PFAS National Drinking Water Assessment Monitoring: UCMR3 and UCMR5 Comparison

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Presentation Outline

- PFAS Introduction
- UCMR5 Introduction
- UCMR5 Detection
- UCMR5 Challenges
- Conclusions

PFAS Have Been around for a Long Time.

- PFOA & PFOS produced

- PFOS phase-out (EPA & 3M, 2002)
- Short-chain PFAS introduced
- EPA Method 537 (2008 – 2009)

- EPA's PFOA Stewardship Program (2010 – 2015)
- No buy/use PFOS (DuPont, 2013)
- Source water assessment
- PFAS treatment
- CCL3 & UCMR3 (2012 – 2016)
- EPA's lifetime HA, PFOA/PFOS = 70 ng/L (2016)
- GenX contamination (2017)
- National Leadership Summit & Engagement (2018)
- EPA Method 537.1 (2018)
- EPA Method 533 (2019)
- EPA's PFAS Action Plan (2019)

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

- Homologues produced
- AFFF implemented (1969)

- PFAS detected by LC/MS/MS

- State PFAS lists & regulations, 2009 –

- Comprehensive National Strategy to Confront PFAS Pollution (2021)
- EPA's new HAs for PFOA, PFOS, PFBS, and GenX (2022)
- Federal MCLs (2022 – 2023)?
- UCMR5 (2022 – 2026)

PFAS Drinking Water Regulations

Currently, ~ 22 States & 11 PFAS

Some regulations are more stringent than the others.



State	Regulation (Unit = ng/L)	PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	GenX	PFOSA	Sum
Alaska	Action Levels				70					70			PFOA+PFOS = 70
California	Notification Levels				5.1					6.5			
Colorado	Tranlation Levels (Water Discharge Permits)				70	70		400,000	700	70			PFOA+PFNA+PFOS = 70 (4 PFOA/PFOS precursors included)
Connecticut	Action Levels			x	x	x			x	x			PFHpA+PFOA+PFNA+PFHxS+PFOS = 70 changed to: 10 ppt PFOS. 12 ppt PFNA, 16 ppt PFOA, and 49 ppt PFHxS by 06/15/2022
Delaware	Proposed MCLs				21					14			
Illinois	Health-Based Guidance Levels		560,000		2	21		2,100	140	14	21		
Iowa	Health Advisories				70					70			PFOA+PFOS = 70
Maine	Interim MCL			x	x	x			x	x			PFHpA+PFOA+PFNA+PFHxS+PFOS = 20
Massachusetts	Established MCL			x	x	x	x		x	x			PFHpA+PFOA+PFNA+PFDA+PFHxS+PFOS = 20
Michigan	Established MCL		400,000		8	6		420	51	16	370		
Minnesota	Health-Based Values	7,000			35			2,000	?	15			
New Hampshire	Established MCLs				12	11			18	15			
New Jersey	Established MCLs				14	13				13			
New York	Established MCLs				10					10			
North Carolina	Health Advisories				70					70	140		PFOA+PFOS = 70
Ohio	Monitoring to establish action levels				70	21		140,000	140	70	700		PFOA+PFOS = 70
Oregon	Proposed Trigger Levels			10,000	500	40				20,000		0.7	
Pennsylvania	Proposed MCLs			x	14	x		x	x	18			
Rhode Island	Interim Standards			x	x	x			x	x			PFHpA+PFOA+PFNA+PFHxS+PFOS = 20
Vermont	Established MCL			x	x	x			x	x			PFHpA+PFOA+PFNA+PFHxS+PFOS= 20
Washington	Action Levels				10	9		345	65	15			
Wisconsin	Proposed MCLs				x					x			PFOA+PFOS = 20

PFAS Drinking Water Regulations (Cont'd)

- **EPA's new health advisories (June, 2022): 0.004 ng/L PFOA, 0.02 ng/L PFOS, 10 ng/L GenX/HFPO-DA, 2,000 ng/L PFBS.**
- **States with drinking water regulations for PFAS**
  - **Established/interim/proposed MCLs: NJ, NH, VT, MA, NY, WI, ME, etc.**
  - **Established NLs: CA**
  - **Proposed HBVs, ALs, or TLs: MI, MN, OH, RI, NC, OR, WA, etc.**
  - **EPA's Lifetime HA: IA, SC, etc.**

