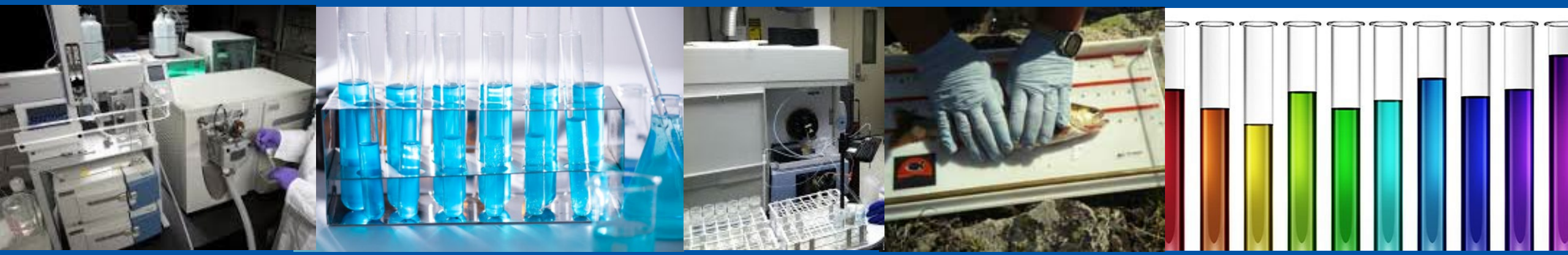


EPA PFAS Analytical Methods: Aqueous and Solid Matrices

Northeast Waste Management Officials' Association (NEWMOA)
September 25, 2024

By Troy Strock
US Environmental Protection Agency
Office of Land and Emergency Management (OLEM)
Office of Resource Conservation and Recovery (ORCR)

Disclaimer

The views expressed in this presentation are those of the author 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.

Presentation Overview

- Background on EPA methods programs
- Recent PFAS-related actions
- Published EPA PFAS analytical methods
- PFAS analytical methods under development
  - Targeted analytical methods
  - Non-targeted analysis
  - Aqueous leaching methods

EPA Headquarters Offices

Office of the Administrator (AO)

202-564-4700

About the Office of the Administrator

AO Organization Chart

Office of Inspector General (OIG)

202-566-0847

About the Office of Inspector General

Office of International and Tribal Affairs (OITA)

202-564-6600

About the Office of International and Tribal Affairs

OITA Organization Chart

Office of Air and Radiation (OAR)

202-564-7404

About the Office of Air and Radiation

OAR Organization Chart

Office of Land and Emergency Management (OLEM)

202-566-0200

About the Office of Land and Emergency Management

OLEM Organization Chart

Office of Water (OW)

202-564-5700

About the Office of Water

Office of Chemical Safety and Pollution Prevention (OCSPP)

202-564-2902

About the Office of Chemical Safety and Pollution Prevention

OCSPP Organization Chart

Office of Research and Development (ORD)

202-564-6620

About the Office of Research and Development

ORD Organization Chart

Office of the Chief Financial Officer (OCFO)

202-564-1151

About the Office of the Chief Financial Officer

OCFO Organization Chart

Office of Enforcement and Compliance Assurance (OECA)

202-564-2440

About the Office of Enforcement and Compliance Assurance

OECA Organization Chart

Office of General Counsel (OGC)

202-564-8040

About the Office of General Counsel

OGC Organization Chart

Office of Mission Support (OMS)

202-564-4600

About the Office of Mission Support

OMS Organization Chart

Office of Environmental Justice and External Civil Rights (OEJECR)

202-564-8040

About the Office of Environmental Justice and External Civil Rights

OEJECR Organization Chart

Offices with blue borders have published analytical methods

https://www.epa.gov/aboutepa/epa-organization-chart

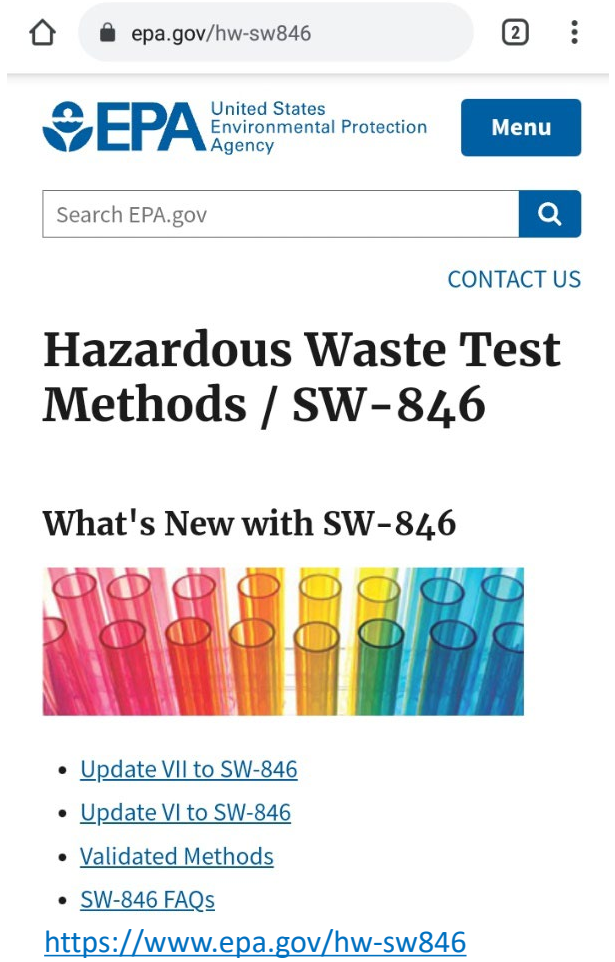
Office of Land and Emergency Management (OLEM) Program Offices

