Clean Water Act Methods

Overview of EPA's CWA PFAS Method Activities

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

SW-846 PFAS Methods Updates

Troy Strock
EPA Office of Resource Conservation and Recovery

Federal Remediation Technologies Roundtable Virtual Meeting February 2024

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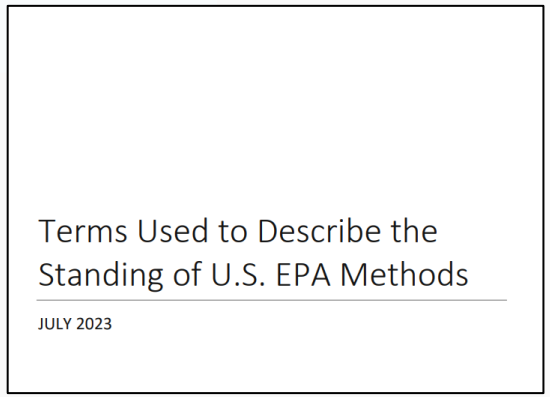
EPA Offices that publish most analytical methods

- 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

Methods Update Rules (MURs)

- Plan to propose and finalize MURs more frequently
  - Smaller rules
  - Less wait time for revisions, Alternate Test Procedures (ATPs), corrections
- A “Routine MUR” every 1-3 years
  - Routine MURs will contain non-controversial items
  - ATPs, minor editorial updates and revisions to methods (EPA, VCSBs, etc.)
- Non-routine MURs will contain more controversial items (i.e., new methods) and be proposed separately and less frequently

Routine MURs

- 2023 Routine MUR
  - Proposed February 21, 2023
  - Accepted public comments through April 24, 2023

  https://www.epa.gov/cwa-methods/methods-update-rules#current
  - Proposed standardized language to revise EPA membrane filtration Methods 1103.2, 1106.2, 1600.1, and 1603.1 found in Tables IA and IH
  - 7 ASTM method revisions, 39 SM revisions
  - 5 New SM methods – same as previously approved technologies
  - 2 Alternate Test Procedures for Dioxins and Furans (EPA Method 1613B)

Full MURs

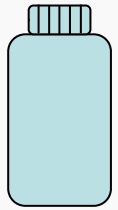
- 2024 Full MUR
  - Initiating the rulemaking now
  - Difficult to predict when the proposal will occur
    - Goal is by the end of 2024
  - Will contain PFAS Method 1633 and Adsorbable Organic Fluorine Method 1621
  - Other methods are possible
  - VCSBs will be contacted if they have any potential methods
    - Multi-laboratory data is necessary

PFAS Method 1633 Validation

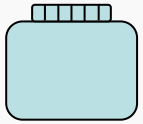
- Based on an SOP originally developed by SGS AXYS
- Partnership with Department of Defense's (DoD) Strategic Environmental Research and Development Program
  - DoD is funding and managing both single and multi-laboratory validation studies of the method, EPA OW and OLEM are providing review
- The goal is 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

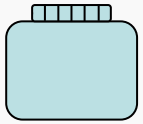
PFAS Method 1633 Validation

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

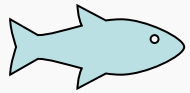


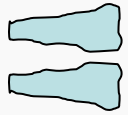
- 500 mL
- 28 days @ 0-6° C
- 90 days @ ≤ -20° C
- Measure TSS
- Invert sample to homogenize
- Sample volume determined by weight
- Spike with EIS
- Check pH
- Ready for SPE
- ~1 mL of extract for analysis





- 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



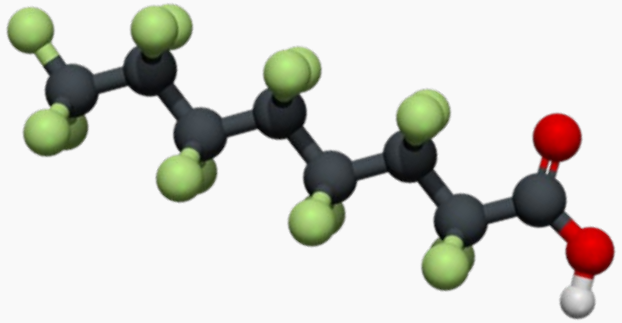


- 2 g homogenized tissue
- 90 days @ ≤ -20° C
- Transfer to centrifuge tube
- Spike with EIS
- Solvent extraction and first carbon cleanup
- Evaporation and reconstitution
- Ready for SPE and cleanup
- ~1 mL of extract for analysis

