



PFAS National Drinking Water Assessment Monitoring: UCMR3 and UCMR5 Comparison

Yongtao (Bruce) Li
Eurofins Eaton Analytical, LLC

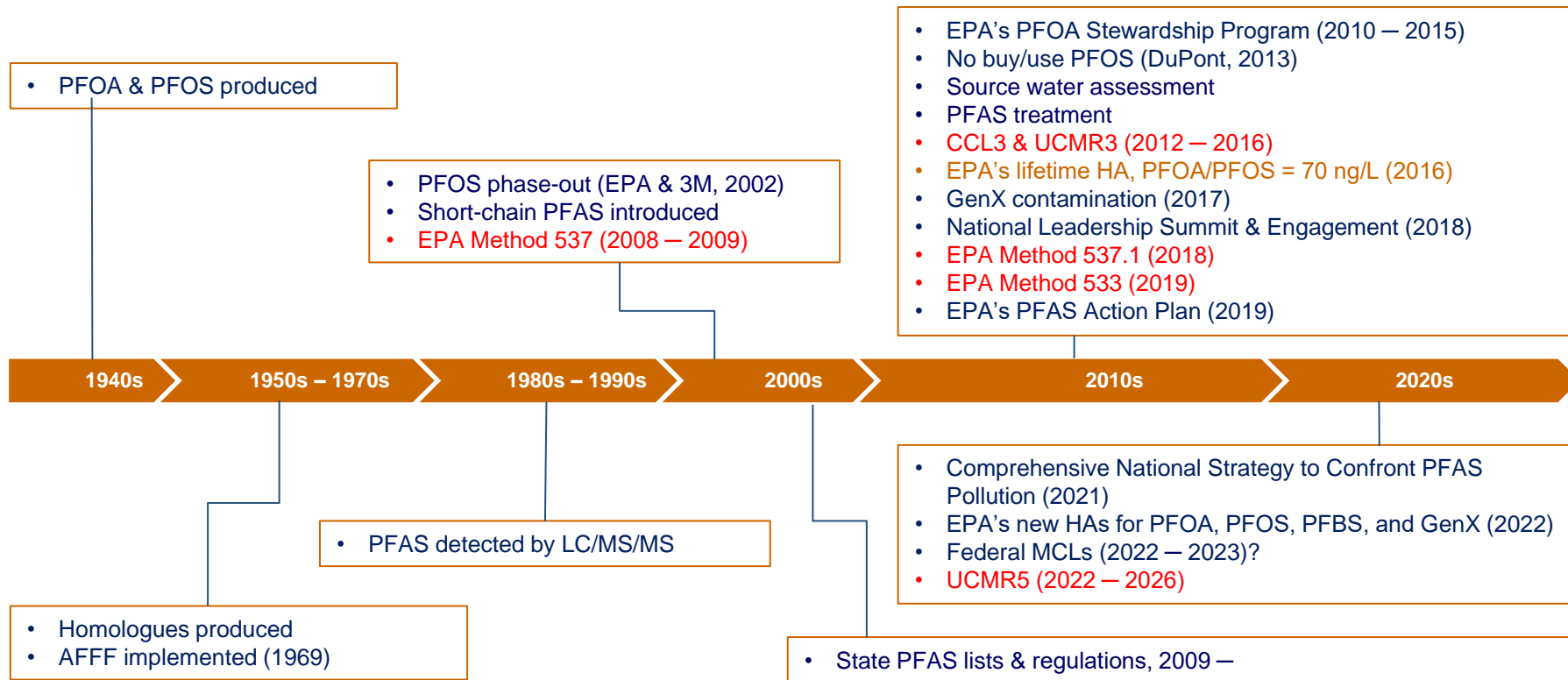


Presentation Outline



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

PFAS Have Been around for a Long Time.



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 |



- 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 <ul style="list-style-type: none"> Manage Lab Approval Program Organize Partnership Agreements and State Monitoring Plans Begin PWS SDWARS registration/inventory Review GWRMP submittal Conduct outreach/trainings | Sampling Period <div> <div>←</div> <div>EPA Implementation Activities</div> <div>→</div> </div> <ul style="list-style-type: none"> Provide compliance assistance Implement small system monitoring Post data quarterly to NCOD PWS Sample Collection; Laboratory Analysis; Reporting <ul style="list-style-type: none"> 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 <ul style="list-style-type: none"> Complete resampling, as needed Conclude data reporting EPA <ul style="list-style-type: none"> Complete upload of UCMR 5 data to NCOD |

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 |
|-----------------|-----|-----|-----|-----|
| 1 st | SE1 | SE1 | SE1 | SE1 |
| 2 nd | SE2 | SE2 | SE2 | SE2 |
| 3 rd | SE3 | | SE3 | SE3 |
| 4 th | 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)