- Office of Resource Conservation and Recovery (**ORCR**)
  - RCRA methods program (SW-846)
- Office of Superfund Remediation and Technology Innovation (**OSRTI**)
- Federal Facilities Restoration and Reuse Office (**FFRRO**)
- Office of Emergency Management (**OEM**)
- Office of Underground Storage Tanks (**OUST**)
- Office of Brownfields and Land Revitalization (**OBLR**)
- Office of Mountains, Deserts and Plains (**OMDP**)
- **OMIS, PARMS**, **OPM**, **OCPA**

https://www.epa.gov/aboutepa/organization-chart-office-land-and-emergency-management

The SW-846 Compendium

- EPA's official collection of test methods for compliance with Resource Conservation and Recovery Act (RCRA)
- 220+ test methods and guidance on project planning, sampling, quality assurance
- A few methods are incorporated by reference in RCRA regulations – Method Defined Parameters (MDPs)
- Remaining methods are performance-based, "non-regulatory"
- Methods and data used by:
  - OLEM program offices, other EPA offices
  - States, other federal agencies, foreign governments
  - Commercial, government testing laboratories
  - Industry



Recent EPA PFAS Rulemakings, Guidance:

- **Resource Conservation and Recovery Act (RCRA):**
  - 40 CFR Part 261 Appendix VIII PFAS Hazardous Constituents rulemaking: 89 FR 8606, proposed rule released 2/08/2024
  - §264 Statutory Definition of Hazardous Waste Applicable to Corrective Action for Releases From Solid Waste Management Units: 89 FR 8598, proposed rule released 02/2024
- **Comprehensive Environmental Responsibility, Compensation and Liability Act (CERCLA):**
  - §302 Designation of PFOA and PFOS as CERCLA Hazardous Substances (89 FR 39124, final rule effective 7/8/2024)
  - Interim PFAS Destruction and Disposal Guidance; Notice of Availability for Public Comment (89 FR 26879, released 4/16/2024) – comment period ends on 10/15/2024
- **Safe Drinking Water Act (SDWA):**
  - §141, §142 National Primary Drinking Water Regulation established Maximum Contaminant Levels (MCLs) for six PFAS in public drinking water systems (89 FR 32532, final rule effective 6/25/2024, 5 year implementation timeframe)

For current info on EPA rulemakings and other actions: https://www.reginfo.gov/public/

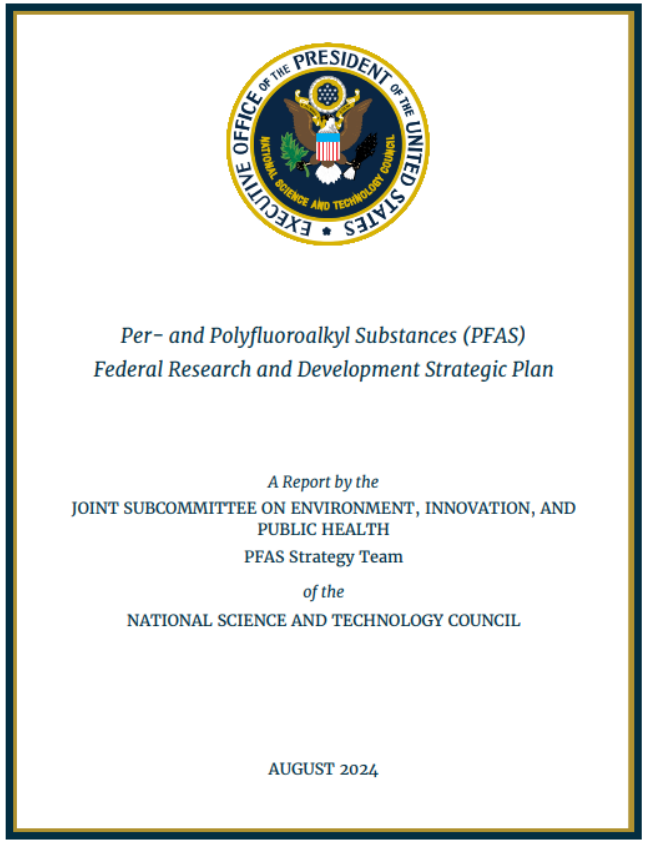
PFAS Federal Research and Development Strategic Plan

