Clean Water Act Methods

Overview of the EPA's CWA PFAS Method Activities

Adrian Hanley and S. Bekah Burket, Ph.D.
EPA OW/OST/Engineering and Analysis Division

Toxic Contaminants Workgroup Meeting June 12, 2024

The views expressed in this presentation are those of the author(s) and do not necessarily represent the views or policies of the Agency. Any mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.

EPA Offices that publish most analytical methods

- Office of Air and Radiation (OAR)
  - Office of Air Quality Planning and Standards (OAQPS): Clean Air Act
    - Stationary Source Methods
    - Ambient Air Methods
- Office of Water (OW)
  - Office of Science and Technology (OST)
    - Clean Water Act Methods
  - Office of Groundwater and Drinking Water (OGWDW):
    - Safe Drinking Water Act Methods
- Office of Land and Emergency Management (OLEM)
  - Office of Resource Conservation and Recovery (ORCR)
    - Resource Conservation and Recovery Act Methods (SW-846)
- Other important EPA sources of methods:
  - Office of Research and Development, EPA Regional Laboratories
  - Office of Chemical Safety and Pollution Prevention

Recently published EPA white paper, available at: https://www.epa.gov/system/files/documents/2023-09/TERMS%20USED%20TO%20DESCRIBE%20THE%20STANDING%20OF%20US%20EPA%20METHODS.PDF

CWA Analytical Methods Program

- Many industries and municipalities are permitted to discharge pollutants under the CWA NPDES
- They use analytical methods to analyze the chemical, physical, and biological components of wastewater and other environmental samples for monitoring compliance
- CWA requires that EPA establish test procedures to measure pollutants for CWA programs through rulemaking, including taking public comments
- EPA promulgates test procedures in 40 CFR Part 136. A method is approved for national use in NPDES permits when it is promulgated.



EPA's CWA Methods Team

Kevin Tingley– Branch Chief and Manager for method activities in the Engineering and Analysis Division

Team Members:

Adrian Hanley – Methods Team Leader, Chemist

Lemuel Walker – National ATP Coordinator, Chemist

Bekah Burket – Chemist

Tracy Bone – Microbiology Lead, Microbiologist

Meghan Hessenauer – Whole Effluent Toxicity Lead, Biologist

Method 1633

"Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS"

PFAS Method 1633 Validation

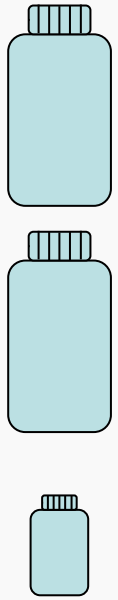
- Based on an SOP originally developed by SGS AXYS
- Partnership with Department of Defense's (DoD) Strategic Environmental Research and Development Program
  - DoD funded and managed both single and multi-laboratory validation studies of the method, EPA OW and OLEM are provided review
- The goal was to provide EPA OW with the documentation needed to consider publication of this method as a CWA method
  - OLEM plans to leverage the validation data to support an SW-846 method

PFAS Method 1633 Validation

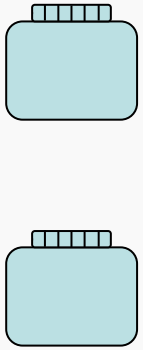
- Targeted method with 40 analytes
- Method validation included:
  - Wastewater (7 sources: POTWs and industrial dischargers), surface water (3 sources: freshwater lake, freshwater creek, saltwater bay), groundwater (3 sources)
  - Soil (TN, MN, NM)
  - Sediment (freshwater silty-sand, freshwater sandy, and marine silty-sand)
  - Landfill leachate, biosolids
  - tissue (freshwater and marine fish, and clams)

PFAS Method 1633 Validation

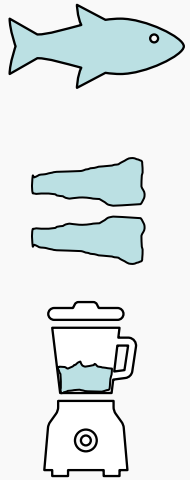
- Solid-phase extraction isotope dilution method
- Analysis by LC-MS/MS