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

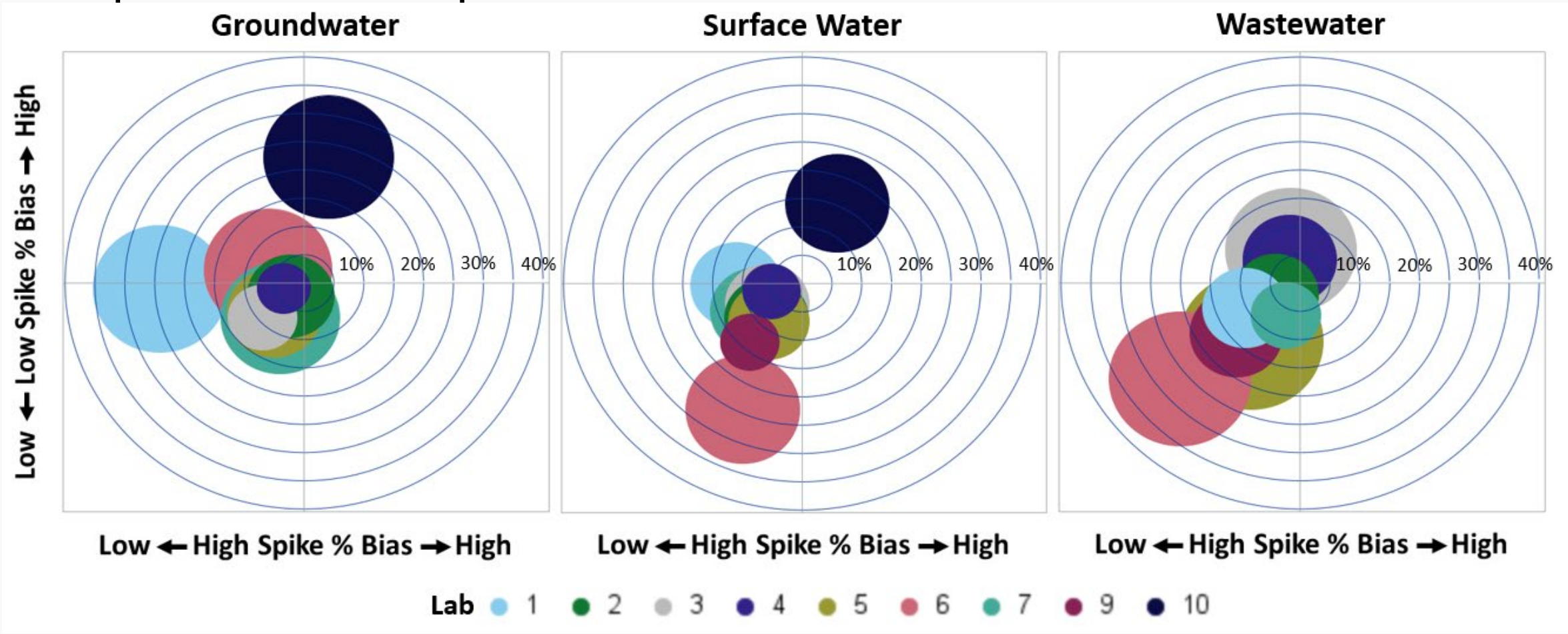
- Ongoing Precision and Recovery (OPR) Low-Level OPR (LLOPR)
  - The performance was about the same for the OPR and LLOPR, so the data were combined and used to develop a single set of criteria
  - Most criteria are inclusive of the highest and lowest observed data point from all 10 laboratories
  - 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.

