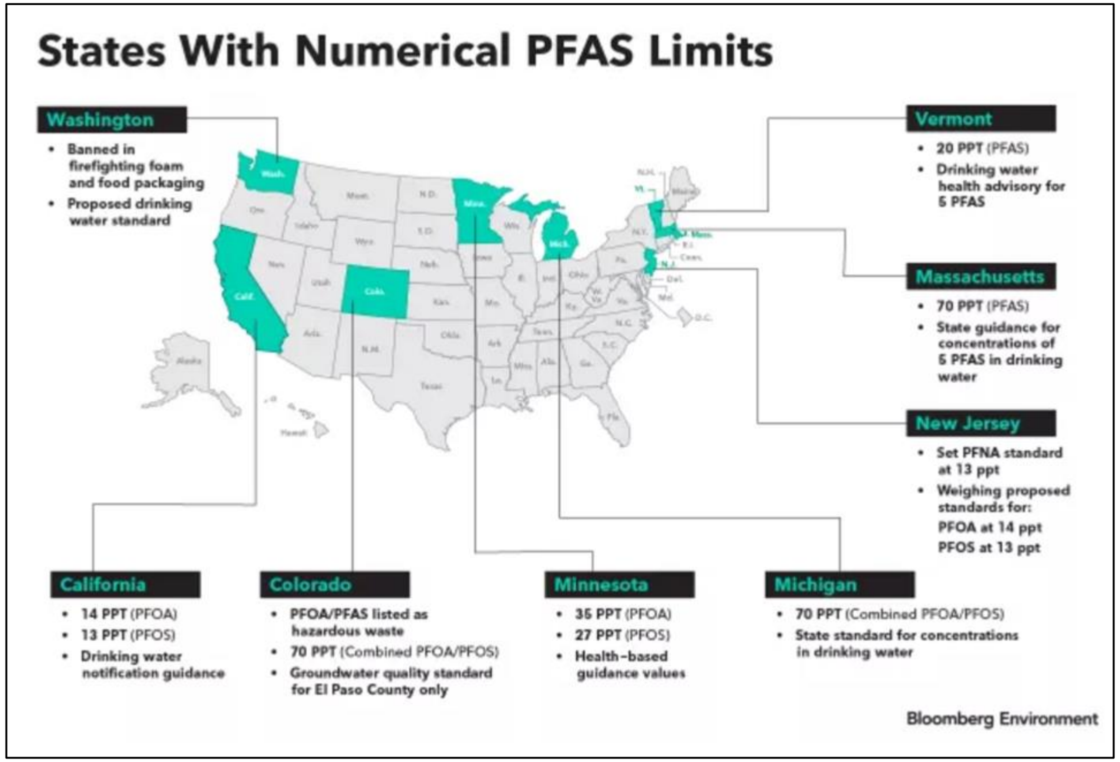
Hu et al., Environ Sci Technol Lett. 2016 Oct 11; 3(10): 344–350.

- 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.

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 regular 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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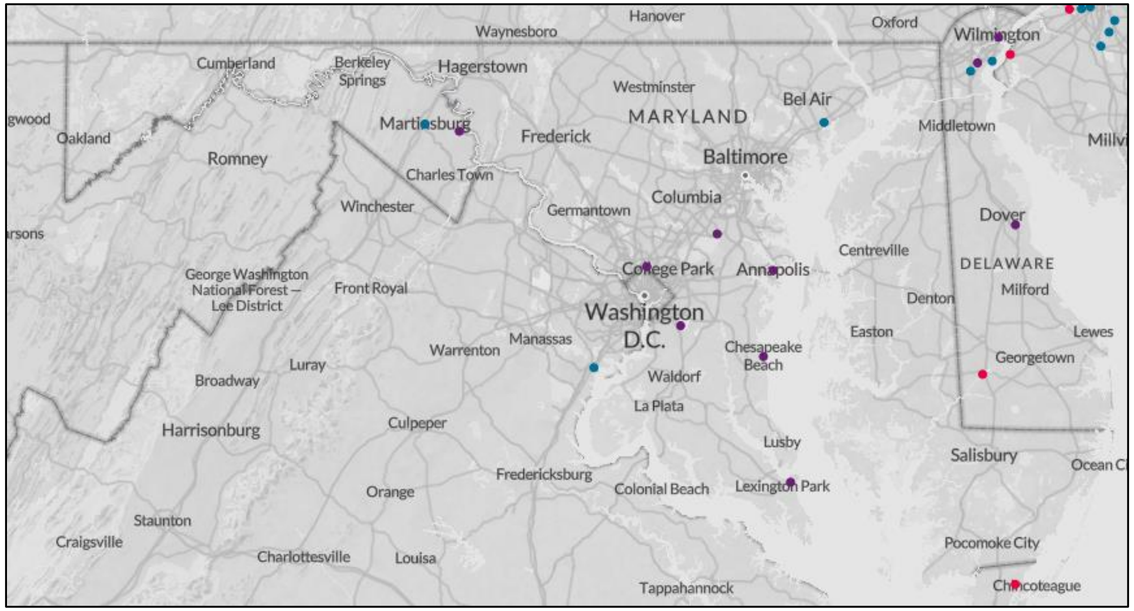
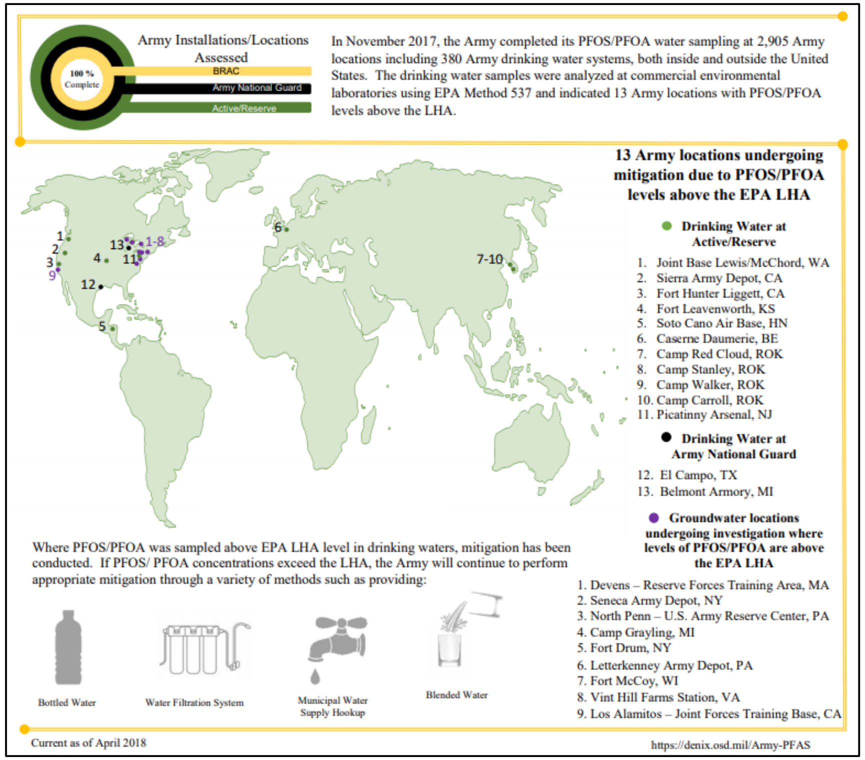
What is going on in Maryland?

- Maryland does not have specific policies for PFAS in drinking water supplies.



https://www.ewg.org/interactive-maps/2019_pfas_contamination/map/

Purple – Military Sites; Blue – Drinking water; Pink - Other



- No army facilities listed among the locations with PFAS concentrations in the drinking water supply above EPA's HA.