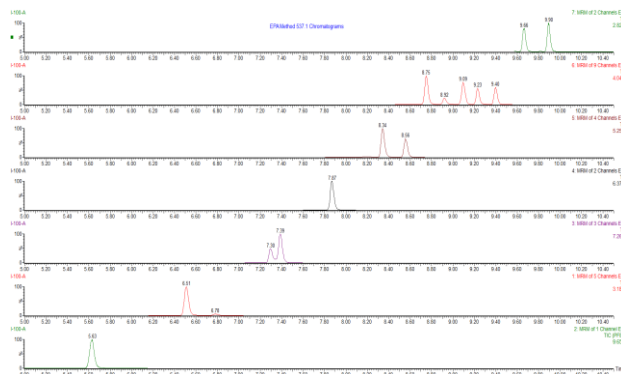
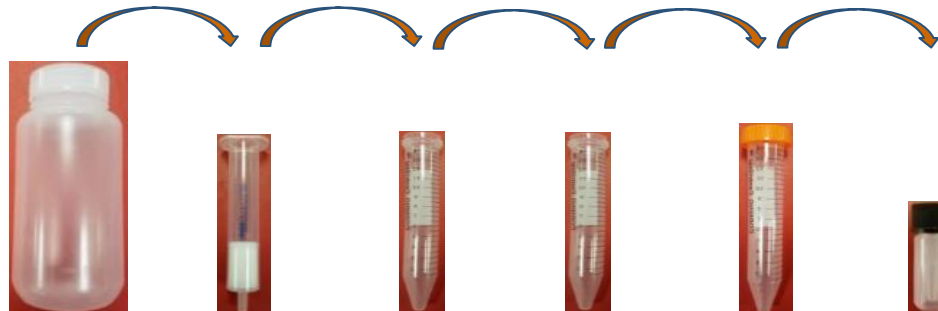


| | | | | | |
|--|--------------------------|---------------------------|---------------|---------------------------|--------------------------|
| EPA 533 (2 – 5 ng/L) | PFBA 5 | PFPeA 3 | PFHxA 3 | PFHpA 3 (10 for UCMR3) | PFOA 4 (20 for UCMR3) |
| | PFNA 4 (20 for UCMR3) | PFDA 3 | PFUnA 2 | PPDoA 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 |
| | 9CI-PF3ONS 2 | 11CI-PF3OUdS 5 | PFMBA 3 | PFMPA 4 | NFDHA 20 |
| EPA 537.1 (5 – 8 ng/L) | | MMeFOSAA 6 | NEtFOSAA 5 | PFTTrDA 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