- 500 mL
- 28 days @ 0-6˚ C
- 90 days @ ≤ -20˚ C
- Measure TSS
- Invert sample to homogenize
- Sample volume determined by weight
- Spike with EIS
- Check pH
- Ready for SPE
- ~1 mL of extract for analysis



- 5 g dry weight (soil and sediment)
- 0.5 g dry weight (biosolids)
- 90 days @ 0-6˚ C or ≤ -20˚ C
- Measure % solids
- Mix with stainless steel spoon
- Remove rocks, invertebrates, foreign objects
- Transfer to centrifuge tube
- Spike with EIS
- Solvent extraction and first carbon cleanup
- Evaporation and reconstitution
- Ready for SPE and cleanup
- ~1 mL of extract for analysis

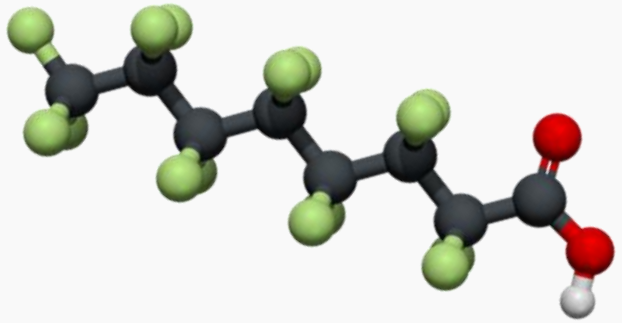


- 2 g homogenized tissue
- 90 days @ ≤ -20˚ C
- Transfer to centrifuge tube
- Spike with EIS
- Solvent extraction and first carbon cleanup
- Evaporation and reconstitution
- Ready for SPE and cleanup
- ~1 mL of extract for analysis

PFAS Method 1633 Validation

- Multi-Laboratory Validation
  - Final Method 1633 and the Multi-Laboratory Validation Study Report posted on January 31, 2024

    https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas
  - Included 10 participant laboratories, referee laboratory, data validators, and statisticians
  - The Multi-Laboratory Validation Report is available in 4 volumes, by matrix



PFAS Method 1633 Validation

- Method Detection Limit – Blank Calculation (MDL_b)
  - MDL_b values rarely impacted the MDL for any laboratory
  - The pooled MDL values were almost entirely calculated from the MDL_s values
- Pooled Method Detection Limit (MDL)
  - Most aqueous values were below 1 ng/L
  - The highest were NMeFOSE - 3.8, NEtFOSE - 4.8, 7:3FTCA - 8.7, and 5:3 FTCA - 9.6
  - Leachate MDLs are assumed to be about 10 times higher
  - Most of the solid MDLs were below 0.2 ng/g
  - The highest were 5:3 FTCA – 0.86 ng/g, and 7:3 FTCA – 0.87 ng/g
  - Biosolid MDLs are assumed to be about 5 times higher
  - Most of the tissue MDLs were below 0.4 ng/g
  - The highest were NEtFOSE – 1.77, 7:3FTCA – 2.38, and 5:3 FTCA – 2.02