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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

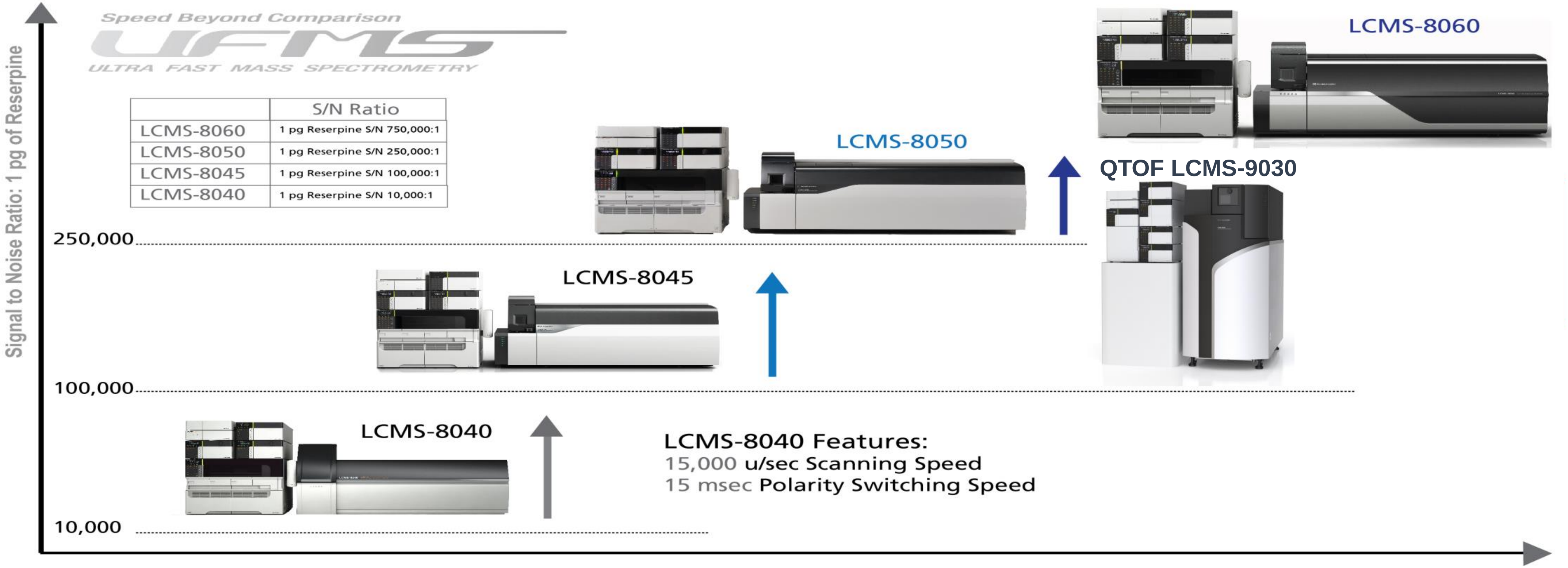
Draft Method 533	Both Methods	Method 537.1
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)[1]	N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)
1H, 1H, 2H, 2H- perfluorohexane sulfonic acid (4:2 FTS)	9-chlorohexadecafluoro-3-oxanone-1-sulfonic 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

Shimadzu’s Solutions for PFAS quantitation



	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

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	EPA 8328	EPA 8329	EPA "Short Chain"
				TO BE PUBLISHED	TO BE PUBLISHED Meets DOD QSM	TO BE PUBLISHED	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	Isotopic dilution
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

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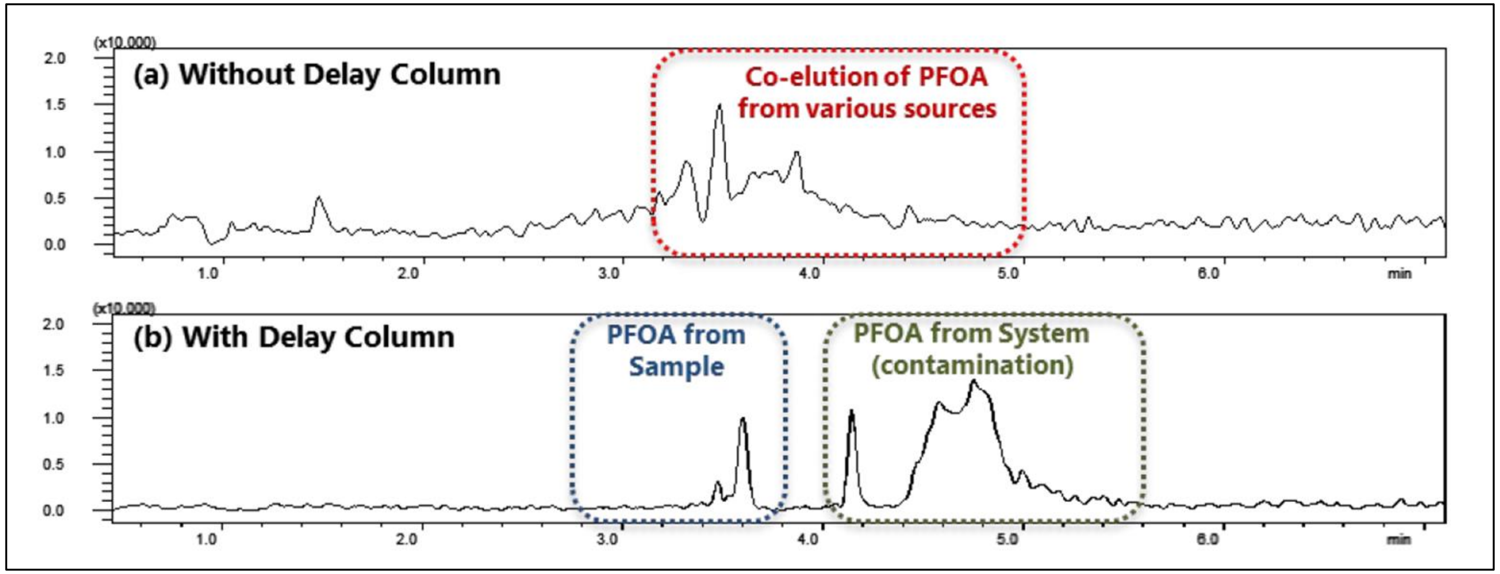
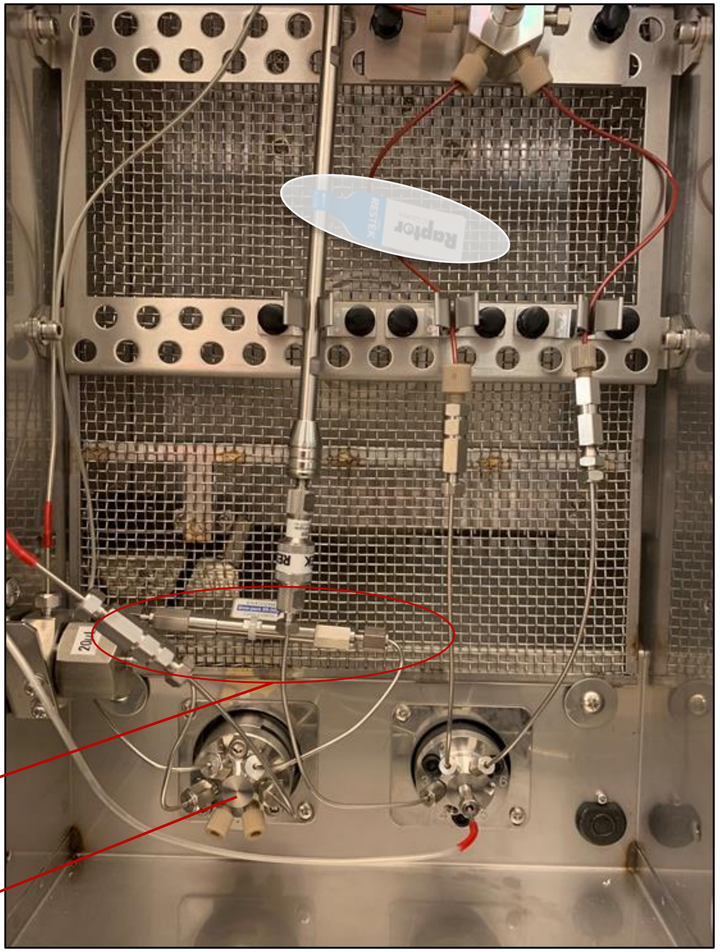
EPA 533