- Published in August 2024
- **Strategy 2:** Address current PFAS measurement challenges through the development of standards, advanced sampling and analytical methodologies

Section	Method Development Needs
Objective 2.1: Further improve targeted and non-targeted analytical methods for identifying, detecting, and quantifying PFAS in a variety of sample types.	• Ultrashort chain PFAS • Neutral semivolatile PFAS • Cationic and zwitterionic precursors • Nontargeted analysis

Objective 2.2: Advance the science of total fluorine and PFAS summations with method-defined analyses and protocols	• Aggregate/class-based methods
	  • Extractable organic fluorine
	  • Total Oxidizable Precursors (TOP) assay

Objective 2.3: Foster the development of new technologies for efficiently measuring and identifying, quantifying, and modeling PFAS occurrence in the environment.	• Aqueous leaching methods



Per- and Polyfluoroalkyl Substances (PFAS)
Federal Research and Development Strategic Plan

A Report by the
JOINT SUBCOMMITTEE ON ENVIRONMENT, INNOVATION, AND PUBLIC HEALTH
PFAS Strategy Team
of the
NATIONAL SCIENCE AND TECHNOLOGY COUNCIL

AUGUST 2024

https://www.whitehouse.gov/wp-content/uploads/2024/09/PFAS-STRAT-PLAN-FINAL.pdf

Categories of PFAS Test Methods

- Targeted analytical methods
  - Quantitative analysis of known analytes
  - Need certified reference materials
  - Not suitable for detecting PFAS not on the analyte list
- Aggregate/Class-based analytical methods
  - Provide information beyond targeted methods
  - Cannot identify specific chemical structures
- Non-target analytical methods
  - Identify known and unknown analytes
  - Qualitative, semiquantitative
- Aqueous leaching methods
  - Evaluate mobility in groundwater, better model transport in subsurface
  - Evaluate immobilization strategies prior to deployment

PFAS Analytical Methods in Aqueous and Solid Samples

Methods program	Method	Type	Matrices	Publication date:
Safe Drinking Water Act (OW)	Method 533	Targeted	Drinking water	2019
	Method 537.1	Targeted	Drinking water	2020
SW-846 (OLEM)	SW-846 Methods 3512 and 8327	Targeted	Non-potable water	2021
Clean Water Act (OW)	Method 1633	Targeted	Non-potable water Solids	2024
	Method 1621	Aggregate	Non-potable water	2024

Clean Water Act Method 1633

Sample Preparation:

- Aqueous: Solid phase extraction (WAX)
- Solid: Triplicate basic solvent extraction

Cleanup:

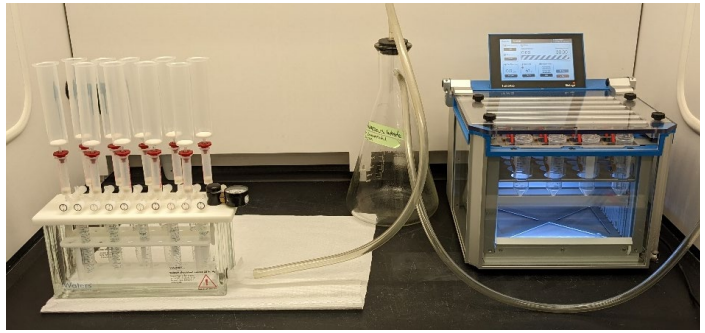
- Aqueous: non-porous graphitized carbon
- Solid: WAX SPE and graphitized carbon

Determinative Analysis:

- Liquid chromatography-tandem mass spectrometry (triple quad)
- 40 target analytes
- 24 isotopically labeled extracted internal standards
- Isotope dilution calibration

Validation study matrices:

- Wastewater (influent and effluent)
- Groundwater
- Surface water
- Landfill leachate
- Soil
- Sediment
- Biosolids
- Fish and shellfish tissues



Validated Limits of Quantitation (for most sensitive targets):

- 1-4 ng/L (aqueous)
- 0.16-0.4 ug/kg (soil/sediment)
- 0.05-2 ng/g (solids)

Clean Water Act methods team lead:
Adrian Hanley, EPA OW
hanley.adrian@epa.gov

SW-846 Methods 3512 and 8327

Method 3512, aqueous sample prep:

- Dilute 1:1 with methanol, filter, add 0.1% acetic acid
  - Rapid, simple, few opportunities for contamination or loss