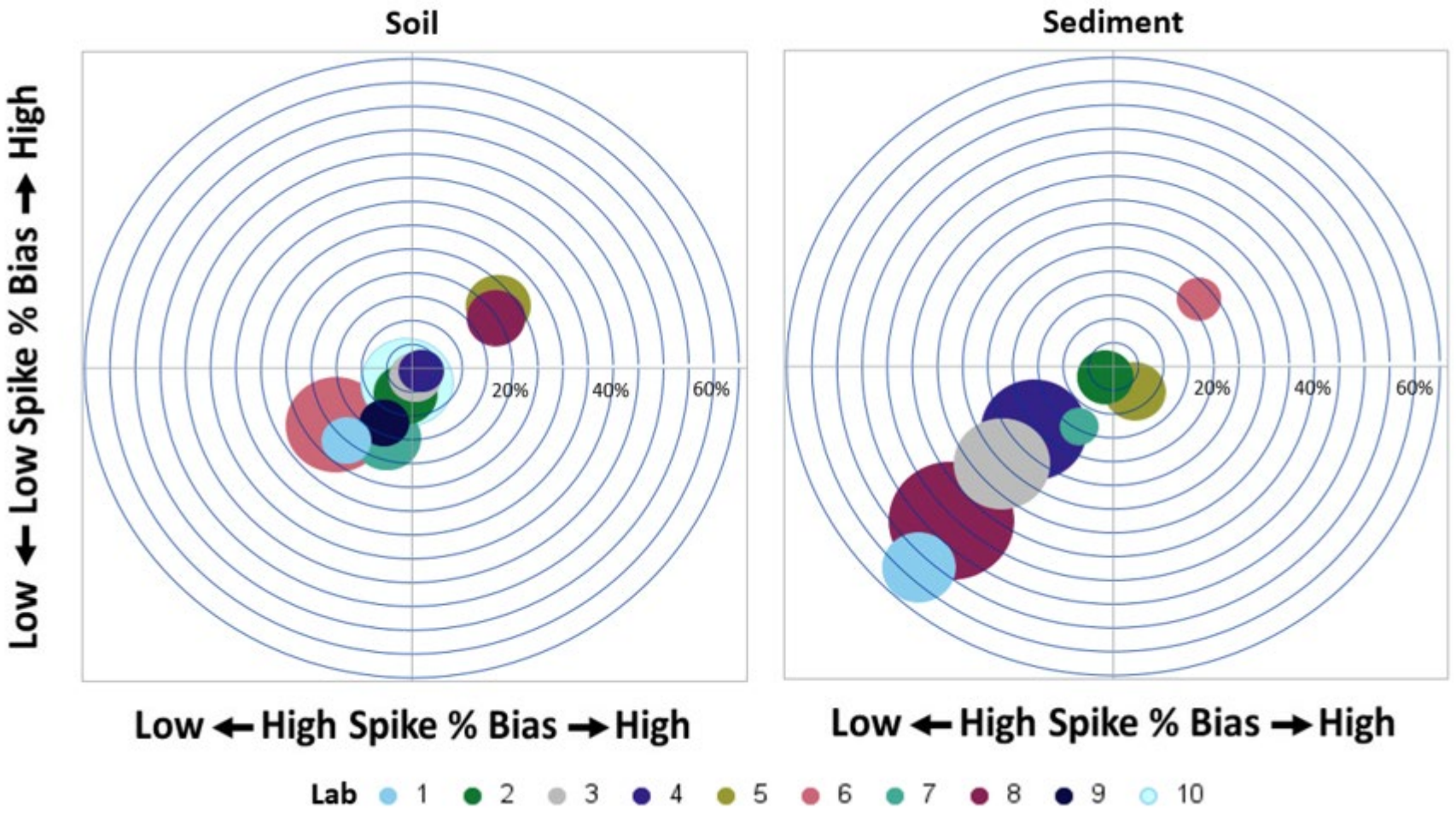
PFAS Method 1633 Validation

- Aqueous Matrix Spike Results



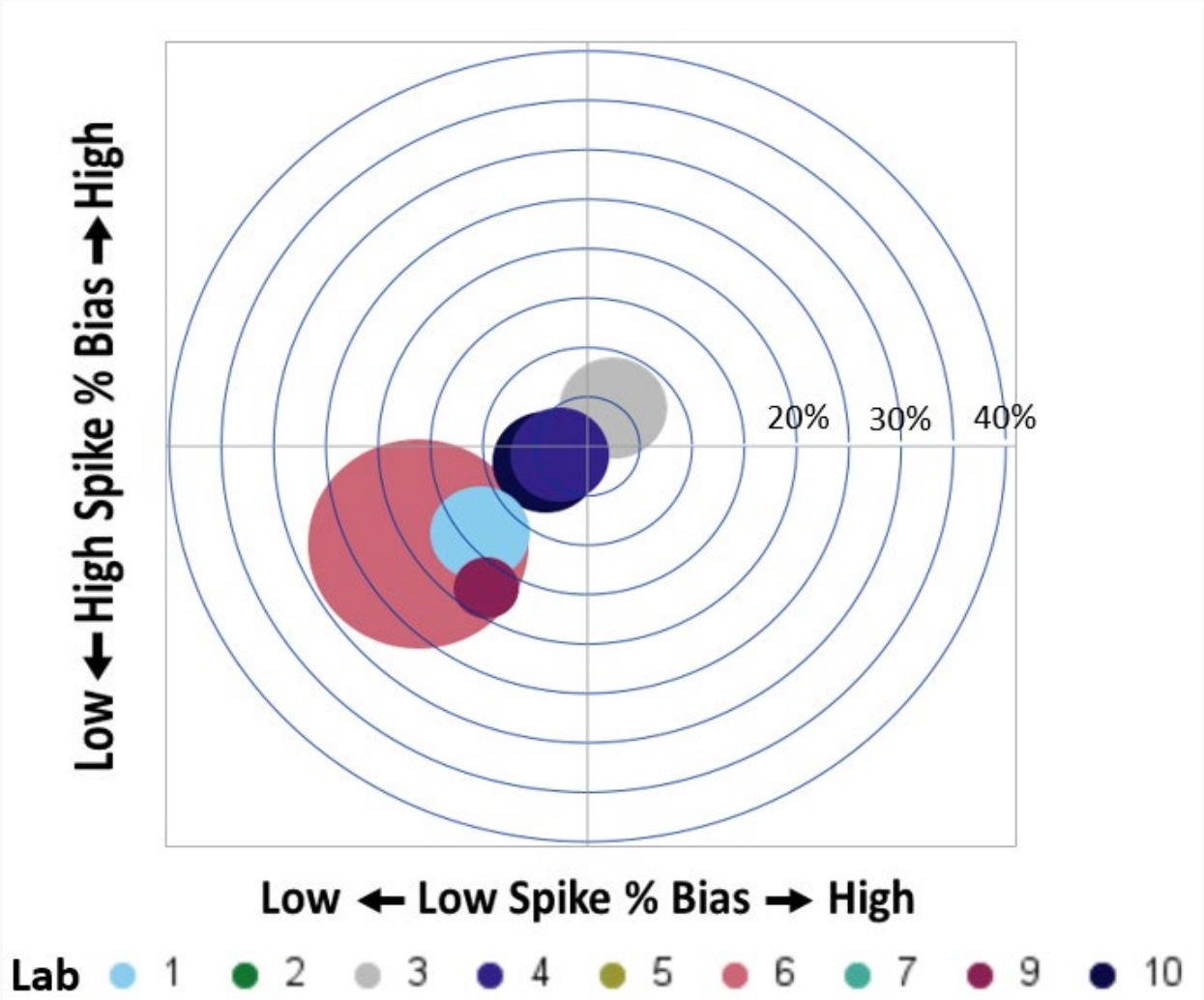
PFAS Method 1633 Validation

- Solid Matrix Spike Results



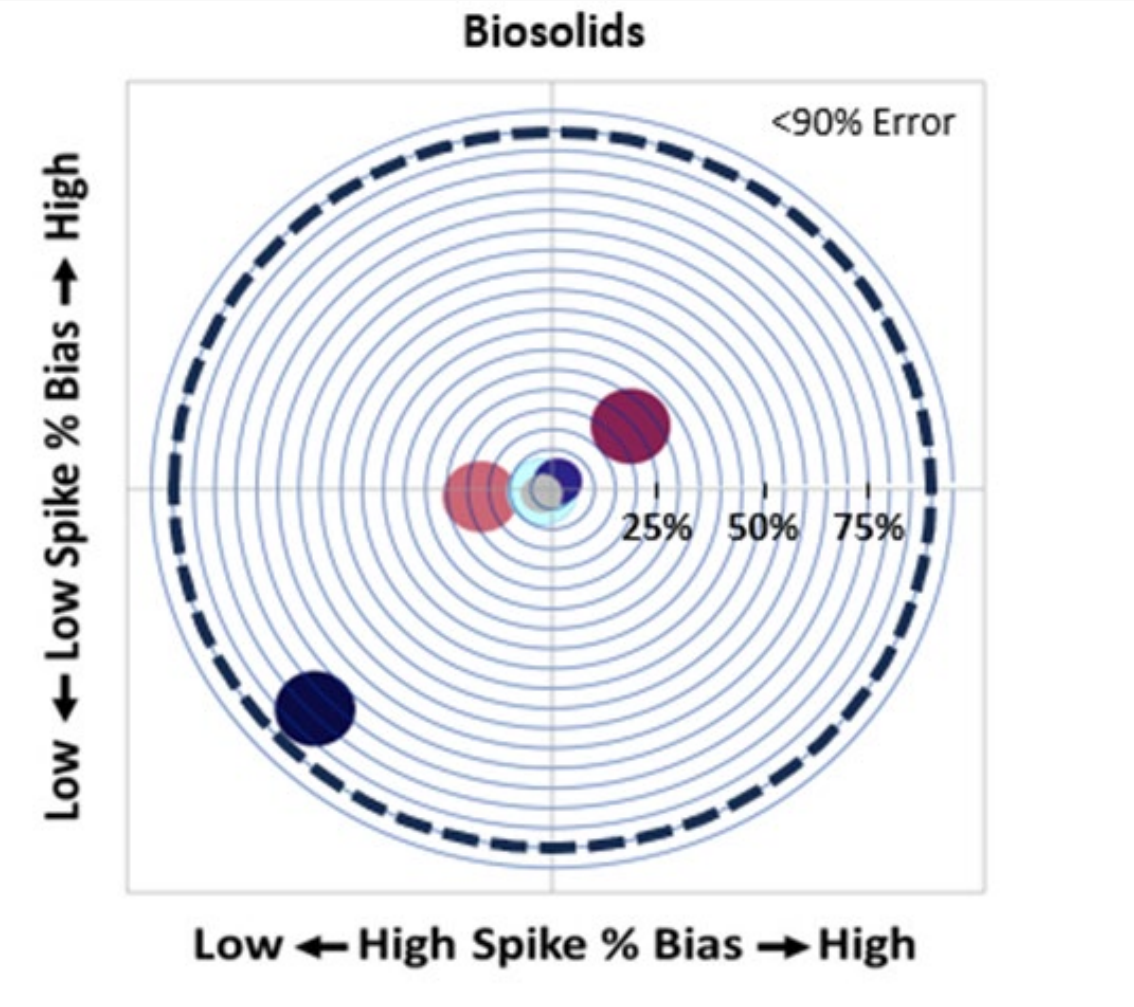
PFAS Method 1633 Validation