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

How to minimize background PFAS





PFAS and cyanotoxins methods
(i.e. EPA 544 and EPA 545) can be run
In the same instrument

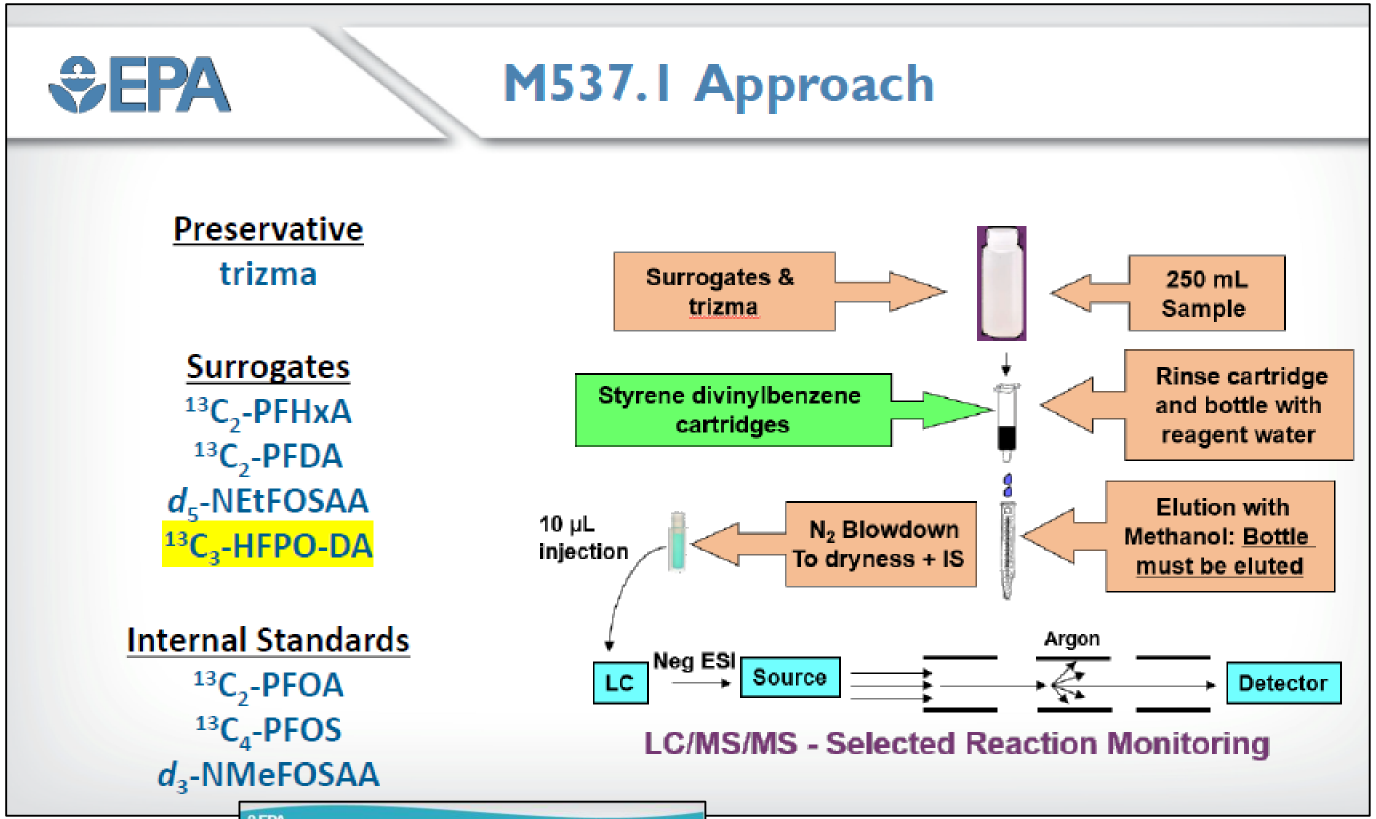
Delay column for PFAS background minimization

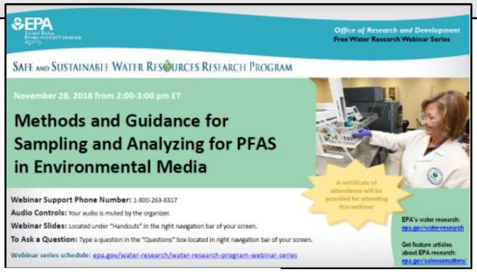
Optional switching valve for alternating methods

EPA 537 and EPA 537.1 – Sample preparation

PFBS
PFHxA
PFHpA
PFHxS
PFOA
PFNA
PFOS
PFDA
N-MeFOSAA
N-EtFOSAA
PFUnA
PFDoA
PFTriA
PFTreA

PFBS
PFHxA
HFPO-DA
PFHpA
PFHxS
ADONA
PFOA
PFNA
PFOS
9Cl-PF3ONS
PFDA
N-MeFOSAA
N-EtFOSAA
PFUnA
11Cl-PF3OUdS
PFDoA
PFTriA
PFTreA