Cleanup:

- None

Method 8327, determinative analysis:

- Liquid chromatography-tandem mass spectrometry (triple quad)

Validated Limits of Quantitation (for most sensitive targets):

- 10-20 ng/L

Planned SW-846 updates (using data from ASTM D8421, 1633 validation studies):

- Add target analytes, performance data
- Add isotope dilution calibration

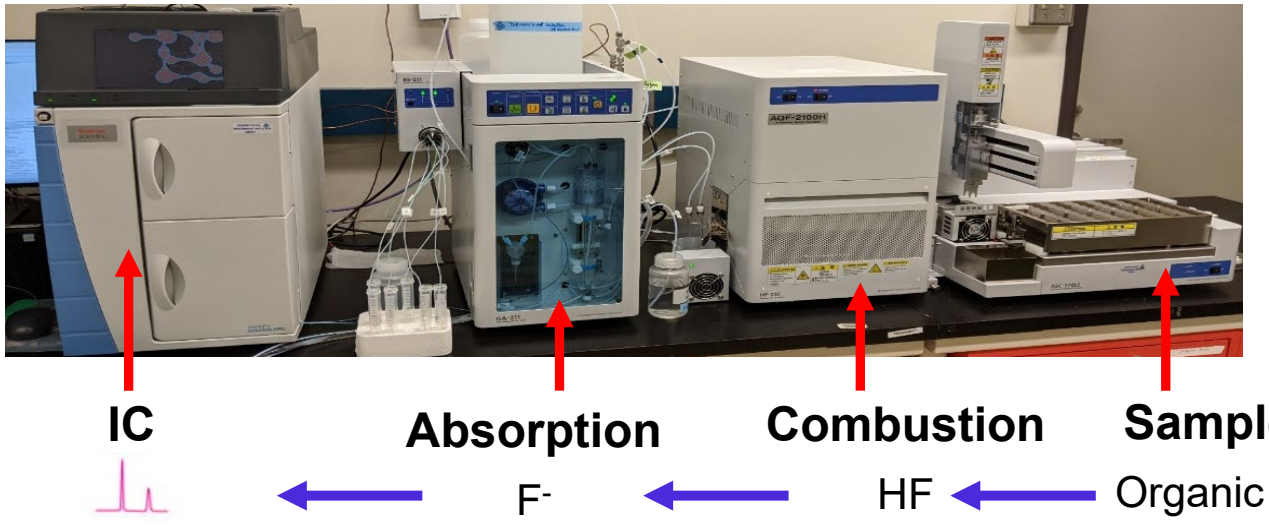
ASTM D8421-24 Validation Study

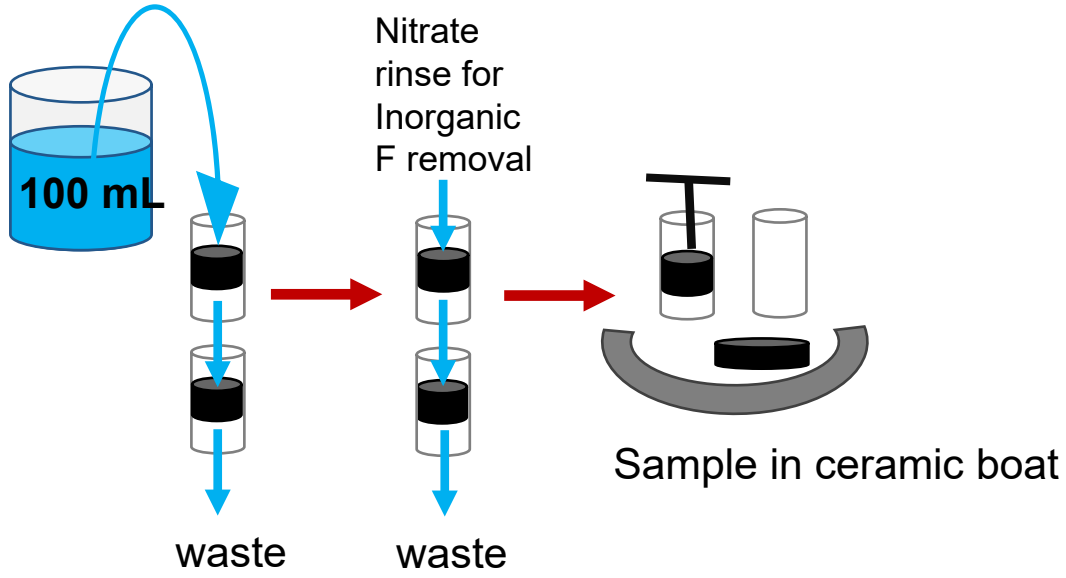
- Matrices:
  - Wastewater (influent and effluent)
  - Groundwater
  - Surface water
  - Landfill leachate
- 44 target analytes, including a couple of ultrashort chain PFAS (PFPrA, TMSI)

