Clean Water Act Methods

Overview of EPA's CWA PFAS Method Activities

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SW-846 PFAS Methods Updates

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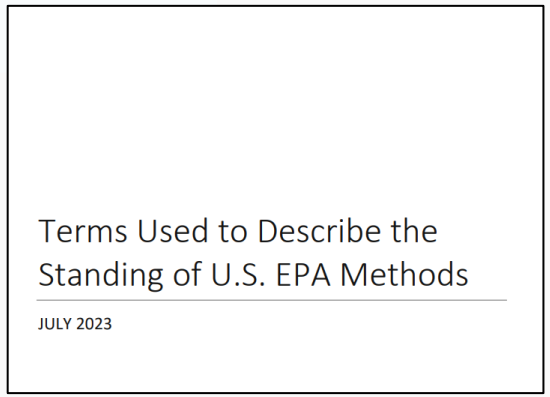
EPA Offices that publish most analytical methods

- Office of Radiation and Indoor Air (ORIA)
  - 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

- 2021 Routine MUR
  - Proposed October 2019
  - Signed on May 3, 2021 by Administrator Michael S. Regan
  - Effective July 19, 2021

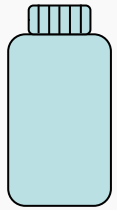
  https://www.epa.gov/cwa-methods/methods-update-rule-2021
- Current Routine MUR
  - Materials received by VCSBs and ATP applicants
  - Proposed on February 21, 2023
  - Public comments accepted through April 24, 2023
  - Plan to finalize in 2024

PFAS Method 1633 Validation

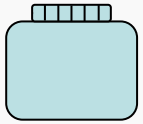
- Based on an SOP originally developed by SGS AXYS
- Partnership with Department of Defense's (DoD) Strategic Environmental Research and Development Program
  - DoD is funding and managing both single and multi-laboratory validation studies of the method, EPA OW and OLEM are providing review
- The goal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

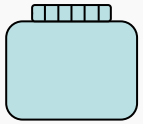
PFAS Method 1633 Validation

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

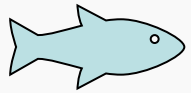


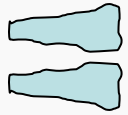
- 500 mL
- 28 days @ 0-6° C
- 90 days @ ≤ -20° C
- Measure TSS
- Invert sample to homogenize
- Sample volume determined by weight
- Spike with EIS
- Check pH
- Ready for SPE
- ~1 mL of extract for analysis





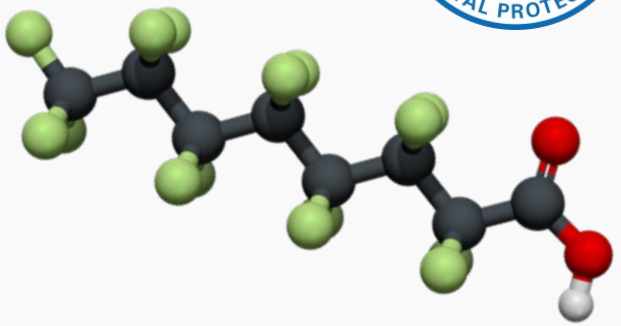
- 5 g dry weight (soil and sediment)
- 0.5 g dry weight (biosolids)
- 90 days @ 0-6° C or ≤ -20° C
- Measure % solids
- Mix with stainless steel spoon
- Remove rocks, invertebrates, foreign objects
- Transfer to centrifuge tube
- Spike with EIS
- Solvent extraction and first carbon cleanup
- Evaporation 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