PFAS Method 1633 Validation

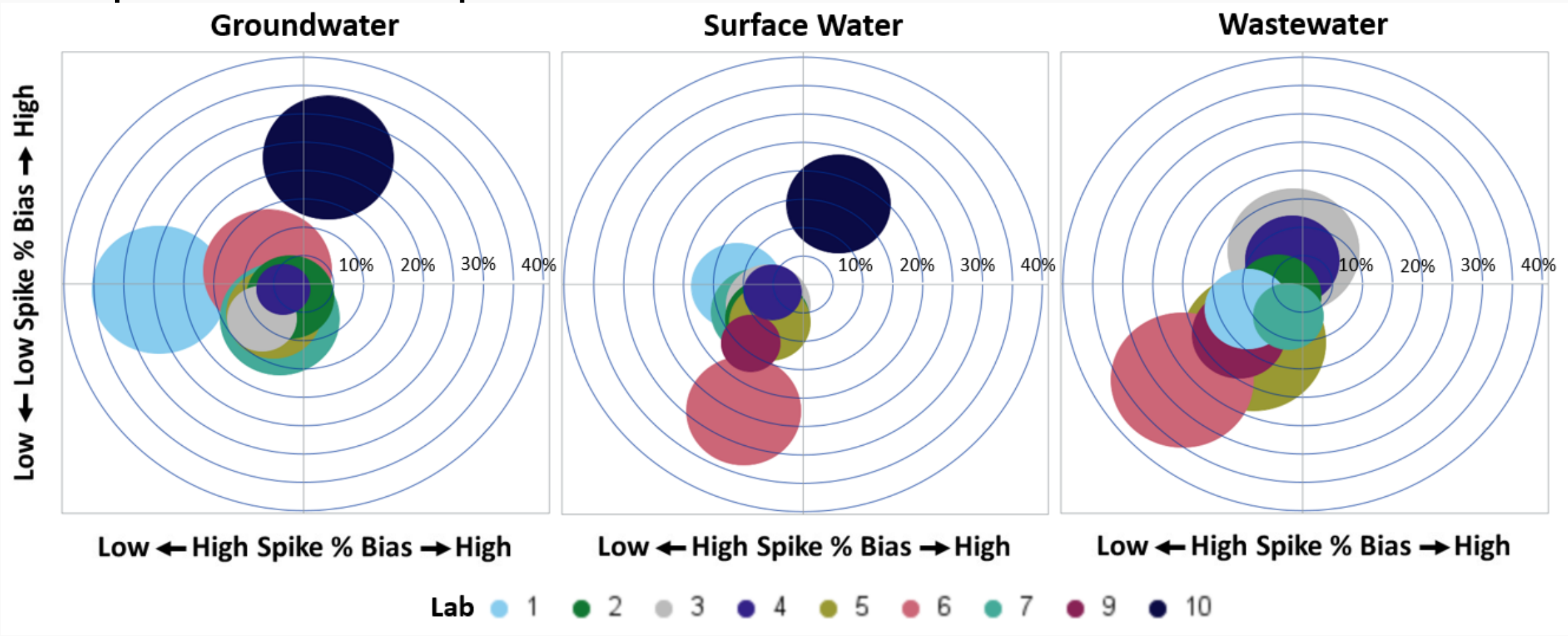
- Ongoing Precision and Recovery (OPR) Low-Level OPR (LLOPR)
  - The performance was about the same for the OPR and LLOPR, so the data were combined and used to develop a single set of criteria
  - Most criteria are inclusive of the highest and lowest observed data point from all 10 laboratories
  - No criteria are more stringent than 70-130%
  - The vast majority of the analytes were able to meet a 50-150% criteria for OPR and LLOPR analysis

PFAS Method 1633 Validation

- 24 Extracted Internal Standards (EIS)
  - Single set of EIS criteria made from only matrix samples (no blank spikes)
  - Used a non-parametric approach (p1 and p99) and professional judgement (e.g., eliminate the EIS compound recoveries from 1 to 2 laboratories for a specific parameter)
  - No criteria are more stringent than 40-130%
  - Lower aqueous limits: 15 at 40%, 1 at 30% ($^{13}C_7$-PFUnA), 1 at 25% (D_5-NEtFOSAA), 6 at 10% ($^{13}C_2$-PFDoA, $^{13}C_2$-PFTeDA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE, and D_9-NEtFOSE), and 1 at 5% ($^{13}C_4$-PFBA)
  - Upper aqueous Limits: 17 at 130%, 3 at 135%, 1 at 170% (D_3-NMeFOSAA), 2 at 200% ($^{13}C_2$-4:2FTS and $^{13}C_2$-6:2FTS), and 1 at 300% ($^{13}C_2$-8:2FTS)
  - The trends were similar for the other matrices. Fish tissue was the most challenging matrix.