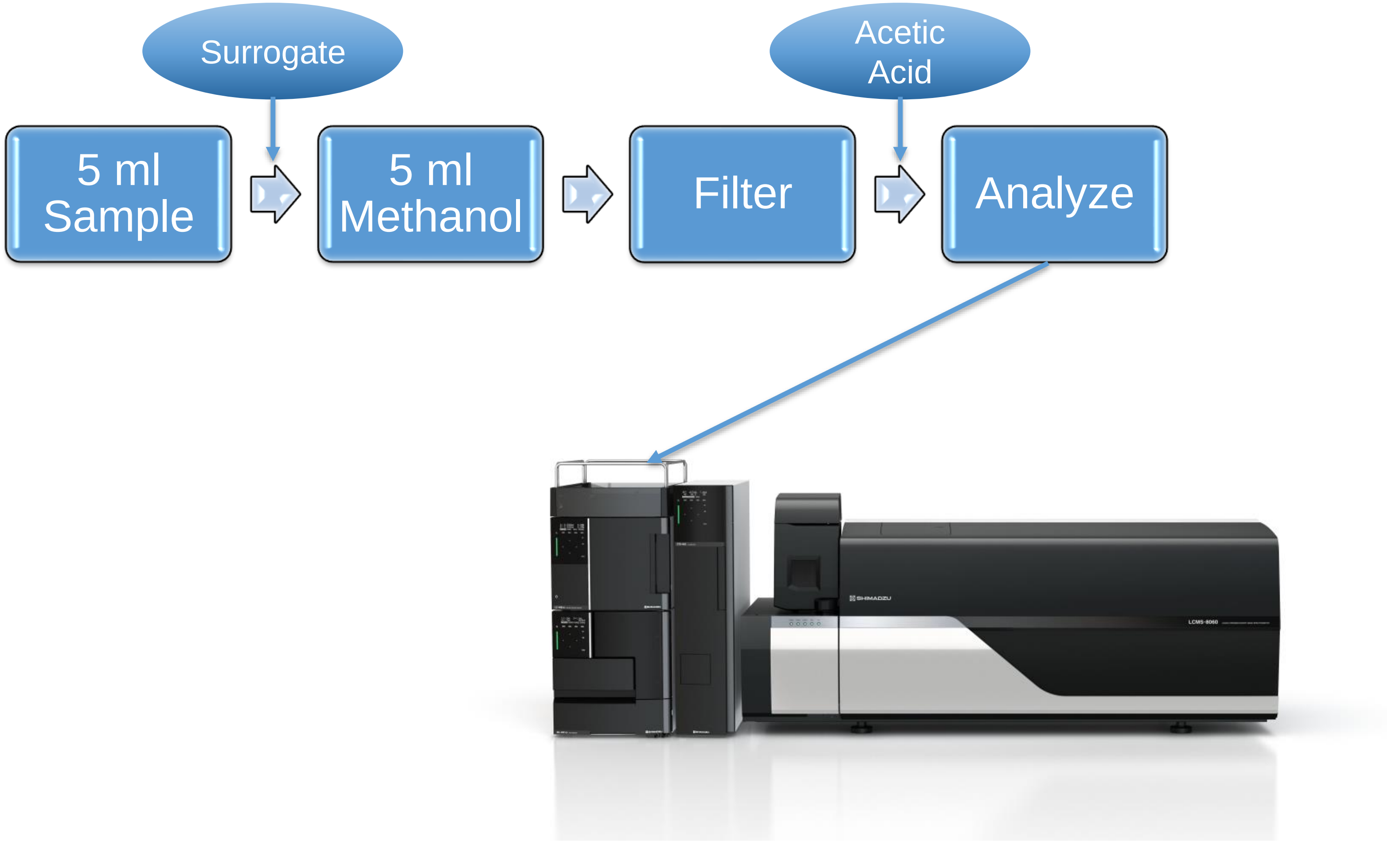


Info from Dr. Shoemaker's presentation on 11/28/2018

Draft EPA 8327: Targets and Sample preparation

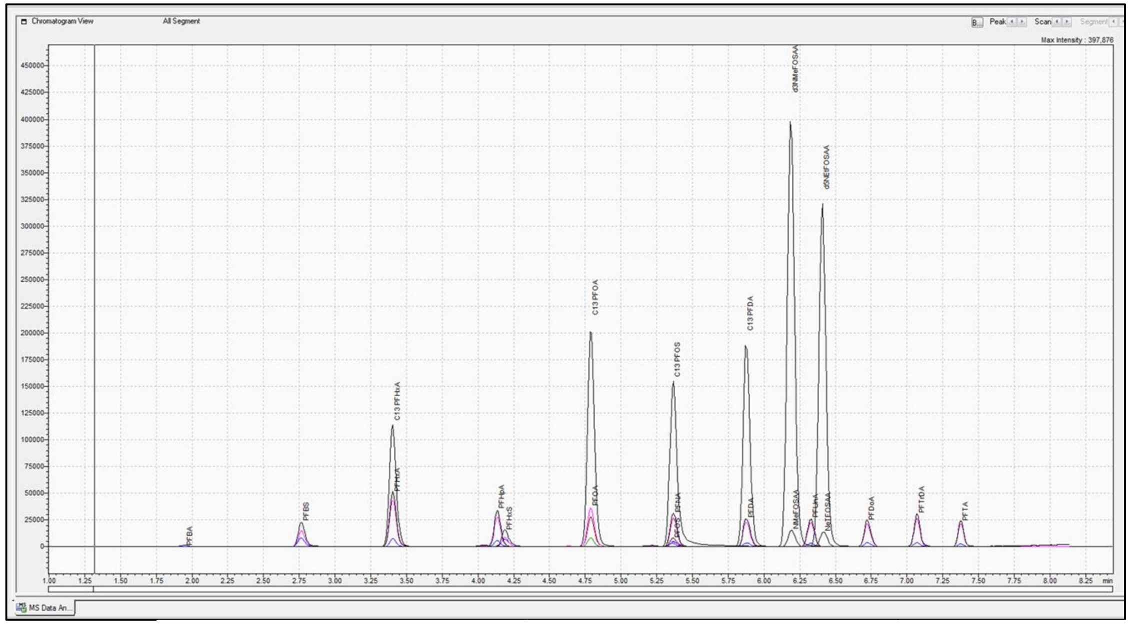
Target	Surrogate
PFBS	13C3-PFBS
PFHxS	13C3-PFxS
PFOS	13C8-PFOS
4:2 FTS	13C2-4:2 FTS
6:2 FTS	13C2-6:2 FTS
8:2 FTS	13C2-8:2 FTS
L-PFPeS	-
L-PFHpS	-
L-PFNS	-
L-PFDS	-
PFBA	13C4-PFBA
PFPeA	13C5-PFPeA
PFHxA	13C5-PFHxA
PFHpA	13C4-PFHpA
PFOA	13C8-PFOA
PFNA	13C9-PFNA
PFDA	13C6-PFDA
PFUnA	13C7-PFUnA
PFDoA	13C2-PFDoA
PFTriA	-
PFTreA	13C2-PFTreA
N-EtFOSAA	D3-N-EtFOSAA
N-MeFOSAA	D3-N-MeFOSAA
FOSA	13C8-PFOSA

Similar to ASTM D7979-17



Addressing monitoring requirements

- High throughput running an 8.5 min gradient for method EPA 537 with LCMS 8050.
- Reporting limits suitable for current limits for PFAS in potable water. Injection volume: 3 µL.



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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EPA 537.1: same performance with new compounds

Information provided by Brahm Prakash and Jerry Byrne (Shimadzu)

- Source conditions modified for EPA 537.1 to achieve required sensitivity for GenX.
- Similar results obtained with QTOF LCMS-9030.

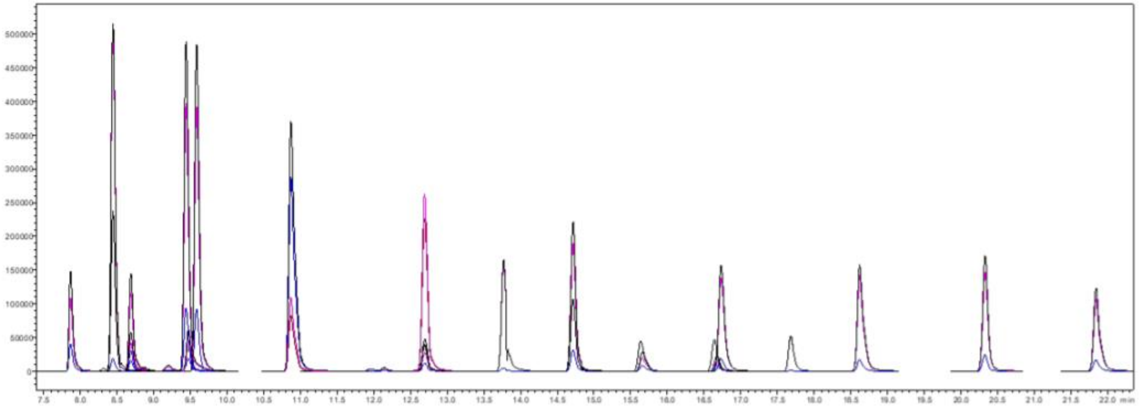


Figure 1: MRM (Pink and Blue) and TIC (black) chromatograms of all PFAS in EPA 537.1 at 80 ppt sample concentration