Extraction Elution Evaporation Reconstitution Transfer



| 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.**

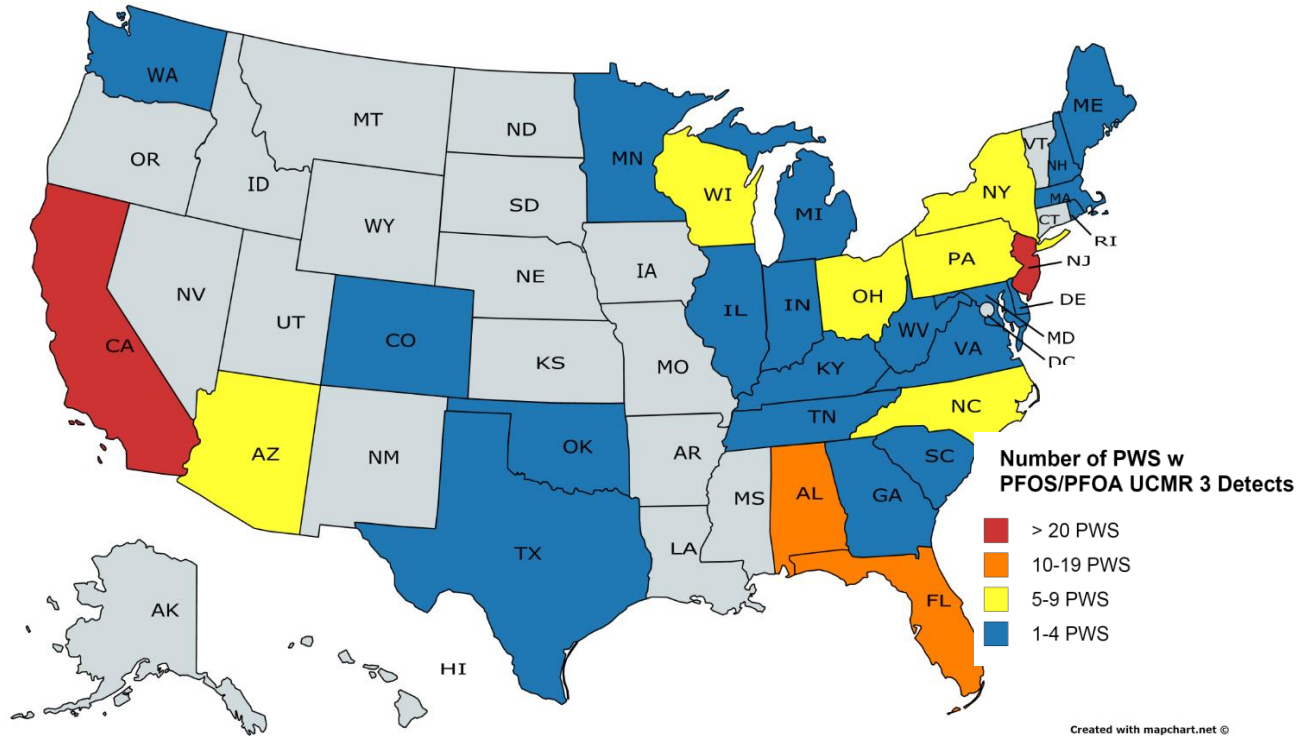
UCMR3 Frequency of Detection

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

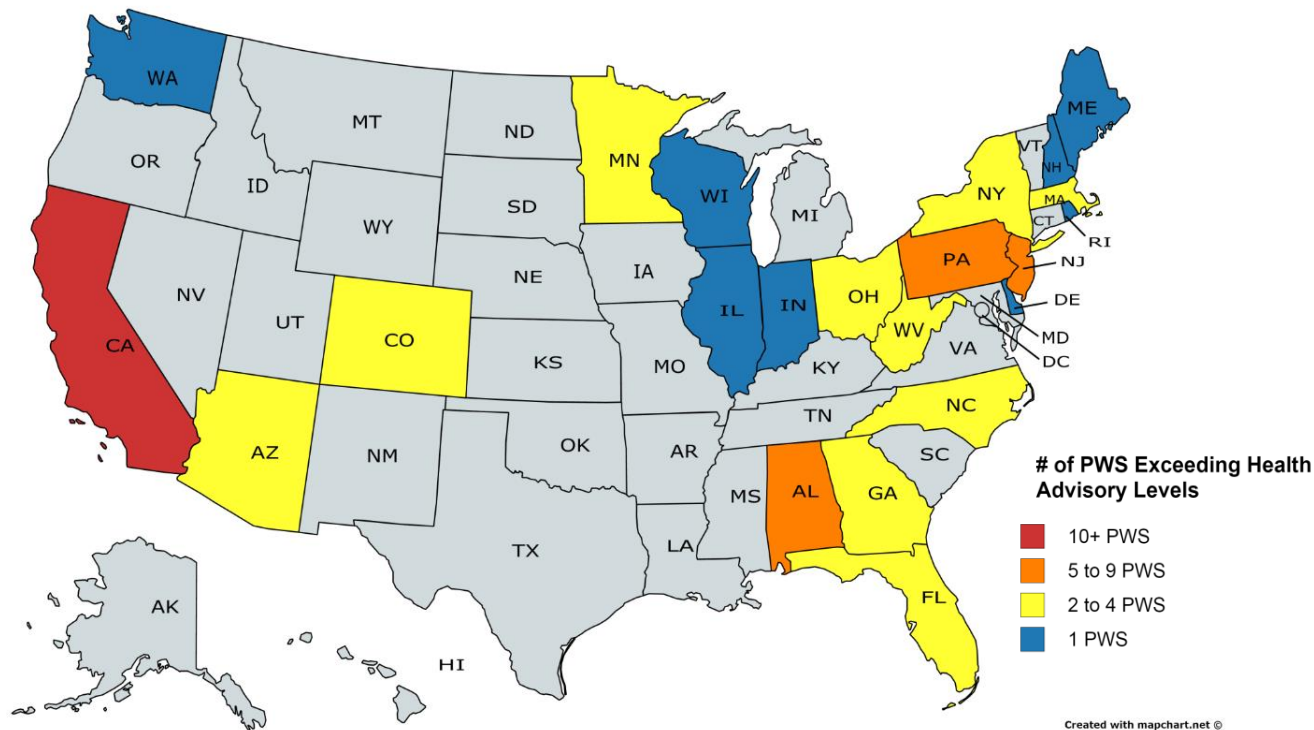


| Analyte | UCMR3 MRL (ng/L) | UCMR3 NCOD % of Results (≥ UCMR3 MRL) | UCMR3 NCOD % of PWS (≥ UCMR3 MRL) |
|---------|------------------|---|---|
| PFBS | 90 | 0.05 | 0.2 |
| PFHxS | 30 | 0.6 | 1.1 |
| PFOS | 40 | 0.8 | 1.9 |
| PFHpA | 10 | 0.6 | 1.7 |
| PFOA | 20 | 1.0 | 2.4 |
| PFNA | 20 | 0.05 | 0.3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