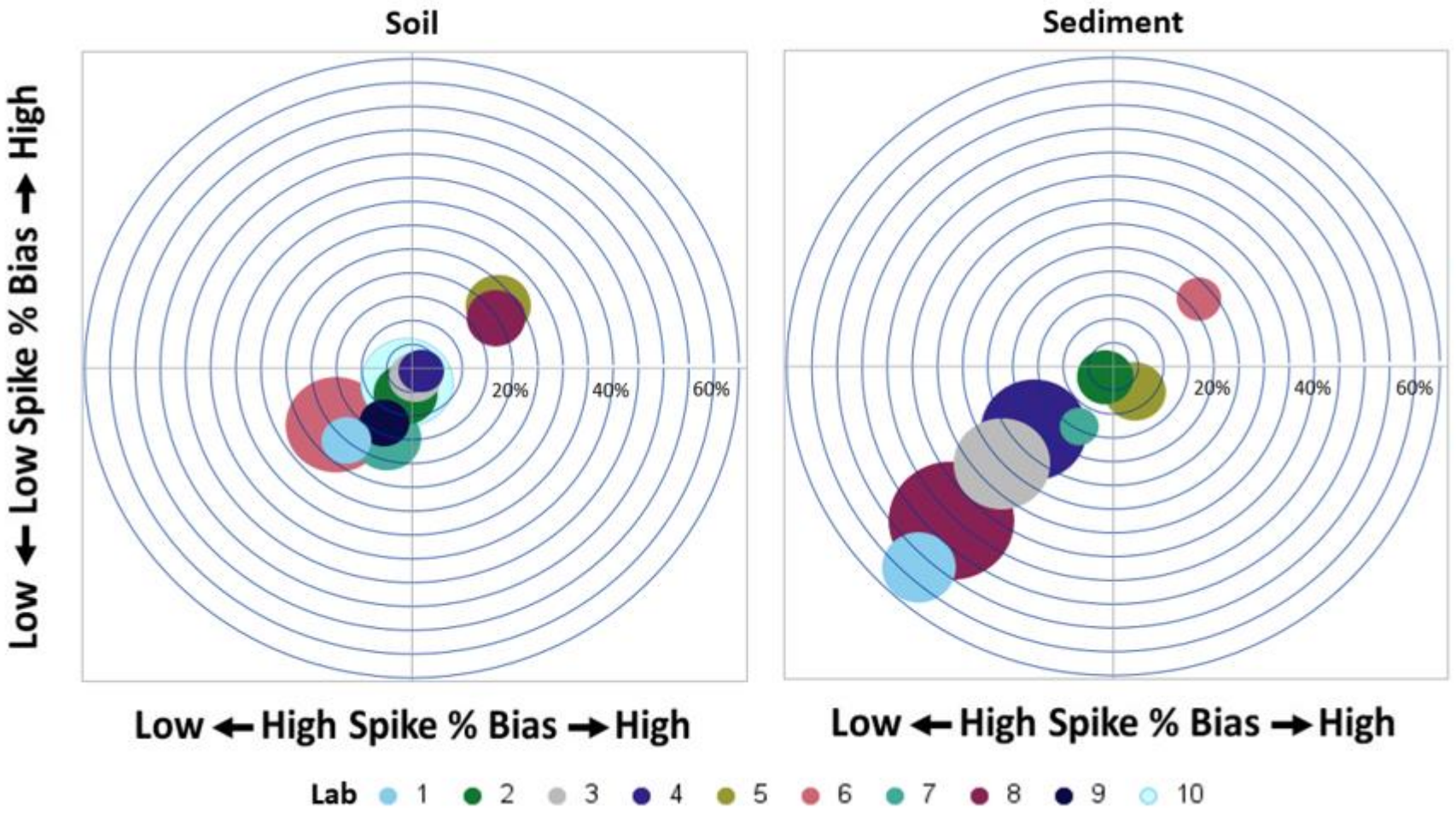
PFAS Method 1633 Validation

- Aqueous Matrix Spike Results



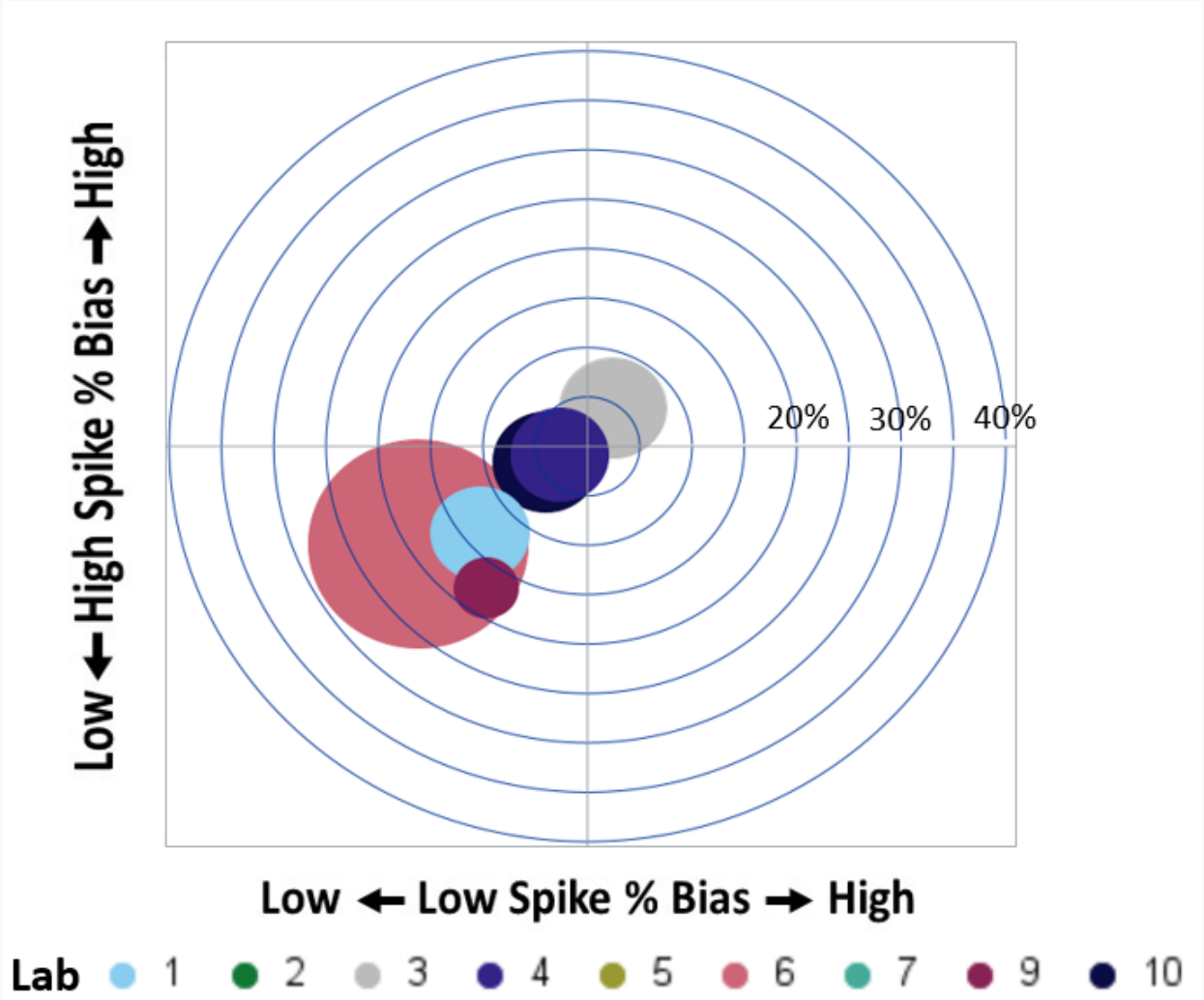
PFAS Method 1633 Validation

- Solid Matrix Spike Results



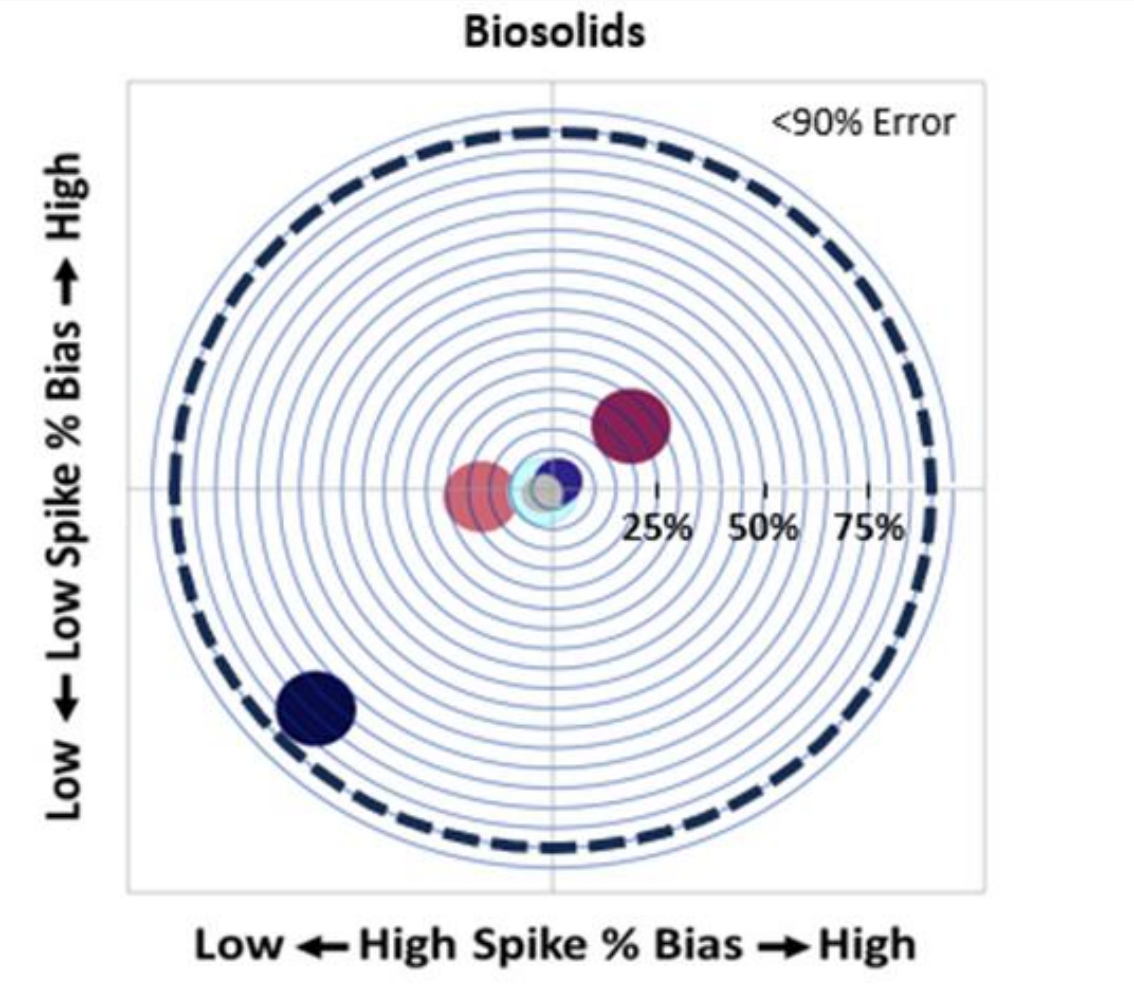
PFAS Method 1633 Validation

- Landfill Leachate Matrix Spike Results



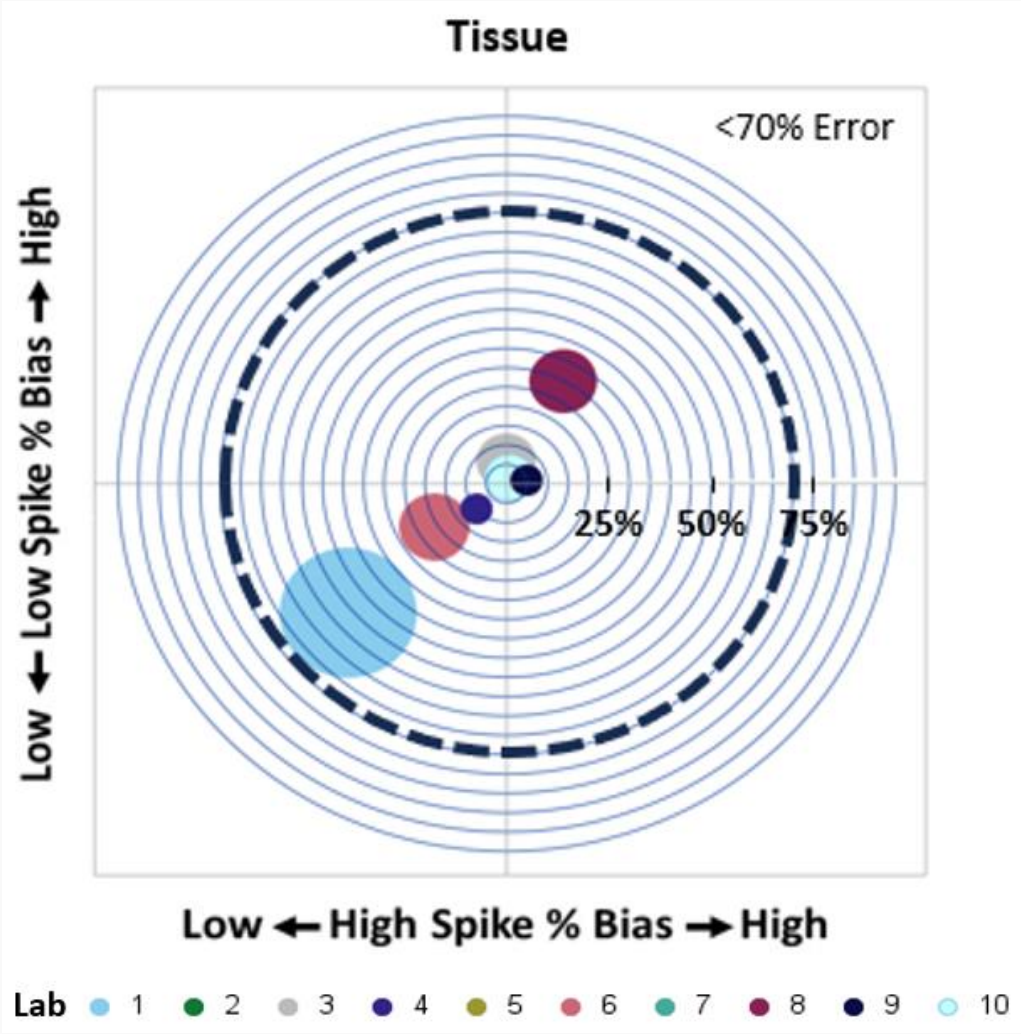
PFAS Method 1633 Validation

- Biosolid Matrix Spike Results