- Landfill Leachate Matrix Spike Results



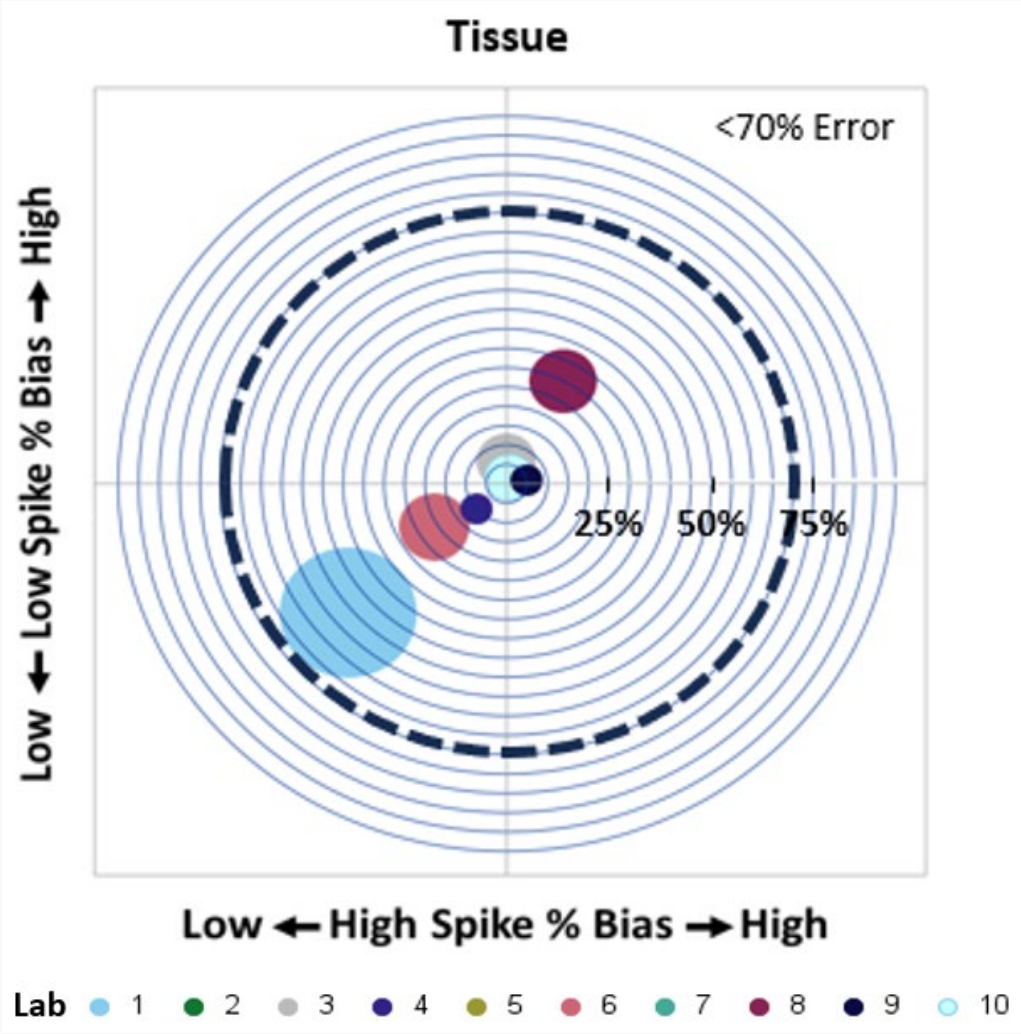
PFAS Method 1633 Validation

- Biosolid Matrix Spike Results



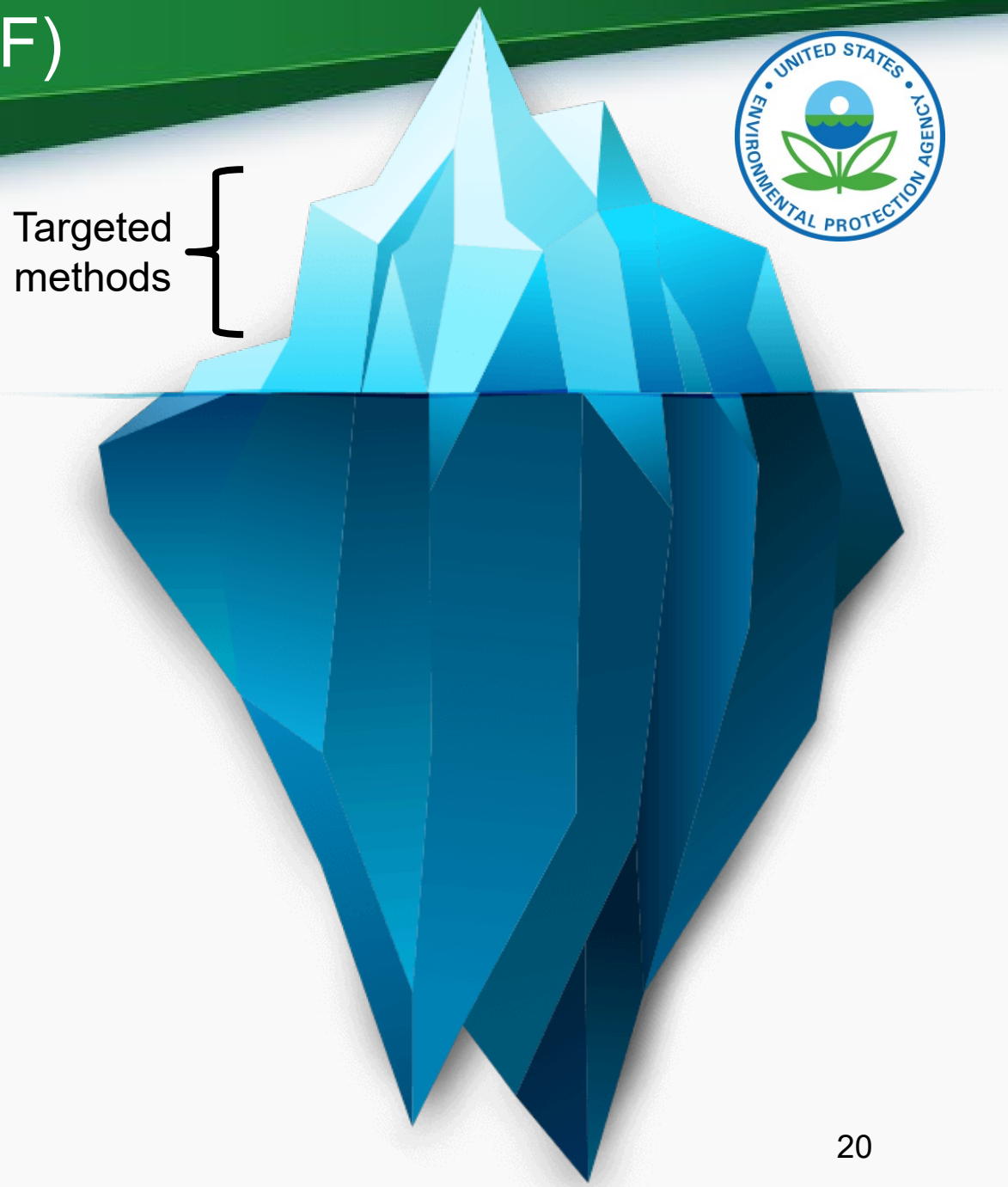
PFAS Method 1633 Validation

- Tissue Matrix Spike Results



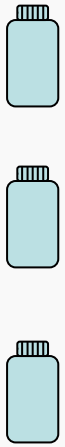
Adsorbable Organic Fluorine (AOF) Method 1621

- Increasing demand for aggregate methods like AOF
- Naturally occurring organofluorines are rare
- Collaborated with ASTM D19 and EPA ORD on single-laboratory validation of AOF screening method
- Method Finalized January 2024!