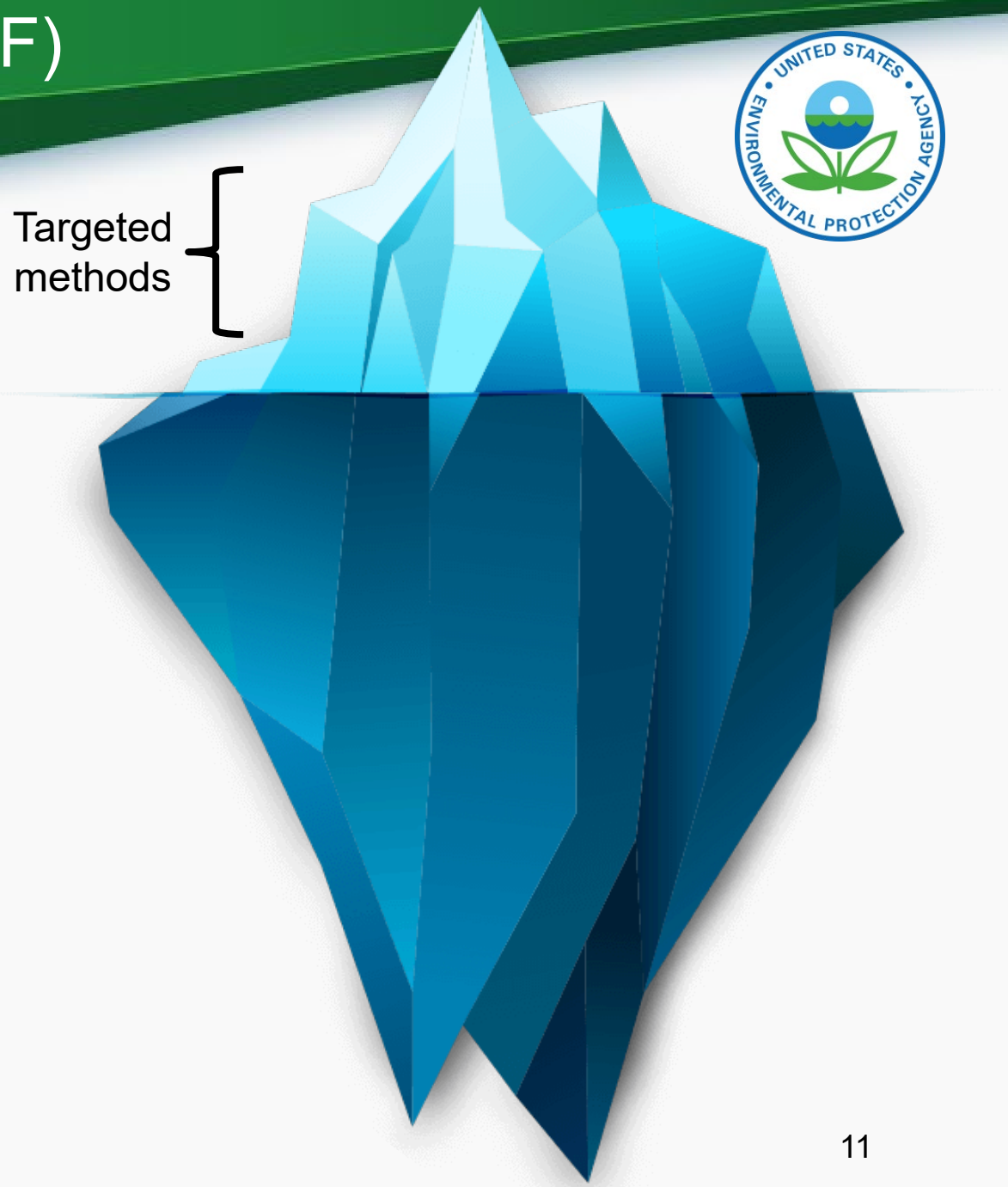
PFAS Method 1633 Validation



- QC samples are important
- Include bile salt interference check standard
- Single-Laboratory Validation completed
  - Draft Method 1633 and single laboratory validation study report are both posted on the web: https://www.epa.gov/cwa-methods
- Multi-Laboratory Validation underway
  - July 2023: 4th draft of method and first MLV study report posted, incorporating QC acceptance criteria for all aqueous matrices, and derived from MLV study data
  - Anticipated late 2023: final version of method with QC criteria for all matrices and a second MLV study report

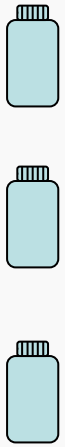
Adsorbable Organic Fluorine (AOF) Draft Method 1621

- 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



AOF, Draft 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

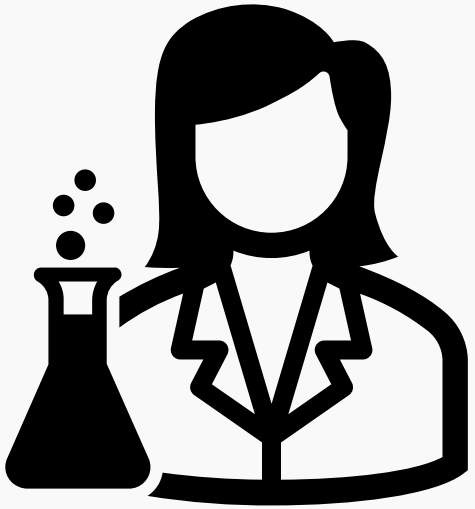
- Slowly load sample onto GAC columns
- Wash GAC columns with 25 mL of 0.01 M sodium nitrate
- Rinse with 20 mL reagent water
- Dry columns
- Transfer carbon to combustion boats
- Sample ready for combustion and analysis

AOF, Draft Method 1621 (cont.)