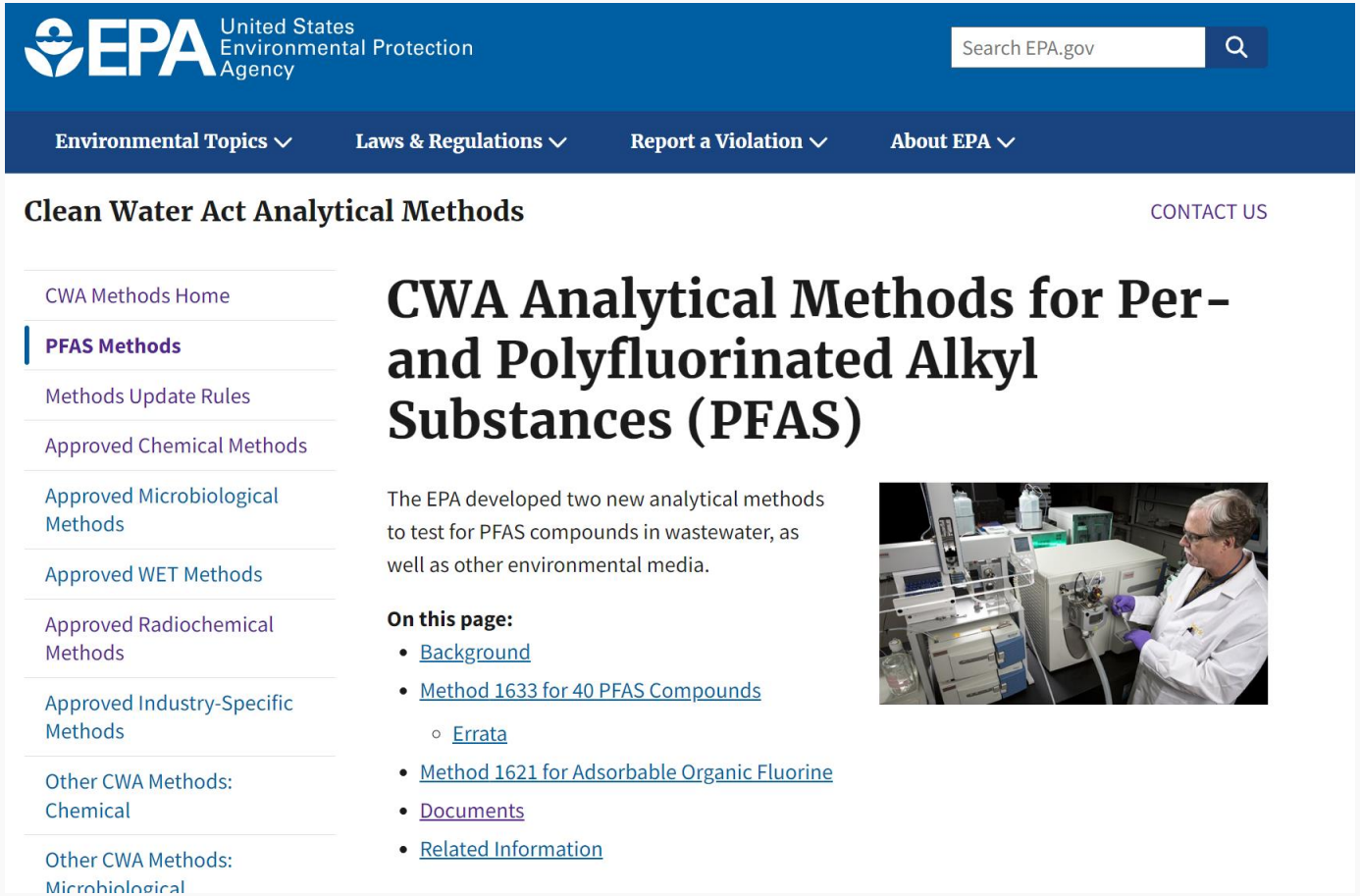
PFAS Method 1633 Validation

- Tissue Matrix Spike Results



PFAS Method 1633 Validation

- https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas



What's next? Full MUR

- CWA Section 304(h) requires EPA, through rulemaking, to establish test procedures to measure pollutants for use under CWA programs
- EPA codifies these analytical methods at 40 CFR Part 136 through notice and comment rulemakings
- Adding new methods or updating existing approved methods occurs via what is called a Methods Update Rule
- The 2024 proposed update to 40 CFR Part 136 includes new parameters and methods
- Adding a parameter to 40 CFR Part 136 does not require the permitting authority to require monitoring that parameter, but it informs the permitting authority that there is an available method that has been validated and tested in a wide variety of wastewater types

Full MUR

- The proposed Full Methods Update Rule includes new EPA methods for:
  - PFAS Method 1633 (DoD collaboration)
  - Adsorbable organic fluorine (AOF) Method 1621
  - Polychlorinated biphenyl (PCB) congeners Method 1628
- These methods have all been fully multi-laboratory validated by EPA

Thank you!

For more information or additional feedback, please contact:

Adrian Hanley
Clean Water Act Methods Team Leader
Senior Chemist
Engineering and Analysis Division
Office of Science and Technology
Office of Water
Phone: 202-564-1564
E-Mail: hanley.adrian@epa.gov

S. Bekah Burket, Ph.D.
Chemist
Engineering and Analysis Division
Office of Science and Technology
Office of Water
Phone: 202-566-2539
E-Mail: burket.sarah@epa.gov