Examples:

- **Individual PFAS**

  NJ MCLs: 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

Unregulated Contaminant Monitoring Rule (UCMR)

Once every 5 years for 30 or fewer unregulated contaminants aligned with the Contaminant Candidate List (CCL)



UCMR 1
- **2001 – 2005, 26 chemicals**

UCMR 2
- **2007 – 2011, 25 chemicals**

UCMR 3
- **2012 – 2016, 28 chemicals & 2 viruses – Six high priority PFAS**

UCMR 4
- **2017 – 2021, 30 chemicals & groups**

UCMR 5
- **2022 – 2026, 30 chemicals – 29 PFAS and lithium**

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

Courtesy to EPA UCMR5 shareholder meeting presentation, 04/16/2022.

UCMR5 Sampling Requirements

SW, GU and MX PWSs: Collect 4 times (~ 3 months apart) during the year of sampling.

GW PWSs: Collect 2 times (5 – 7 months apart) during the year of sampling.

Sample Point Type Code: EP

Sample Event Codes: SE1, SE2, SE3, and SE4.

Field Reagent Blanks (FRB): Must be collected along with all samples.

Sampling Period	SW	GW	GU	MX
1st	SE1	SE1	SE1	SE1
2nd	SE2	SE2	SE2	SE2
3rd	SE3		SE3	SE3
4th	SE4		SE4	SE4

UCMR5 Assessment Monitoring Scopes

UCMR 5 Applicability to PWSs per AWIA

System[1] Size (# of people served)	National Sample: Assessment Monitoring Design	Total # of Systems per Size Category
Small Systems (25 – 3,299)	800 randomly selected systems (CWSs and NTNCWSs)	800
Small Systems (3,300 – 10,000)	All systems (CWSs and NTNCWSs)	~5,100
Large Systems (10,001 and over)	All systems (CWSs and NTNCWSs)	~4,400
TOTAL	**Totally, ~ 64,000 (60,000 – 68,000) samples.**	**~10,300**

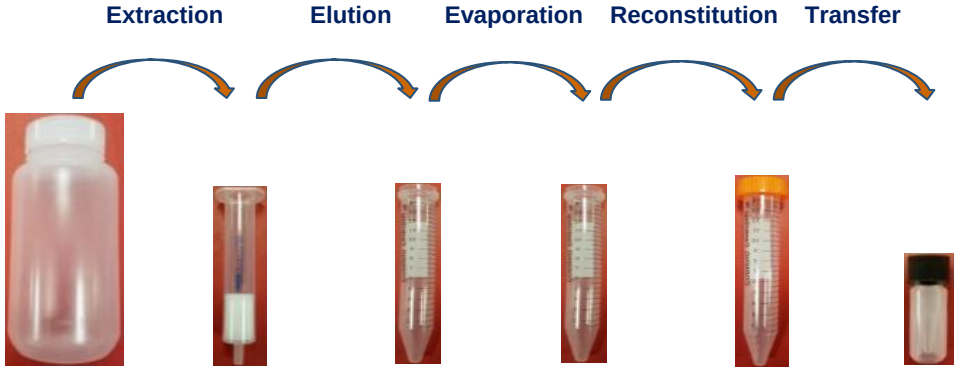
[1] Systems provide water for human consumption through pipes or other constructed conveyances to at least 15 service connections or serves an average of at least 25 people for at least 60 days a year

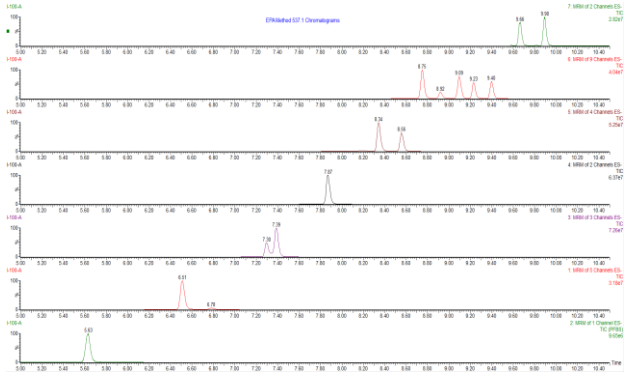
UCMR 3 PWSs
800 randomly selected small systems (CWSs and NTNCWSs) serving 10,000 or fewer people.
All large systems (CWSs and NTNCWSs) serving more than 10,000 people.
Totally, 4,920 PWSs and 36,972 samples analyzed.