3512/8327, ASTM D8421
Method developer:
Larry Zintek, EPA Region 5
zintek.lawrence@epa.gov

Clean Water Act Method 1621: Adsorbable Organic Fluorine (AOF)

- Screening method, adsorbs contaminants onto granular activated carbon, removes inorganic fluoride with nitrate solution, followed by combustion of the carbon
- **Adsorbable Organic Fluorine** compounds are converted to fluoride in the combustion process and measured by ion chromatography





Clean Water Act project lead:
Bekah Burket, EPA OW
burket.sarah@epa.gov

Validation study, Minimum Level (LOQ) = 5 µg/L (as fluoride)

Drinking Water Method Development

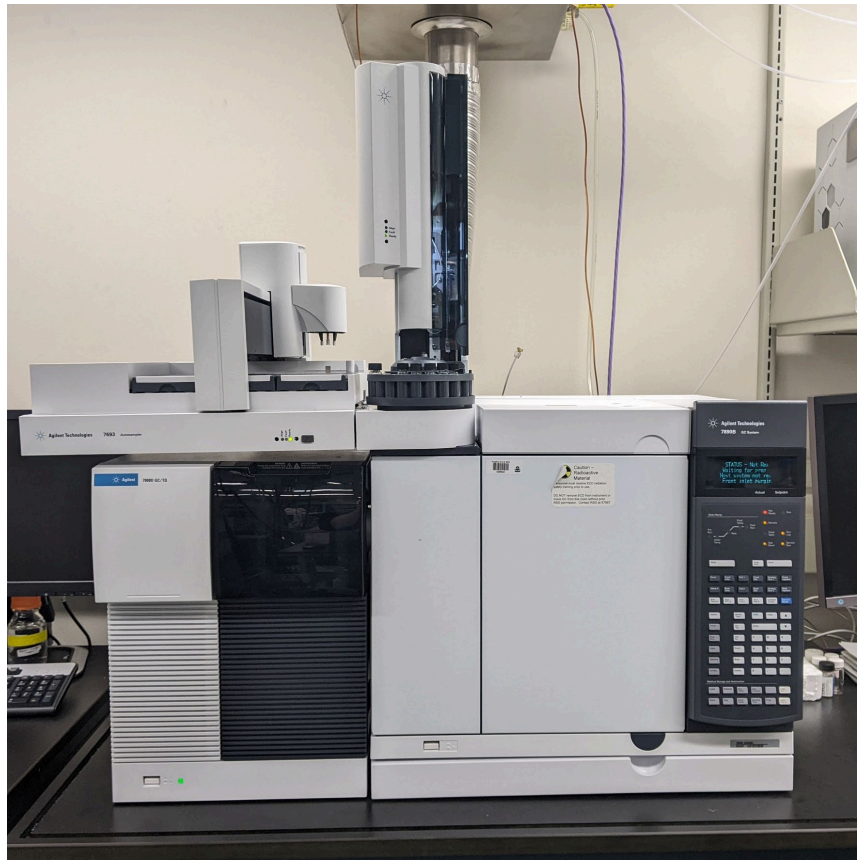
- **EOF/CIC**
  - Interference from inorganic fluoride/fluoridation is removed >99.99%
  - Optimization of inorganic fluoride rinse of SPE cartridge and evaporation parameters is ongoing
  - Recovery limitations for ultra short chain PFAS, volatile PFAS, sulfonamides
  - Expect lower method detection limit (MDL) than 1621
  - Screening method that may not be appropriate for regulatory purposes
- **Drinking water method for ultrashort chain PFAS**
  - Select C1-C3 PFAS
  - Solvent dilution/Direct injection
  - In-line solid phase extraction to LC-MS/MS

EOF/CIC project lead:
Dan Tettenhorst
tettenhorst.dan@epa.gov

OW PFAS methods lead:
Will Adams
adams.william@epa.gov

Analytical method development project: Semivolatile PFAS in soil and groundwater

- Target analytes: neutral, semi-volatile, precursor PFAS
  - Fluorotelomer alcohols, acrylates
- Liquid-liquid extraction or liquid-solid extraction with ethyl acetate
- Analysis: GC-MS/MS, positive chemical ionization
- Single lab detection limits: 30-300 ng/L



FTOHs/FTACs ORD project lead:
Jean Van Buren
vanburen.jean@epa.gov

Non-Targeted Analysis

- Conduct non-targeted analysis for PFAS
  - Technical support to states and tribes
  - EPA research and sampling activities
- Advancing tools and resources for non-targeted analysis
  - Best practices for non-targeted analysis (BP4NTA)
    - Working group to address challenges in non-targeted analysis studies using mass spectrometry
    - Co-chairs from FDA and Shimadzu
  - Practical application guide for the discovery of novel PFAS in environmental samples using high resolution mass spectrometry (2023)
- Technology transfer to states and EPA regional labs