EPA 537.1

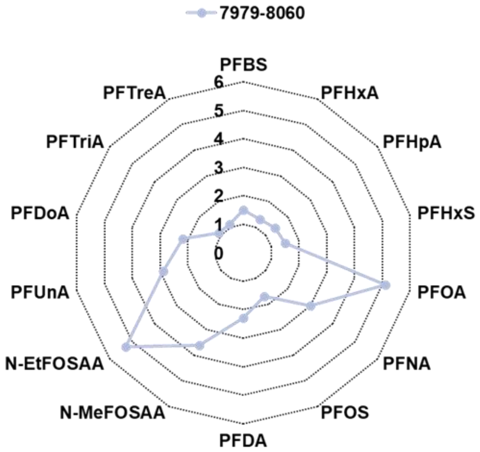
Compound	Spiked Conc (ppt)	Calculated Conc (ppt)	Accuracy	%RSD (n=8)	MDL (ppt)
PFBS	4	3.84	96.0	4.4	0.48
PFHxA	4	3.70	92	7.3	0.79
HFPO-DA	**4**	**3.55**	**89**	**8.6**	**0.88**
PFHpA	4	3.87	97	6.2	0.69
PFHxS	4	3.74	93	5.7	0.61
ADONA	**4**	**3.72**	**93**	**5.4**	**0.58**
PFOA	4	3.71	93	5.5	0.59
PFNA	4	3.79	95	5.2	0.57
PFOS	4	3.76	94	11.1	1.21
9Cl-PF3ONS	**4**	**3.63**	**91**	**7.9**	**0.82**
PFDA	4	3.67	92	5.7	0.60
N-MeFOSAA	4	3.55	89	15.9	1.64
N-EtFOSAA	4	3.81	95	7.3	0.81
PFUnA	4	3.56	89	10.2	1.05
11Cl-PF3OUdS	**4**	**3.41**	**85**	**12.7**	**1.25**
PFDoA	4	3.73	93	5.4	0.58
PFTriA	4	3.74	93	5.7	0.62
PFTreA	4	3.67	92	5.7	0.60

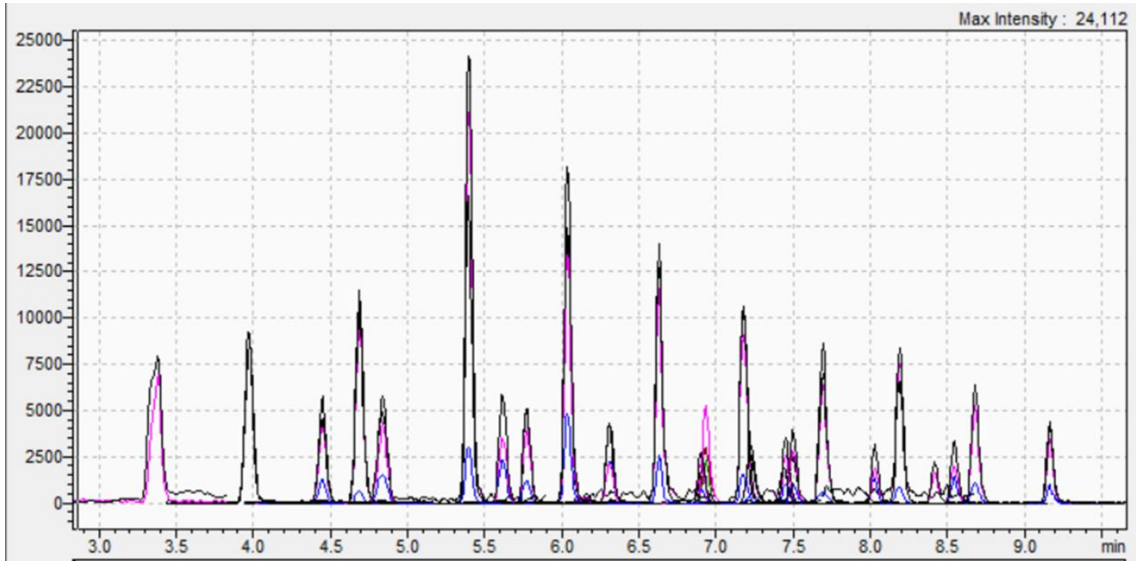
Data acquired with LCMS-8045 with 5 µL injection

Draft EPA 8327 – direct injection for non-potable waters

Information provided by Brahm Prakash and Jerry Byrne (Shimadzu)

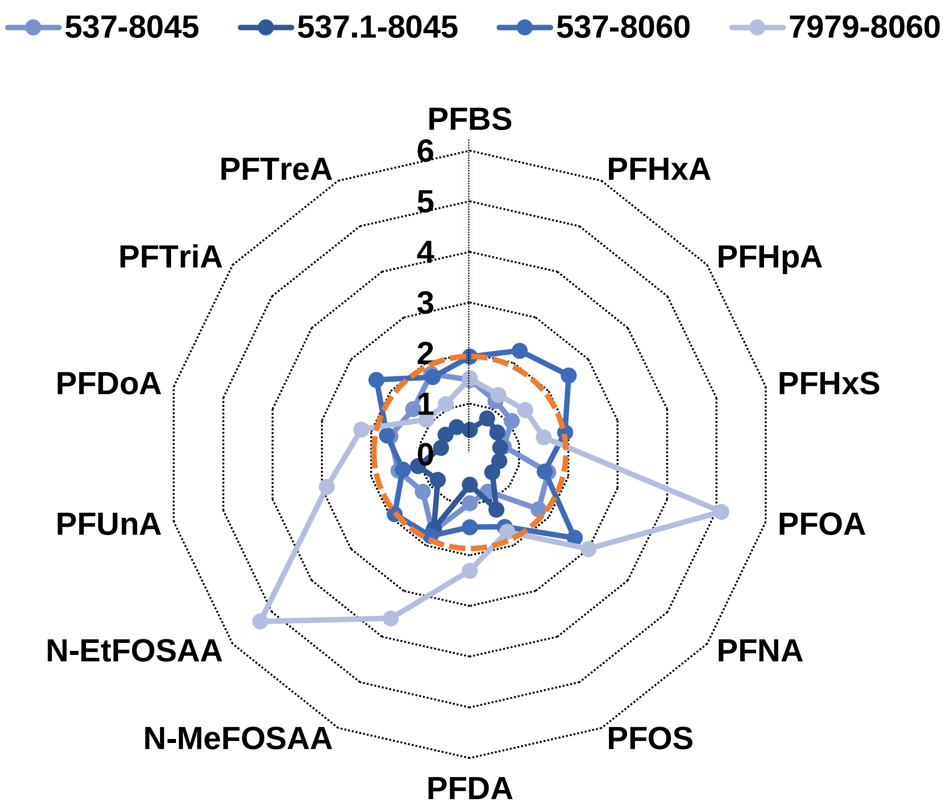
Apparent higher MDLs because there is not sample preconcentration by SPE. Fast turn-around-time because of "dilute and shoot" approach.





Compounds	Measured Concentration, ng/L	%Recovery	S/N
PFBA	5.19	103.71	7.90
PFPeA	5	99.94	5.01
4-2 FTS	5.17	103.43	16.41
PFHxA	5	100.07	6.53
PFBS	4.17	83.38	(INF)
PFHpA	5.02	100.44	(INF)
PFPeS	4.58	91.67	(INF)
6-2 FTS	5.38	107.6	7.87
PFOA	6.37	127.46	12.20
PFHxS	4.98	99.5	1.43
PFNA	5.34	106.89	(INF)
8-2 FTS	4.98	99.56	(INF)
PFHpS	3.85	77.03	(INF)
N-MeFOSAA	5.41	108.22	(INF)
PFDA	5	100.05	4.59
N-EtFOSAA	4.98	99.66	(INF)
PFOS	5.12	102.42	4.29
PFUnA	5.15	103.07	3.84
PFNS	4.81	96.2	7.75
PFDoA	4.87	97.34	(INF)
FOSA	4.19	83.84	(INF)
PFDS	4.75	94.98	(INF)
PFTriA	4.79	95.76	11.78
PFTreA	5.73	114.63	6.16