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



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

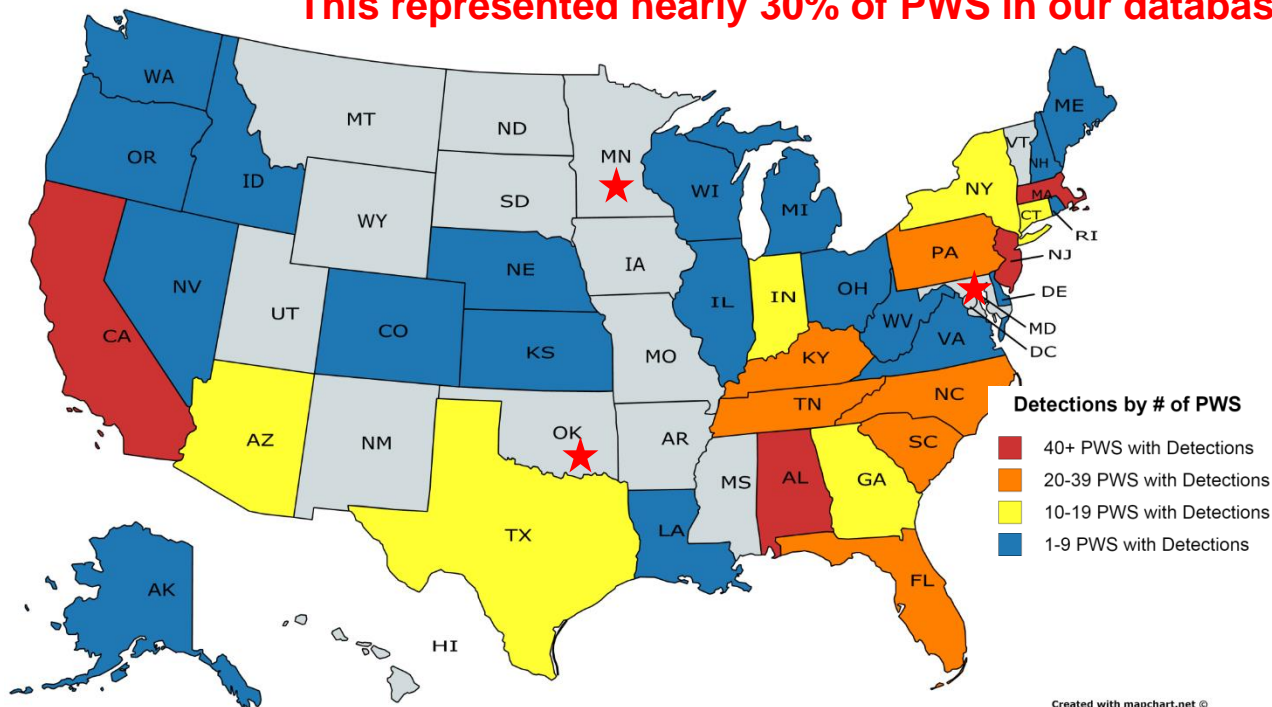


| Analyte | NCOD Results with Detection (UCMR3 MRL) | EEA Subset Data Results \geq UCMR3 MRL | EEA Subset Data Results \geq 5 ng/L | EEA Subset Data Results \geq 2.5 ng/L |
|-------------|---|--|---------------------------------------|---|
| Sample # | ~37,000 | ~10,500 | ~10,500 | ~10,500 |
| PFBS | 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% |

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) | 11CI-PF3ONS | 5 | ~ 0.0 (0.0) |
| PFUnA | 2 | ~ 0.2 (0.6) | 9CI-PF3ONS | 2 | ~ 0.2 (0.1) |
| PFDaA | 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) | | | |

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



| Analyte | UCMR5 MRL (ng/L) | % of Results (\geq 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 |

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) |

Estimated Overall PFAS Detections in UCMR5



| | EPA 533 | EPA 537.1 |
|-------------------------------------|--------------------------|-----------|
| Total Sample # | ~ 64,000 | ~ 64,000 |
| Total PWS # | ~ 10,300 | ~ 10,300 |
| Results \geq UCMR5 MRL | ~ 20 \pm 10% | < 0.5% |
| PWS \geq UCMR5 MRL | ~ 20 \pm 10% | < 0.5% |
| States/Territories \geq 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 \pm 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 $pK_a = -3.7$), carboxylic acid IDAs are less acidic (e.g., PFOA $pK_a = 3.8$) 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, $\sim 20 \pm 10\%$ samples and $\sim 20 \pm 10\%$ 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



Yongtao (Bruce) Li
Yongtao.Li@ET.EurofinsUS.com
574.472.5562

Eurofins Eaton Analytical, LLC
www.EurofinsUS.com/Env