Aggregate/class-based analytical methods Method Development Project: TOP Assay

- Total Oxidizable Precursors (TOP) Assay
  - Alkaline persulfate oxidation to convert PFAS precursors to perfluoroalkyl acids
- Collaborators:
  - EPA, Commercial labs, universities, other federal agencies
- Goal: Complete method development for waters in early 2025, followed by solids

Challenges	Potential Solutions
Ensure efficient oxidation	• Pretreatment to remove DOC • Heat-activated vs UV-activated • Surrogate to monitor oxidation process
Improve fluorine mass balance	• Monitor for ultra-short chain transformation products
Minimize volatile loss	• Closed system
Processes for solids	• Extraction followed by oxidation vs direct oxidation

TOP Assay ORD project lead:
Moha Ateia Ibrahim
ibrahim.mohamed@epa.gov

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

Poll Question:

How many EPA headquarters offices publish test methods?

A) One

B) Four

C) Five

D) Six

Answer: C, five: OAR, OCSPP, OW, OLEM, ORD. However, it may depend on how we define ‘method’ and ‘publish’! Refer to links below for more information about EPA PFAS methods and EPA methods programs.

https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research

https://www.epa.gov/system/files/documents/2023-09/TERMS%20USED%20TO%20DESCRIBE%20THE%20STANDING%20OF%20US%20EPA%20METHODS.PDF

Aqueous leaching methods: SW-846 LEAF Methods

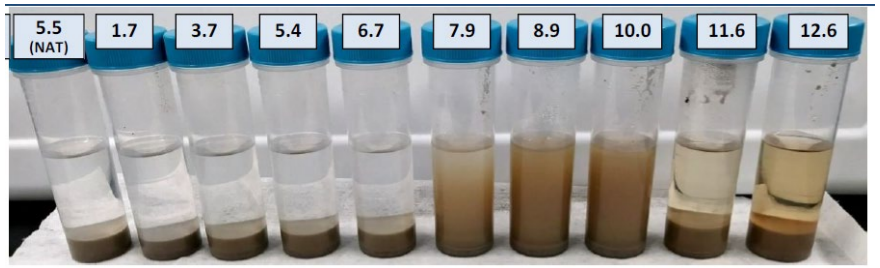
- Methods **1313**, **1316**: Batch equilibrium leaching tests
  - *Method 1313: Varies solution pH (range: 2 to 13)*
  - *Method 1316: Varies liquid-solid ratio (L/S range 0.5 to 10)*
  - *Granular solids*
- Methods **1314**, **1315**: Dynamic leaching tests
  - *Method 1314: Up-flow column percolation test – granular solids*
  - *Method 1315: Tank leaching test - monolithic or compacted granular solids*
- Multi-point aqueous leaching methods
- Used to better model leaching behavior, evaluate immobilization strategies prior to deploying in the field

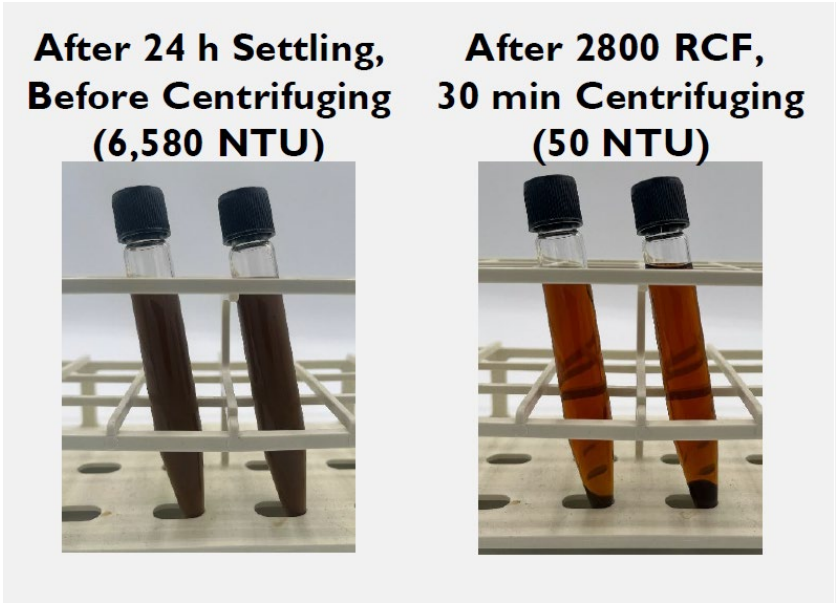
Aqueous Leaching: Adapting LEAF methods to SVOCs and PFAS