UCMR5 Methods, Analytes, and MRLs (Cont'd)

EPA 533 (2 – 5 ng/L)	PFBA 5	PFPeA 3	PFHxA 3	PFHpA 3 (10 for UCMR3)	PFOA 4 (20 for UCMR3)
	PFNA 4 (20 for UCMR3)	PFDA 3	PFUnA 2	PPDoA 3	PFBS 3 (90 for UCMR3)
	PFPeS 4	PFHxS 3 (30 for UCMR3)	PFHpS 3	PFOS 4 (40 for UCMR3)	PFEESA 3
	4:2 FTS 3	6:2 FTS 5	8:2 FTS 5	HFPO-DA 5	ADONA 3
	9Cl-PF3ONS 2	11Cl-PF3OUdS 5	PFMBA 3	PFMPA 4	NFDHA 20
EPA 537.1 (5 – 8 ng/L)		MMeFOSAA 6	NEtFOSAA 5	PFTrDA 7	PFTeDA 8
EPA 200.7, SM 3120 B (2017), SM 3120 B–99 (1999), or ASTM D1976–20					Li 9 µg/L

EPA 537.1 *vs.* EPA 533 SPE–LC/MS/MS





Method	EPA 537.1	EPA 533
250 mL sample	Trizma pH 6 – 8 > 0 & ≤ 6°C 14 days	Ammonium acetate pH 6 – 8 > 0 & ≤ 6°C 28 days
SPE	Reversed-phase	Weak anion change
1 mL extract	96% MeOH/water Room Temp. 28 days	80% MeOH/water Room Temp. 28 days
IS / IPS	Internal standards	Isotope performance standards
SS / IDA	Surrogate standards	Isotope dilution analogues
Calibration	Internal standard calibration	Isotope dilution calibration
QC	UCMR 5	UCMR 5

Anticipate much higher PFAS detection frequencies in UCMR5.