Method Detection Limits



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

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

Method Detection Limit, ng/L (537.1-8045)	
HFPO-DA	0.88
ADONA	0.58
9Cl-PF3ONS	0.82
11Cl-PF3OUdS	1.25

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

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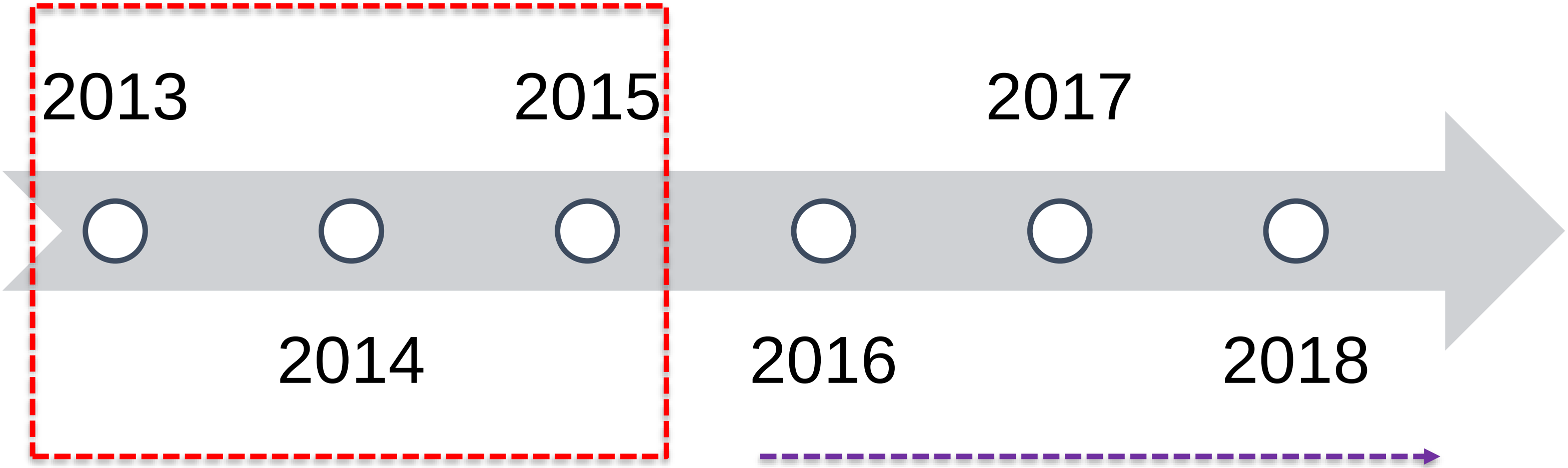
Some results from the field



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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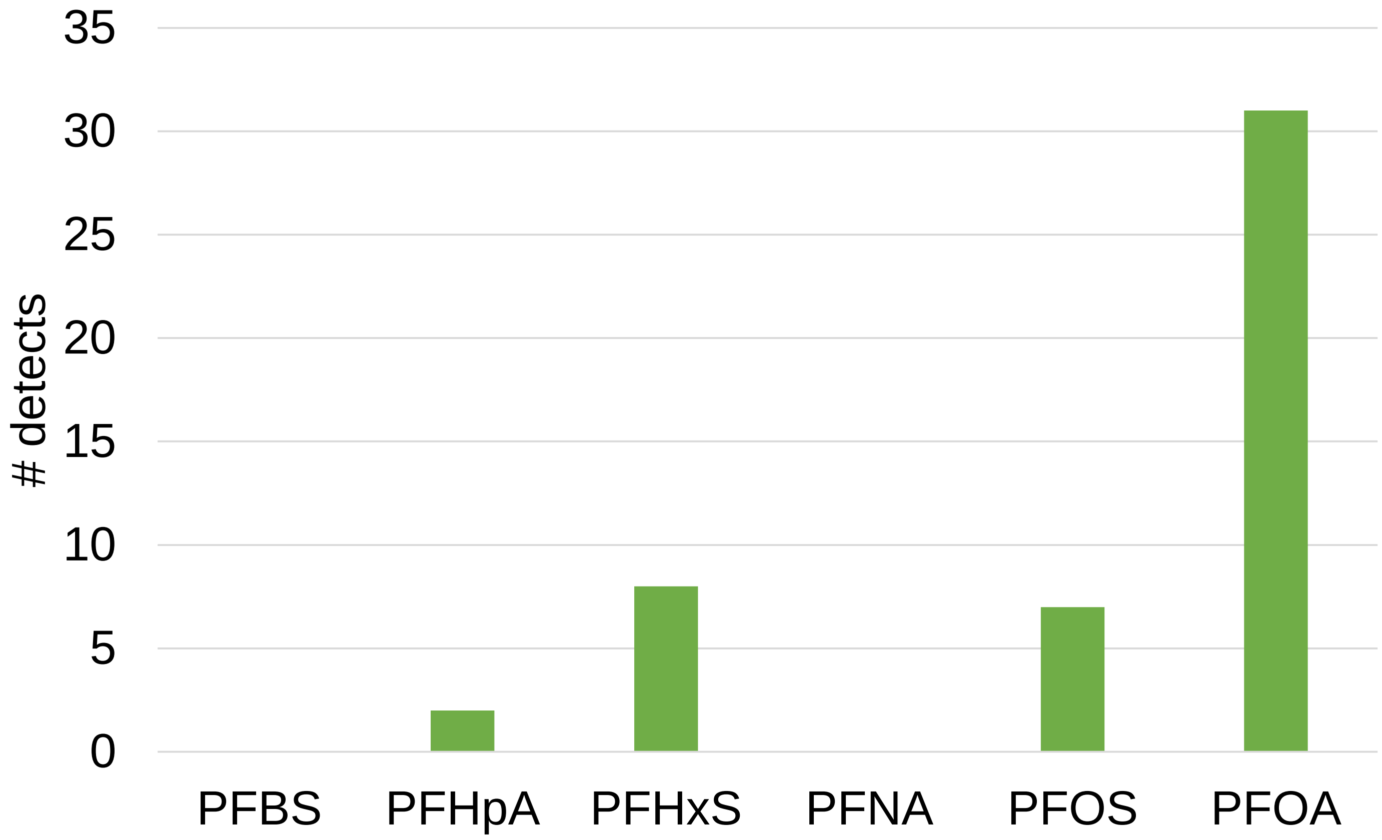
Some results – UCMR3