- Current status: Multi-laboratory validation studies are underway for **1313A** and **1316A**, and **1314A** is starting soon
- Planning to complete Method **1315A** development in the coming year
- Validation study:
  - Four field-contaminated soils, two with SVOCs and two with PFAS
  - Four participating laboratories (commercial, government), with Vanderbilt University as the reference lab
  - Aqueous leachate samples analyzed by a commercial testing laboratory
- Timeline: **1313A**, **1316A**, **1314A** anticipated to be ready to propose for publication in 2025, followed by **1315A**

Aqueous Leaching: SW-846 LEAF Methods Batch equilibration methods 1313A and 1316A

- Advantage: End-over-end mixing to approach equilibrium relatively quickly (e.g., 24 hours for <300 µm particle size), easy to replicate
- Disadvantage: Potential to over-estimate *in situ* leaching
- Challenge: Liquid-solid separations
  - TSS tends to be higher at alkaline pH
  - Aqueous phase not filtered to avoid sorption-related losses, contamination
- Solution: Centrifuge

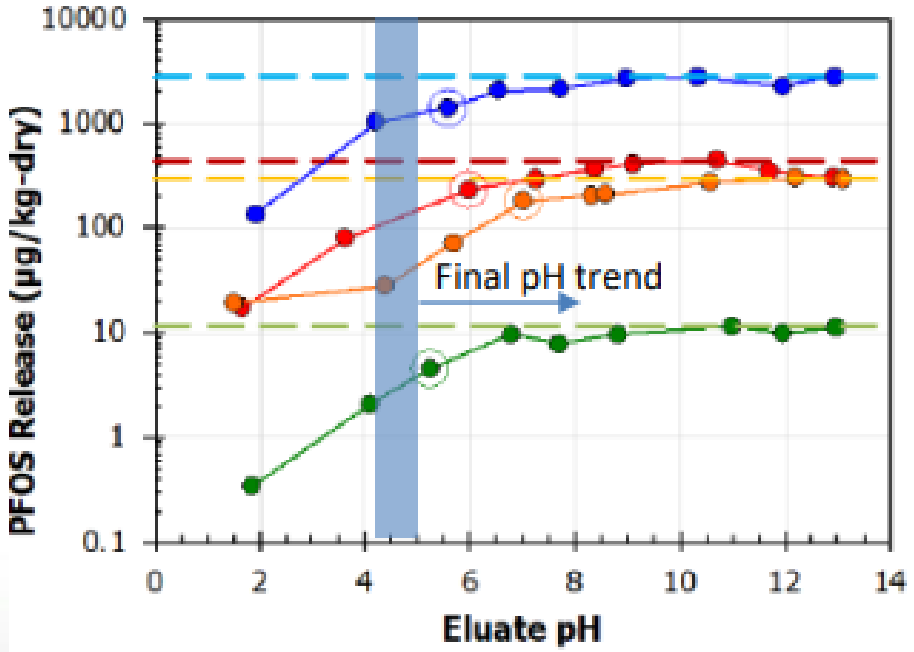


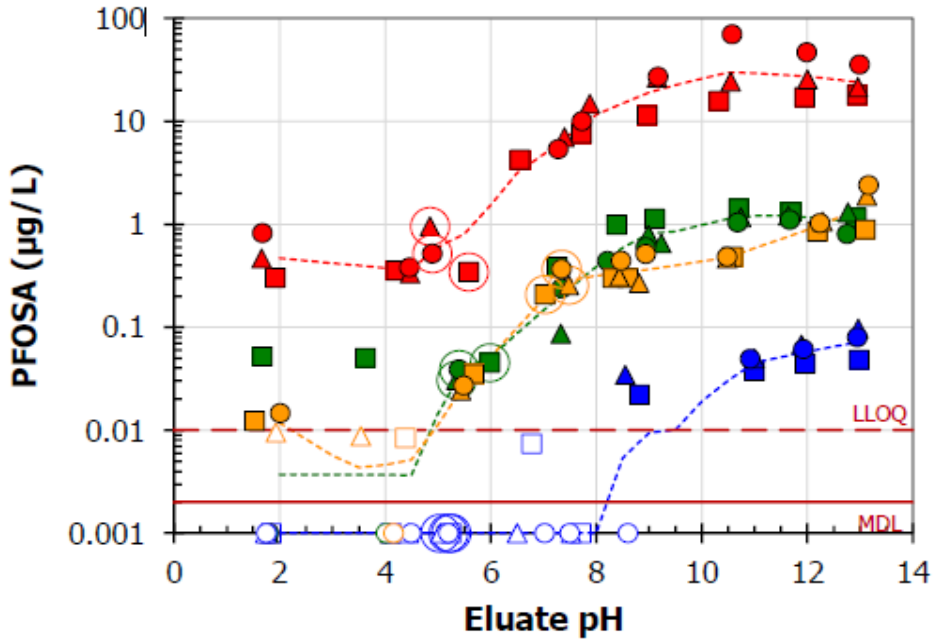


Preliminary info from draft document entitled "Development of Equilibrium Leaching Tests for Materials Containing SVOCs and PFAS Background Information Document", authored by Andrew Garrabrants, Fangfei Liu, Kaelyn Warne, Rosanne DeLapp, Zhiliang Chen, Darlington Yawson, David Kosson (Vanderbilt University), 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