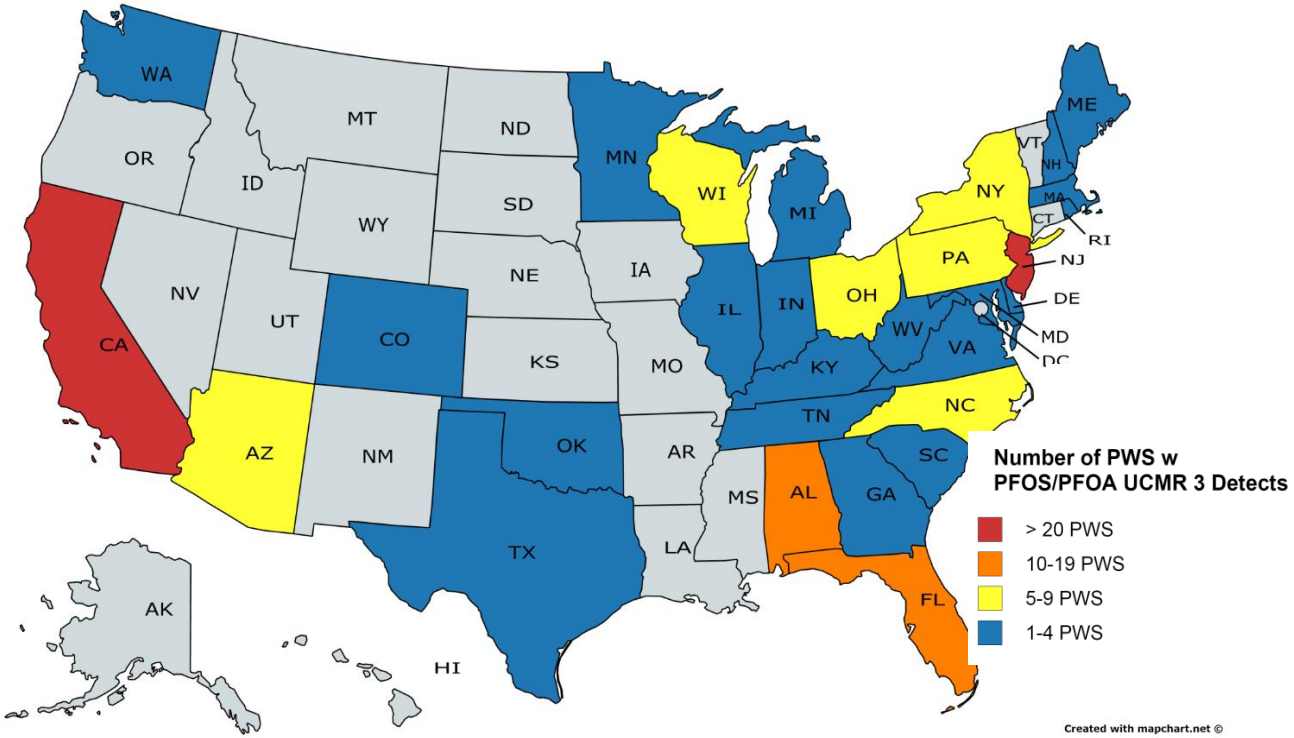
UCMR3 Frequency of Detection

(~37,000 samples, ~4,920 PWS)

Ananlyte	UCMR3 MRL (ng/L)	UCMR3 NCOD % of Results (≥ UCMR3 MRL)	UCMR3 NCOD % of PWS (≥ UCMR3 MRL)
PFBS	90	0.05	0.2
PFHxS	30	0.6	1.1
PFOS	40	0.8	1.9
PFHpA	10	0.6	1.7
PFOA	20	1.0	2.4
PFNA	20	0.05	0.3
Overall	---	1.6 (0.4% > HA of 70 ng/L)	3.3 (1.5% > HA of 70 ng/L)

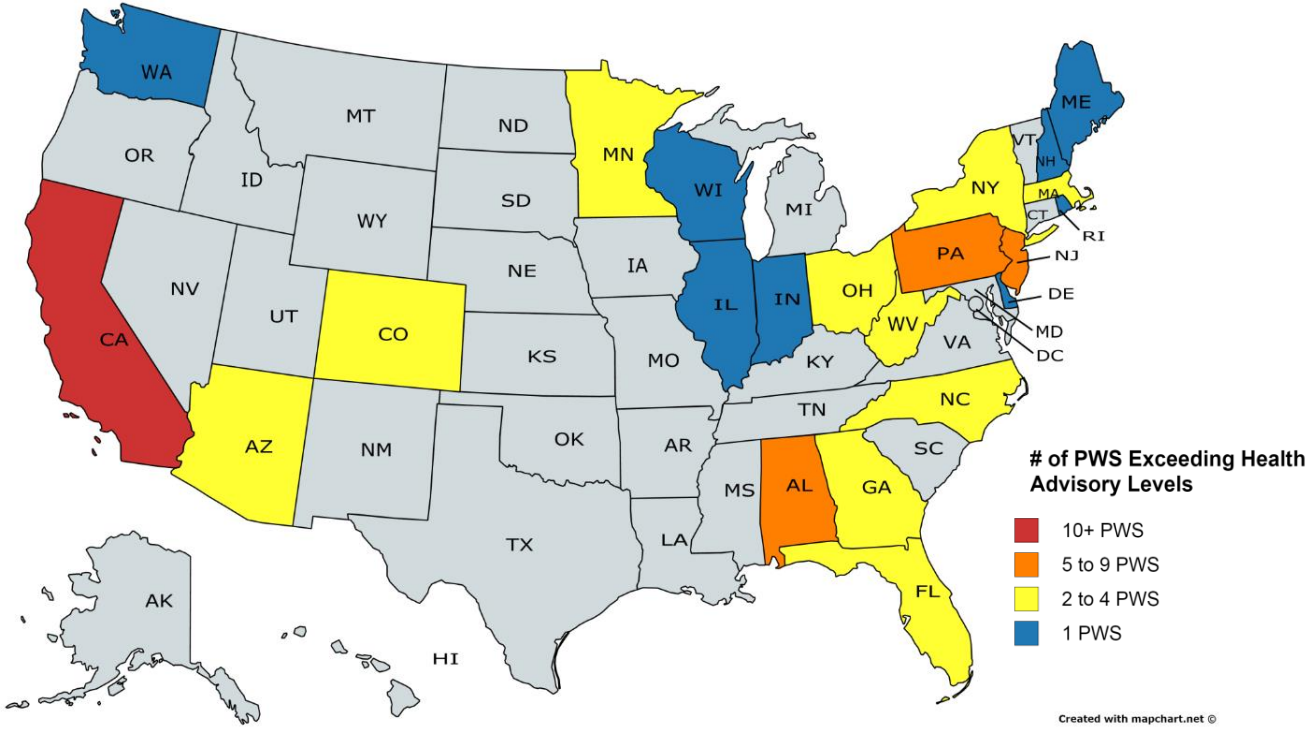
NCOD = National Contaminant Occurrence Database