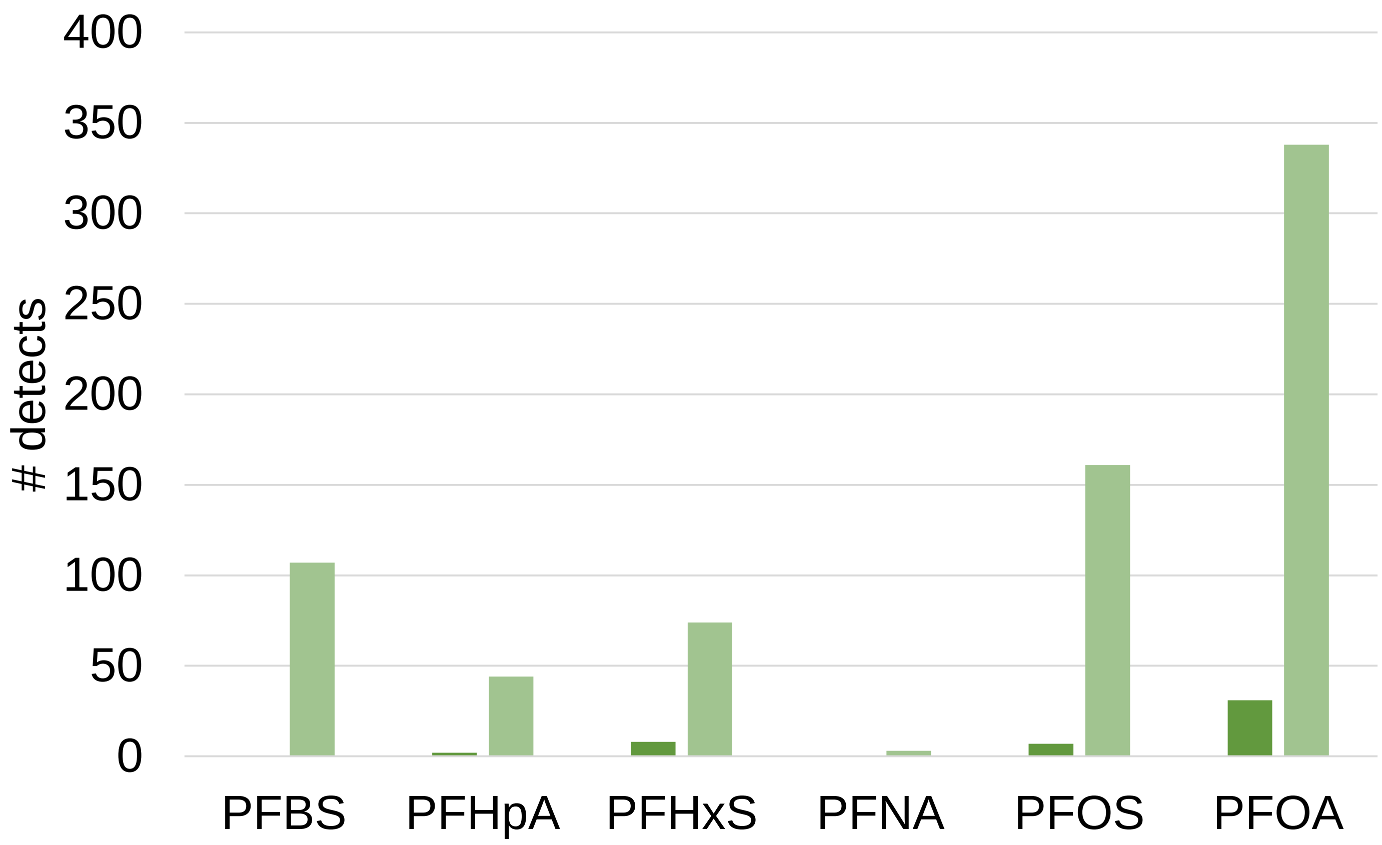


Total # of detects
>MRL: 48

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

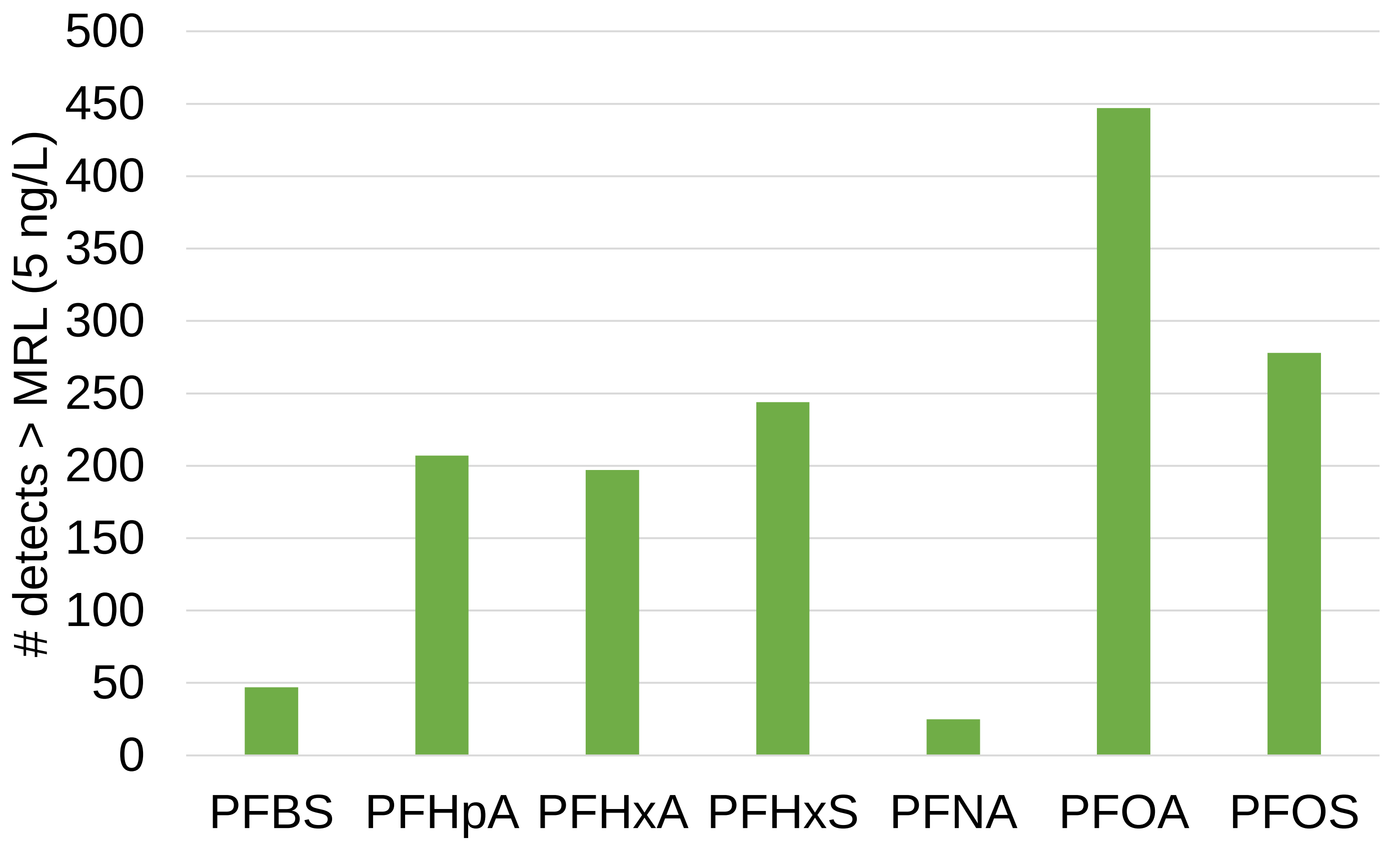


Total # of detects
>MRL: 48
">5 ng/L": 727

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

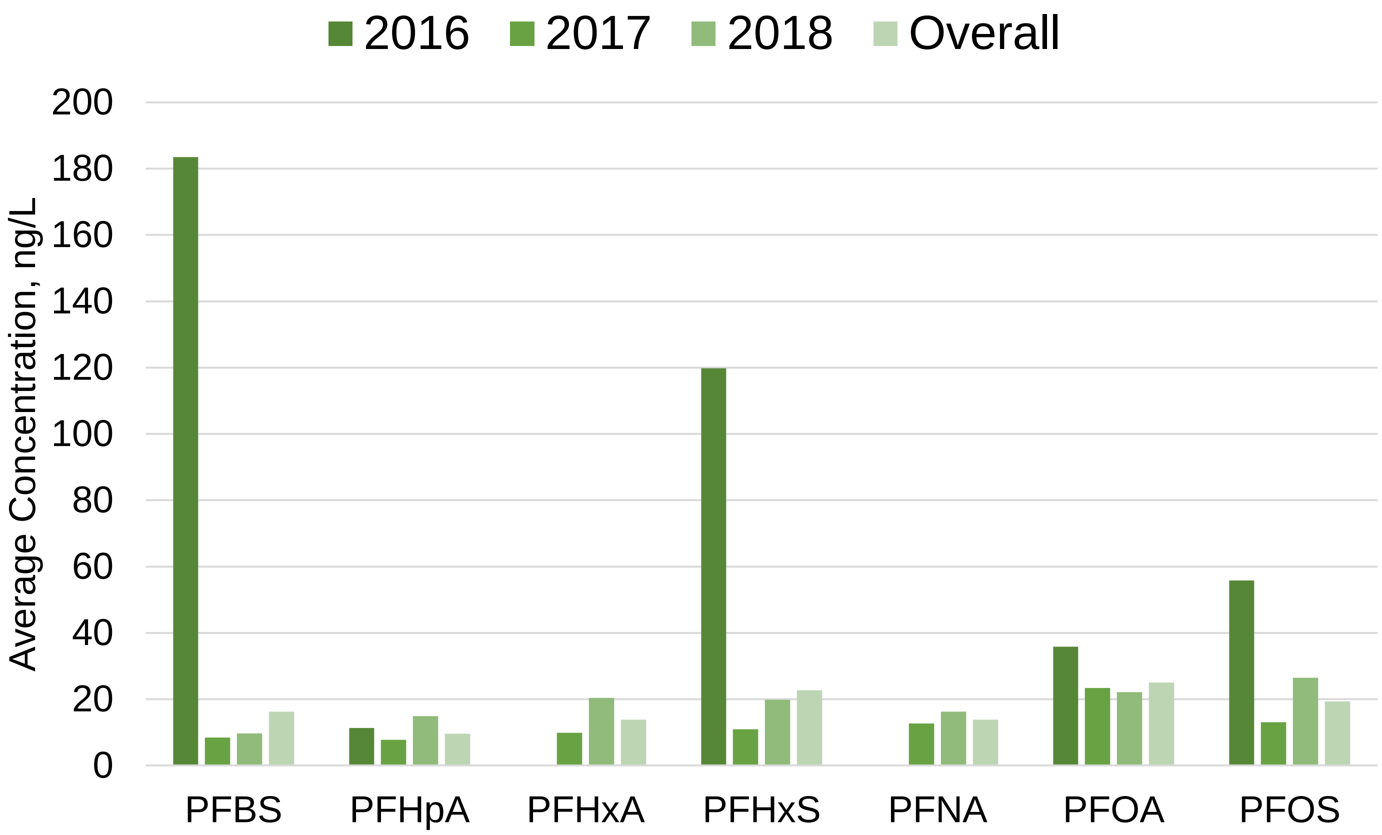
Some results – after UCMR3



PFUnA, PFDoA, PFTrDA, PFTA not detected