AOF, Method 1621 (cont.)

- Samples prepared and passed through two GAC columns
- Analysis via CIC
- Yields a single result that estimates an aggregate concentration of any organofluorine compounds in the sample
- Method defined parameter



- 100 mL
- 90 days @ 0-6° C
- Measure TSS
- Verify sample pH ≥ 5
- Check for chlorine and dechlorinate if needed
- Determine concentration of inorganic fluoride
- Sample volume determined by weight
- Add 0.5 mL of 2M sodium nitrate

- Slowly load sample onto GAC columns
- Wash GAC columns with 25 mL of 0.01 M sodium nitrate
- Rinse with 20 mL reagent water
- Dry columns
- Transfer carbon to combustion boats
- Sample ready for combustion and analysis

AOF, Method 1621 (cont.)

- Single-Laboratory Validation completed April 2022:
  - Calibration and sorbent testing
  - Recovery ranged from about 40-200% for analytes tested:
    - 36 individual PFAS
    - 3 different mixed PFAS standards
    - 3 fluorinated pharmaceuticals
    - 3 fluorinated pesticides
  - Initial precision and recovery and method detection limit studies
  - Ten wastewater and surface water matrices were tested at two spike concentrations
- SLV study report posted:
  - https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

AOF, Method 1621 (cont.)

- Multi-Laboratory Validation completed January 2024:
  - 10 labs, 9 wastewaters and surface water matrices were tested at three spike concentrations
  - Calibration testing (extended range)
  - PFHxS used in every test matrix; PFBA, PFOS, and a mixed standard were also tested
  - Initial precision and recovery and method detection limit
  - % breakthrough

AOF, Method 1621 (cont.)

- 10 lab pooled MDL was 1.5 ppb
  - Maximum MDLs was 2.9 ppb, maximum MDLb was 3.2 ppb
- EPA established an acceptance limit of 80 – 120% for the mean IPR recovery, with an RSD < 20%; retained the interim limit of 70 – 130% for the OPR
- 429 matrix spike results were gathered during this study, 96% of the results had recoveries between 50 and 150 percent. Only 3% of the spiked samples had recoveries below 50% and 1% were above 150%
- MLV study report and method:
  - https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

SW-846 PFAS Methods Updates

Troy Strock

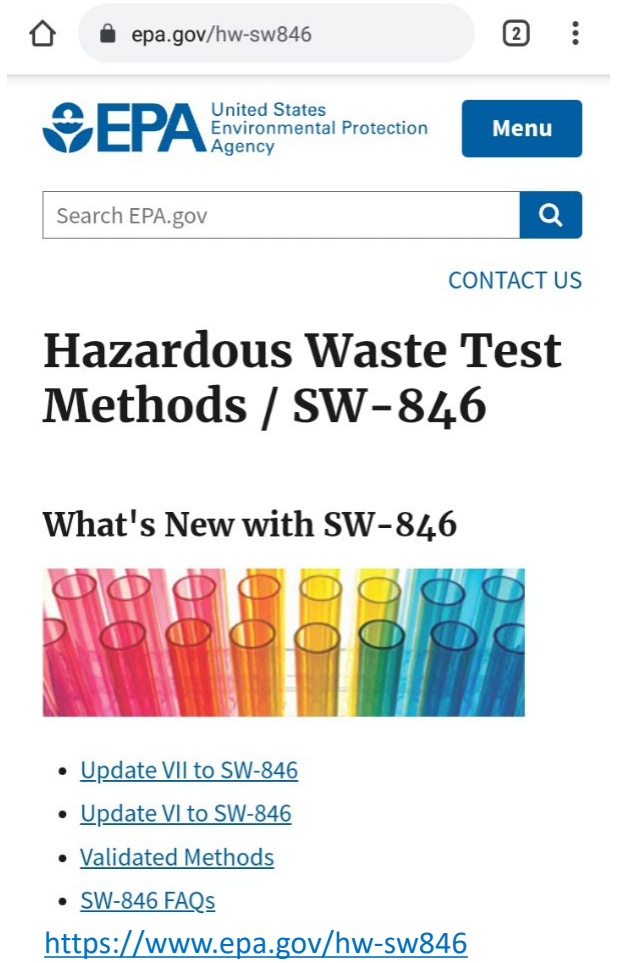
EPA Office of Resource Conservation and Recovery

“Federal Remediation Technologies Roundtable Presents” Webinar

2/28/2024

Background: SW-846

- Official compendium of test methods to support compliance with RCRA regulations
- Collection of 200+ methods, associated guidance
- A few methods are incorporated by reference in RCRA regulations – Method Defined Parameters (MDPs)
- Remaining methods are performance-based, “non-regulatory”
  - Appropriate modifications are permitted
  - Other reliable, published methods may be used
  - Regulated entity is responsible for ensuring results are appropriate, decisions are accurate



Three categories of SW-846 PFAS Methods Projects:

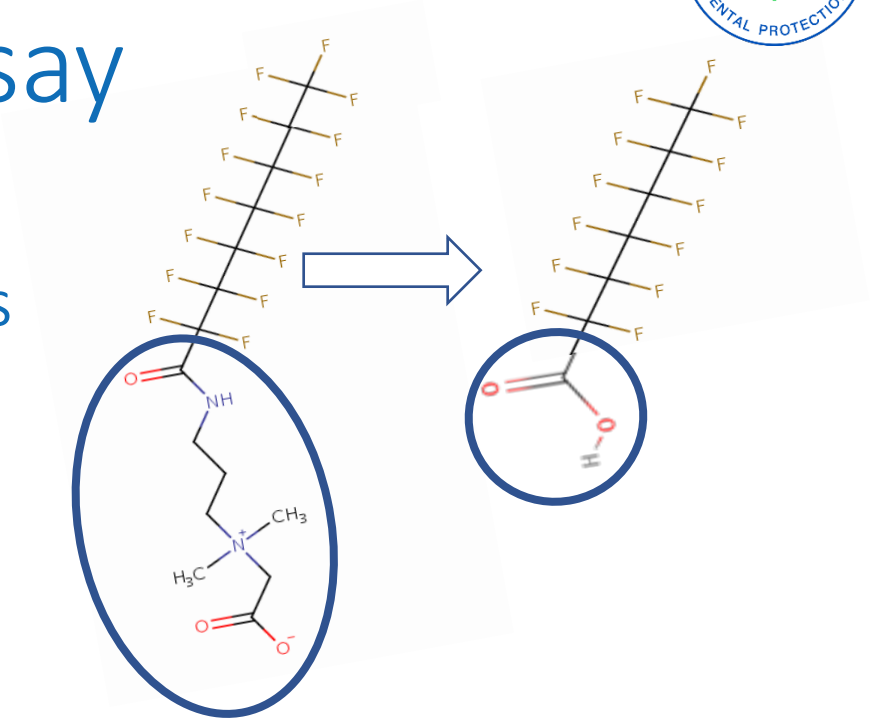
Targeted Analytical Methods	Class-Based Test Methods	Aqueous Leaching Methods
• Expanding range of validated target analytes for quantitative analysis • Provide laboratories with additional tools for sample preparation and cleanup, especially useful for challenging matrices	• Working to develop robust and quality-assured methods like the Total Oxidizable Precursors (TOP) assay • Capable of capturing PFAS precursors that otherwise cannot be measured with current targeted analytical methods	• Adapt SW-846 Leaching Environmental Assessment Framework (LEAF) methods 1313-1316 to PFAS • Updates will improve fate and transport modelling, provide tools to evaluate immobilization strategies on a pilot scale prior to field deployment

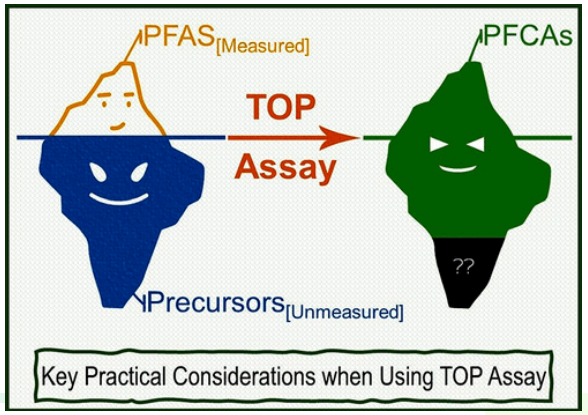
SW-846 PFAS analytical methods

- SW-846 Methods 3512 and 8327 were published in July 2021
  - 3512: “Direct inject” sample preparation method for aqueous samples – dilute 1:1 with methanol, vortex, and filter
  - 8327: Liquid chromatography / tandem mass spectrometry determinative method
- Validation studies:
  - DoD/EPA collaborated on validation study for Method 1633
  - ASTM International/EPA collaborated on validation study for ASTM D8421-22
- Next steps: Publish SW-846 updates
  - Projected timeframe: Complete in 2024
- Revise 3512A, 8327A:
  - Add target analytes, include extracted internal standard/isotope dilution calibration
- New sample preparation and cleanup methods to propose:
  - 3536: Weak anion exchange solid phase extraction - aqueous
  - 3551: Equilibrium basic solvent extraction - solids
  - 3670?: Graphitized carbon cleanup

PFAS Method Development Project: Total Oxidizable Precursors (TOP) Assay

- Original paper published by Erika Houtz and David Sedlak
  - https://doi.org/10.1021/es302274g
- Warm alkaline persulfate oxidation pretreatment to convert PFAS precursors to perfluoroalkyl acids
- Benefits:
  - Retains some structural information
  - Use the same targeted analytical methods
- Some challenges to address:
  - Oxidation efficiency
  - Mole balance/fluoride mass balance
  - Volatile loss
  - Different approaches for aqueous, solid samples
- Goals:
  - Complete development work in 2024
  - Then validate and publish a standardized SW-846 method
- Collaborators: EPA, commercial labs, universities

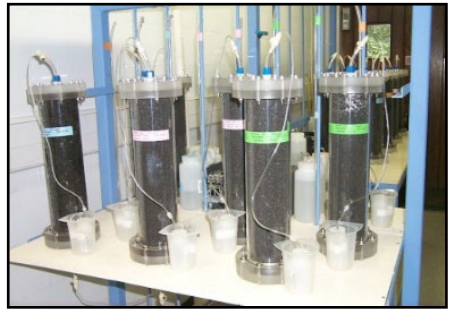




Environ. Sci. Technol. Lett. 2023, 10, 4, 292–301
https://pubs.acs.org/doi/10.1021/acs.estlett.3c00061