UCMR3 NCOD: 36 States/Territories with Detection of One or More PFAS



Plus AS, GU, MP and PR

UCMR3 NCOD: 24 States/Territories with Detection of PFOS/PFOA HA (70 ng/L) Exceedances



How Can We Estimate UCMR5 Detection Frequencies Using UCMR3 Data?

- EEA accounted for ~30% of the UCMR3 PFAS data.
- EEA's in-house MRLs were significantly lower than the UCMR3 required MRLs for all six UCMR3 PFAS.
- We re-examined all of our data, censoring at 5 and 2.5 ng/L for all six UCMR3 PFAS.
- We compared detection frequencies and states with significant detections.
- Then, we could review the pattern changed when the MRLs were reduced.

How Representative Are Our Subset of UCMR3 Data?

Factor	Overall UCMR3 NCOD Data	EEA Subset of UCMR3 Data
# of Samples	~ 37,000	~ 10,500
# of PWS	~ 4920	~ 1100
% of PWS with UCMR 3 Detection	3.3%	5.3%
% of PWS with HA Exceedance	1.5%	1.8%
# of States/Territories with Results	All	All
# of States/Territories with Detection	36	27
# of States/Territories with HA Exceedance	24	18

Comparison of Detection Frequencies by UCMR3 Sample Numbers

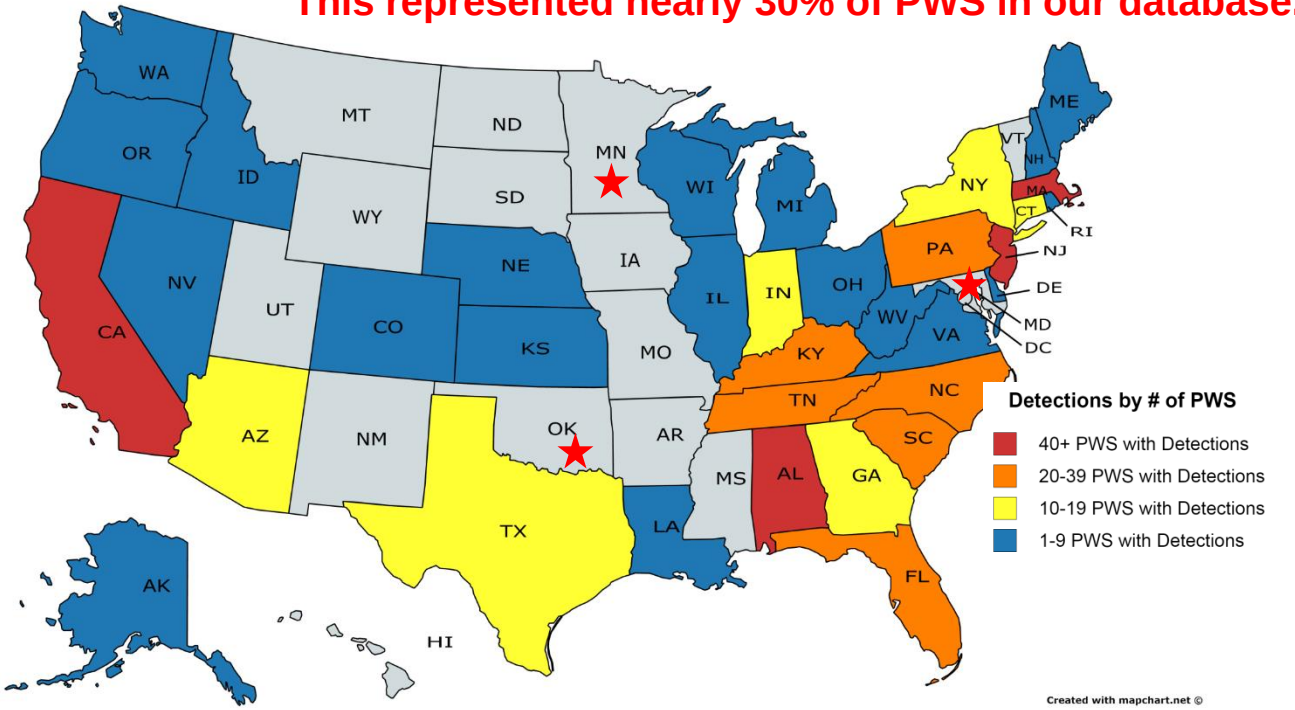
Analyte	NCOD Results with Detection (UCMR3 MRL)	EEA Subset Data Results ≥ UCMR3 MRL	EEA Subset Data Results ≥ 5 ng/L	EEA Subset Data Results ≥ 2.5 ng/L
Sample #	~37,000	~10,500	~10,500	~10,500
PFBS	0.05%	0.2%	5.3%	11.9%
PFHxS	0.6%	1.0%	6.0%	12.3%
PFOS	**0.8%**	**1.3%**	**11.5%**	**20.5%**
PFHpA	0.6%	1.5%	3.3%	8.8%
PFOA	**1.0%**	**1.8%**	**12.5%**	**23.5%**
PFNA	0.05%	0.1%	0.6%	1.9%