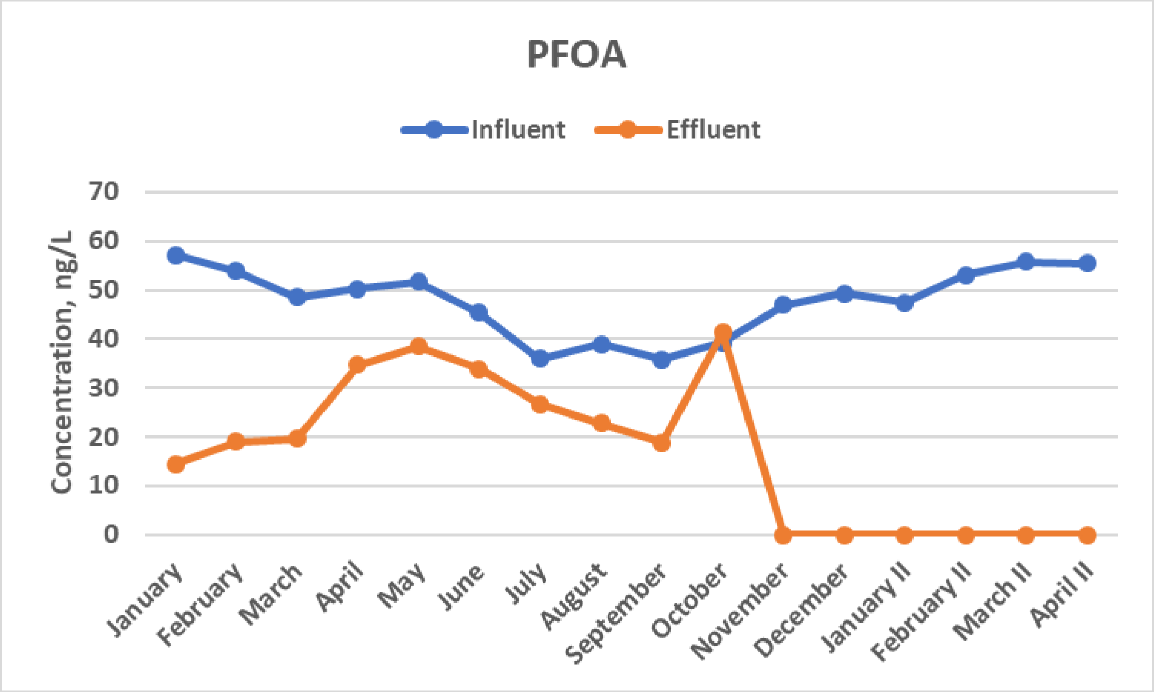
detects (1,445) represents 13% of total data

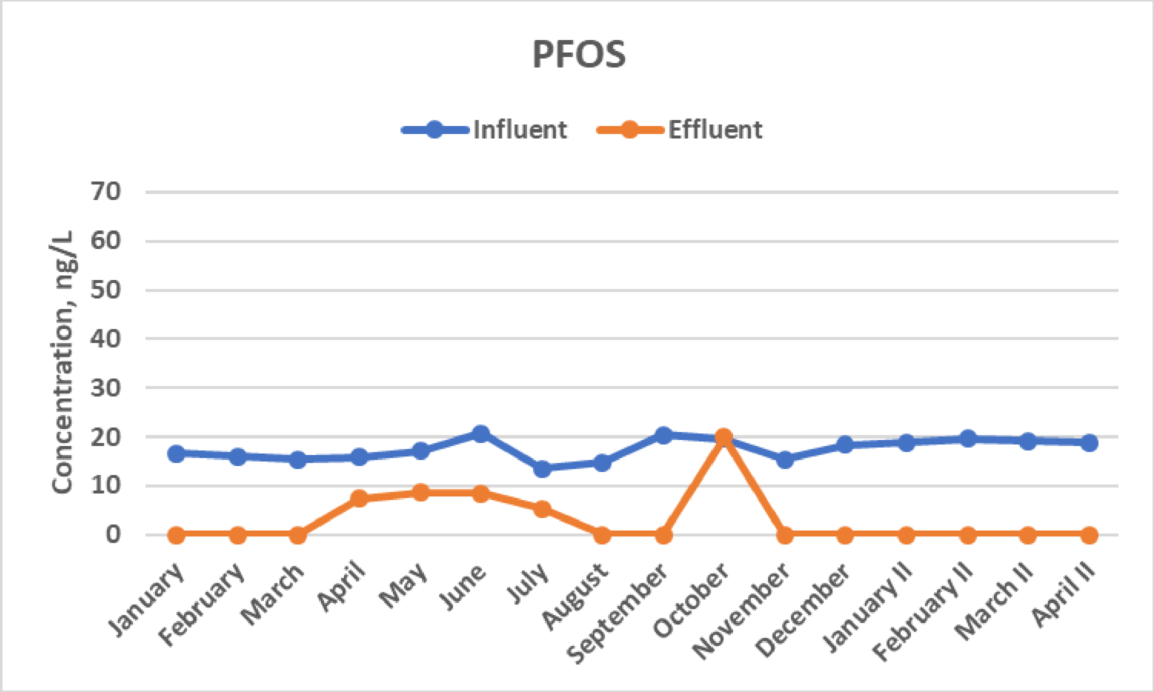
Some results – after UCMR3



		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

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

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!

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