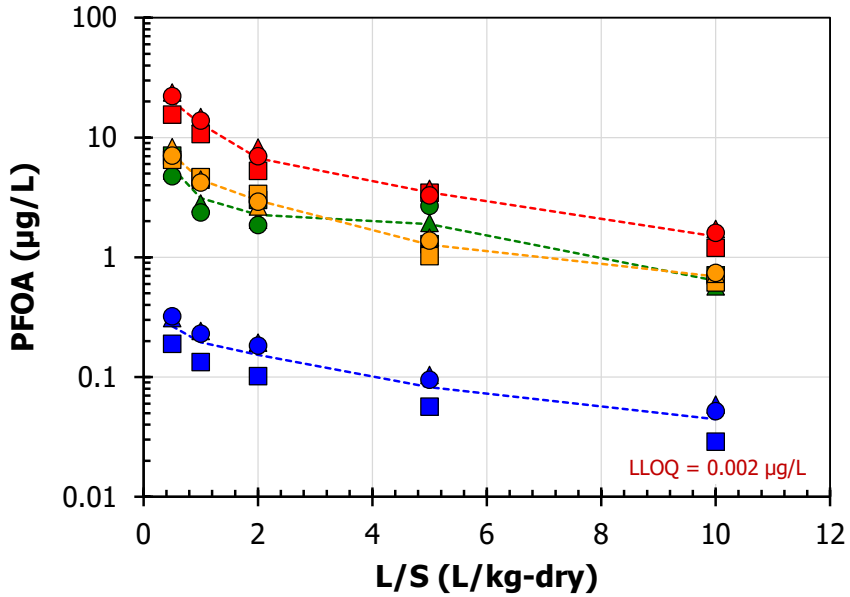
Adapting LEAF Methods for PFAS

- LEAF: Leaching Environmental Assessment Framework
- Methods, data used to:
  - Identify key variable(s) affecting leaching behavior
  - Estimate “source term” i.e., aqueous concentration, release rate, to use as inputs for fate and transport modeling
  - Evaluate/optimize immobilization strategy prior to field deployment
- Non-regulatory (i.e., not replacing TCLP/Method **1311** for hazardous waste determinations)
- Equilibrium-based leaching as a function of eluate pH (**1313**) or liquid-solid ratio (**1316**)
- Up-flow column percolation (**1314**)
- Semidynamic tank leaching test for monolithic or compacted granular materials (**1315**)



Adapting LEAF Methods for PFAS

- Current status:
  - Multi-laboratory validation studies began in January for **1313A**, **1316A** for PFAS and SVOCs
    - Four participating laboratories, two field-contaminated soils
  - Method development work for PFAS is complete or nearly complete for **1314A**
    - Largely performed through SERDP grant - joint effort by Texas Tech and Vanderbilt
  - To do: Finish method development work for **1315A**
- Other EPA PFAS LEAF projects:
  - Leaching from biosolids: Collaborative effort by EPA OW, OLEM, and ORD



Preliminary leaching data from draft document entitled "Development of Equilibrium Leaching Tests for Materials Containing SVOCs and PFAS Background Information Document", authored by Andrew Garrabrants, Fangfei Liu, Kaelyn Warne, Rosanne DeLapp, Zhiliang Chen, Darlington Yawson, David Kosson (Vanderbilt University), Jennifer Guelfo and Md. Isreq Real (Texas Tech University), and Hans van der Sloot (Hans van der Sloot Consultancy), Subcontracted by Abderrahmane Touati (Jacobs Technology, Inc), prepared for Susan Thorneloe USEPA Office of Research and Development, Center for Environmental Solutions and Emergency Response, and Troy Strock, USEPA Office of Land and Emergency Management - manuscript in preparation

PFAS analytical methods and method development projects in other EPA program offices

- OGWDW PFAS analytical methods for drinking water
  - Targeted PFAS analysis by LC-MS/MS
    - Methods 533, 537.1 were published in 2018-2019
    - Method development projects:
      - Solvent dilution/direct inject
      - In-line solid-phase extraction
  - For more information: Will Adams in OW/OGWDW: adams.william@epa.gov
- ORD PFAS analytical method development project for drinking water: Extractable organic fluorine (EOF)
  - For more information: Dan Tettenhorst in ORD/CESER: tettenhorst.dan@epa.gov
- OAQPS PFAS stack sampling and analysis methods:
  - OTM-45 – released Jan. 2021; revisions in progress
  - OTM-50 (volatile PFAS) – released Feb. 2024
  - Method development project: OTM-55 (non-polar longer-chain PFAS)
  - For more information:
    - David Berkowitz in OAR/OAQPS: berkowitz.david@epa.gov
    - Jeff Ryan, Stephen Jackson in ORD/CEMM: ryan.jeff@epa.gov, jackson.stephen@epa.gov

Thank you!

For more information or additional feedback, please contact:

CWA Methods Program:

Adrian Hanley
Engineering and Analysis Division
Office of Science and Technology
Office of Water
Phone: 202-564-1564
E-Mail: hanley.Adrian@epa.gov

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

SW-846 Methods Program:

Troy Strock
Waste Characterization Branch
USEPA OLEM ORCR MRWMD
Phone: 202-566-0504 (office)
E-Mail: strock.troy@epa.gov