Overall ~20% detections ≥ UCMR 5 MRLs.

EEA UCMR3 Data: 40 States/Territories, 511 PWS Detected with PFAS at ≥ 5 ng/L



This represented nearly 30% of PWS in our database.



Plus AS, GU, MP and PR

Plus 3 more states (MN, KS, MD) with NCOD detections but insufficient EEA data

How Can We Estimate UCMR5 Detection Frequencies Using Post-UCMR3 Data?

- EEA in-house MRLs of both EPA 537.1 and 533 were equal to or lower than the UCMR5 required MRLs for all 29 PFAS.
- We selected a fixed period of the drinking water results and re-examined all the data, censoring at the UCMR5 required MRLs.
- The data sets included over 10,000 EPA 537.1 samples and approximately 1000 EPA 533 samples.
- We then determined the detection frequencies.

EEA Post-UCMR3 Data: 17 PFAS were not detected or detected in <1% DW samples.

Analyte	UCMR5 MRL (ng/L)	% of Results (≥ UCMR5 MRL)	Analyte	UCMR5 MRL (ng/L)	% of Results (≥ UCMR5 MRL)
PFDA	3	~ 0.5 (0.5)	11Cl-PF3ONS	5	~ 0.0 (0.0)
PFUnA	2	~ 0.2 (0.6)	9Cl-PF3ONS	2	~ 0.2 (0.1)
PFDoA	3	~ 0.5 (0.2)	NFDHA	20	~ 0.2
PFTrDA	7	~ (0.1)	PFEESA	3	~ 0.2
PFTeDA	8	~ (0.1)	PFMPA	4	~ 0.7
NMeFOSAA	6	~ (0.1)	PFMBA	3	~ 0.5
NEtFOSAA	5	~ (0.3)	4:2 FTS	3	~ 0.6
HFPO-DA	5	~ 0.4 (0.4)	8:2 FTS	5	~ 0.9
ADONA	3	~ 0.2 (0.0)			

EPA 537.1 results in parentheses.

EEA Post-UCMR3 Data: 12 PFAS were detected in ≥1% DW samples.

Analyte	UCMR5 MRL (ng/L)	% of Results (≥ UCMR5 MRL)
PFBS	3	~ 24 (16)
PFHxS	3	~ 28 (16)
PFHpA	3	~ 12 (13)
PFOA	4	~ 22 (25)
PFOS	4	~ 30 (20)
PFNA	4	~ 1.1 (2.6)
PFBA	**5**	**~ 20**
PFPeA	**3**	**~ 33**
PFPeS	4	~ 3.9
PFHxA	**3**	**~ 30 (22)**
PFHpS	3	1.1
6:2 FTS	5	~ 2.5

EPA 537.1 results in parentheses.