- Single-Laboratory Validation completed and included:
  - Calibration and sorbent testing
  - Recovery of individual PFAS, mixed PFAS, and non PFAS organofluorines
  - Initial precision and recovery and method detection limit studies
  - Ten wastewater and surface water matrices were tested at two spike concentrations

- Draft Method and SLV study report posted April 2022:
  - https://www.epa.gov/cwa-methods

Multi-Laboratory Validation



- Nearly complete
- Includes volunteer and contracted laboratories
- Anticipated completion late 2023

SW-846 PFAS Methods Updates

Troy Strock

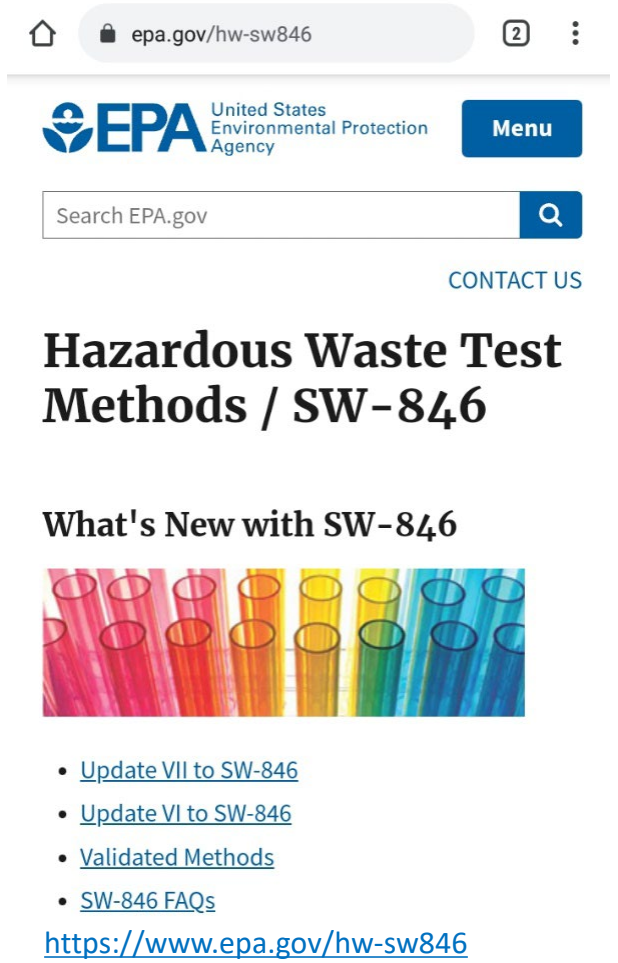
EPA Office of Resource Conservation and Recovery

Federal Remediation Technologies Roundtable meeting

11/7/2023

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"
  - May still be required when specified, e.g., in a RCRA permit, consent decree, regulations by other EPA programs
  - Appropriate modifications are permitted, or other reliable, published methods may be used
  - Regulated entity is responsible for ensuring results are appropriate, decisions are accurate