Post-UCMR3 Data: PFOA & PFOS Detected with HA Exceedance

Analyte	UCMR3 MRL (ng/L)	UCMR3 % of Results	UCMR5 MRL (ng/L)	Post-UCMR3 % of Results
PFOA	20	0.09 (> HA of 70 ng/L)	4	~ 0.7 (1.0) (> HA of 70 ng/L)
PFOS	40	0.3 (> HA of 70 ng/L)	4	~ 2.6 (1.1) (> HA of 70 ng/L)
PFOA & PFOS		0.4 (> HA of 70 ng/L)		~ 3.2 (2.5) (> HA of 70 ng/L)
PFOA			4	~ 37 (37) (≥ 2.0 ng/L)
PFOS			4	~ 38 (31) (≥ 2.0 ng/L)
PFBS			3	~ 0.2 (0) (> HA of 2,000 ng/L)
HFPO-DA			5	~ 0 (0.2) (> HA of 10 ng/L)

EPA 537.1 results in parentheses.

Estimated Overall PFAS Detections in UCMR5

	EPA 533	EPA 537.1
Total Sample #	~ 64,000	~ 64,000
Total PWS #	~ 10,300	~ 10,300
Results ≥ UCMR5 MRL	~ 20 ± 10%	< 0.5%
PWS ≥ UCMR5 MRL	~ 20 ± 10%	< 0.5%
States/Territories ≥ UCMR5 MRL	~ 100%	< 0.5%
Results > EPA's New HAs	All detected PFOS & PFOS	NA
PWS > EPA's New HAs	All detected PFOS & PFOS	NA
# of FRBs Analyzed	~ 20 ± 10%	< 0.5%

Challenge #1: Meet IDA and SS Limits.

- UCMR5 requires passing 50–200% recoveries for EPA 533 IDAs and 70–130% recoveries for EPA 537.1 SS.
- Compared with sulfonic acid IDAs (e.g., PFOS pKa = -3.7), carboxylic acid IDAs are less acidic (e.g., PFOA pKa = 3.8) and more sensitive to the SPE procedures. Slightly lower recoveries were observed for labeled carboxylic acid IDAs likely due to high inorganic salts, hardness and alkalinity.
  - Inorganic salts up to 250 mg/L chloride, 250 mg/L sulfate, and 340 mg/L hardness measured as $CaCO_3$.
- SS-NEtFPSAA-d5 is a long-chain PFAS and has a strong tendency to surface adsorption losses, Li et al. AWWA Wat Sci. 2020; e1234.
- IDA/SS failures may result in a handful of resampling for UCMR5.

Challenge #2: Meet FRB Limits.

- FRBs of > 0.7 ng/L (i.e., 1/3 of MRL 2.0 ng/L) were extremely rare. Most UCMR5 MRLs are > 2 ng/L. Therefore, FRB contamination should not be a major concern.
- The most common FRB issue was due to mislabeling or switching FRB bottles with field sample bottles in the sampling field.
- This problem can be often resolved by re-extracting the other associated bottle(s) if it is permissible.
- Otherwise, the need for resampling is anticipated for UCMR5.

Challenge #3: Meet Reporting Deadlines.

	UCMR3	UCMR5
Laboratories	Must approve analytical results in SDWAS within 120 days from the sample collection date.	Must approve analytical results in SDWAS within 90 days (60 days for small PWS) from the sample collection date.
PWSs	Must review and approve the data posted to SDWARS within 60 days.	Large PWS must review and approve the data posted to SDWARS within 30 days.

Conclusions

- Estimated approximately 12 PFAS likely detected in UCMR5 samples, 17 PFAS not detected or detected in <1% UCMR5 samples.
- Estimated PFAS detections in approximately all states, ~20±10% samples and ~20±10% participating PWS in UCMR5.
- Most frequently detected PFAS may include PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS.
- Expect to have a handful of sample recollection due to various reasons.
  - EPA 533 IDA & EPA 537.1 SS failures
  - FRB/FS bottles switched
  - Sample pH and chlorine verification failures

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