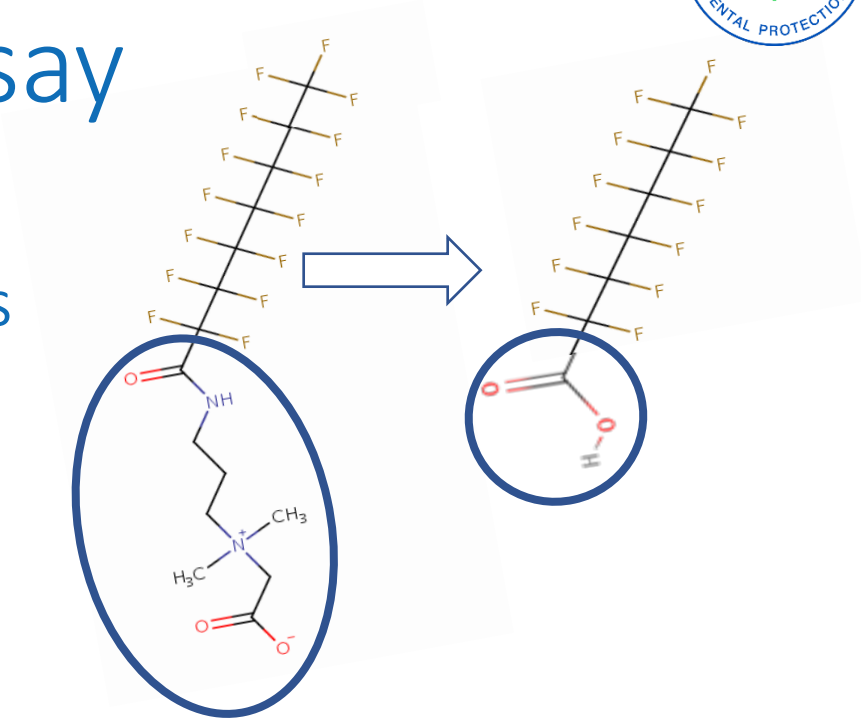


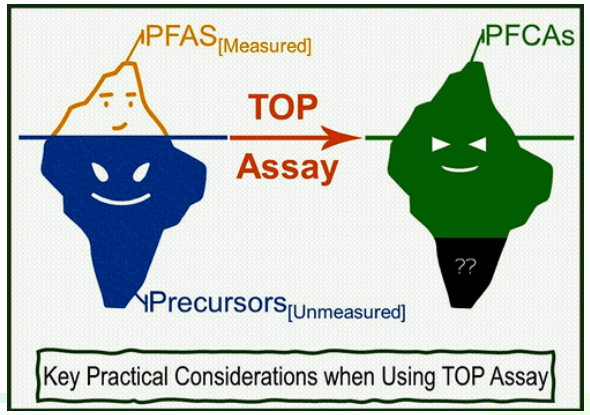
Three categories of SW-846 PFAS Methods Projects in 2023-2024:

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

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 FY24
  - 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

SW-846 PFAS analytical methods

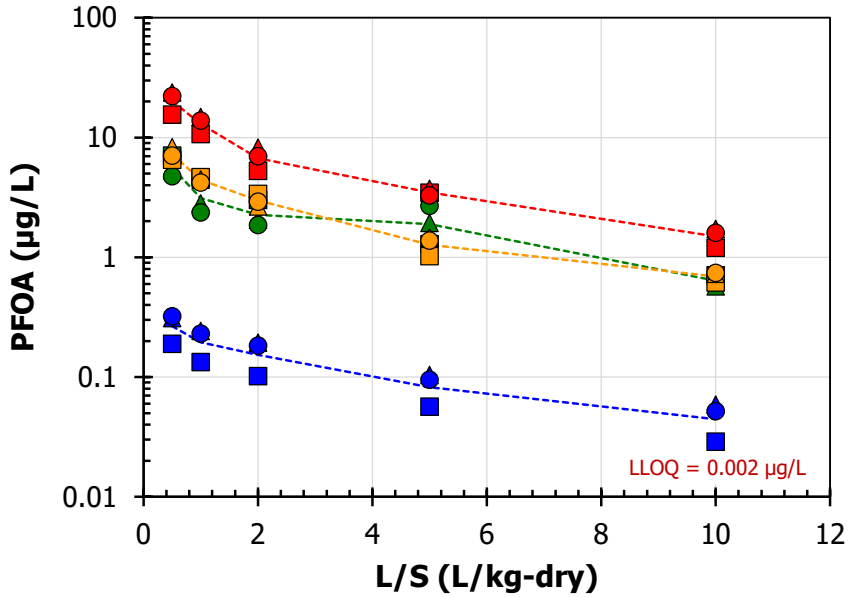
- SW-846 Methods 3512 and 8327 were published in July 2021
  - 3512: “Direct inject” sample preparation method for aqueous samples – dilute 1:1 with methanol, vortex, and filter
  - 8327: Liquid chromatography / tandem mass spectrometry determinative method
- Ongoing validation studies:
  - DoD collaborating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

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 immobilization strategies 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:
  - Method development work for PFAS is complete or nearly complete for **1313A**, **1314A**, **1316A**
    - Largely performed through SERDP grant - joint effort by Texas Tech and Vanderbilt
  - Beginning multi-laboratory validation of **1313A**, **1316A**
    - Labs performing Initial Demonstrations of Proficiency
  - To do: Finish method development work for **1315A**



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

- Starting another PFAS LEAF project: Leaching from biosolids
  - Collaborative effort by EPA OW, OLEM, and ORD

Other EPA PFAS method development projects

- OW/OGWDW PFAS method development for drinking water
  - Targeted PFAS analysis by LC-MS/MS
    - Solvent dilution/direct inject
    - In-line solid phase extraction
- ORD Total organic fluorine method development for drinking water
  - Class-specific
    - Total organic fluorine
  - For more information, contact Dan Tettenhorst: tettenhorst.dan@epa.gov
- OAQPS PFAS method development for stack testing
  - Revised version of OTM-45
  - OTM-50 (volatile PFAS)
  - For more information, contact Ray Merrill: merrill.raymond@epa.gov

Thank you!

For more information or additional feedback, please contact:

CWA Methods Program:

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