Method 1313A example: pH-dependence of PFAS leaching from AFFF-contaminated soils

- pH range: 2 to 13
- Liquid-to-solid ratio: 10:1
- Equilibration time: 24 hr (<300 µm)





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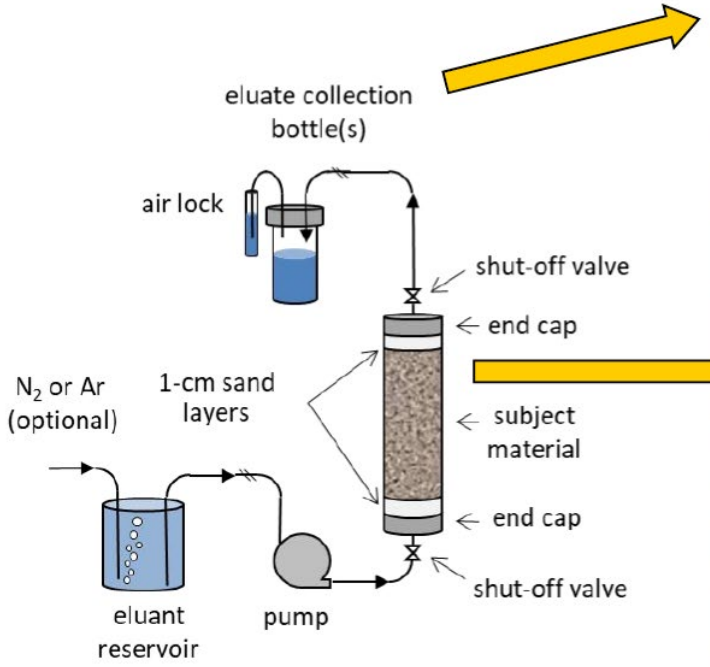
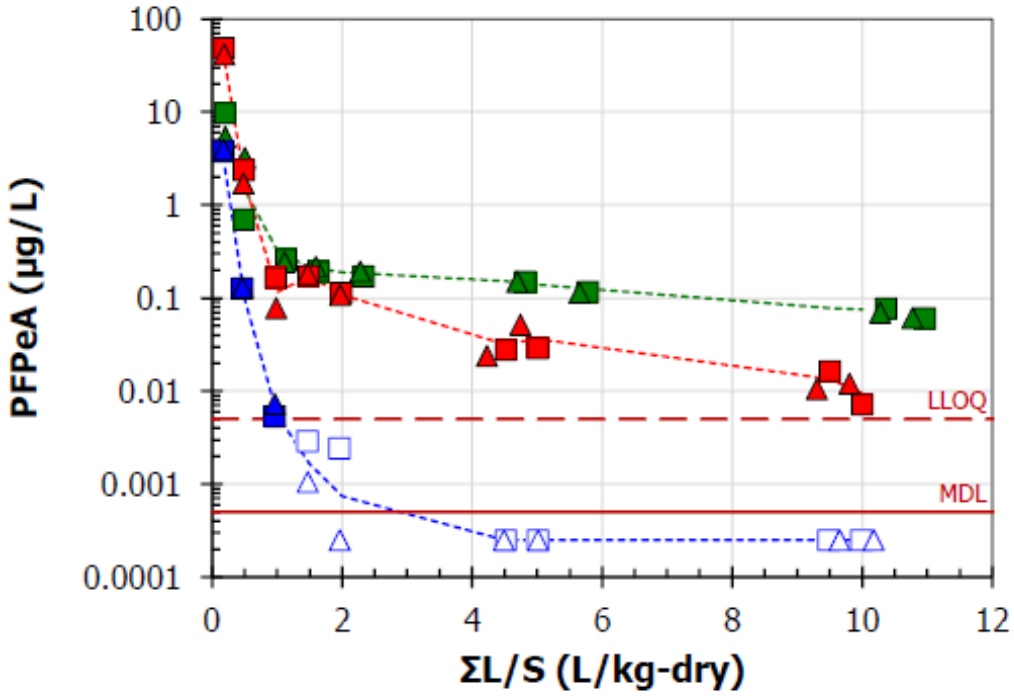
Method 1314A example: Saturated column leaching profile, AFFF-contaminated soil

- Flow rate: 0.5-1.0 L/S (L/kg) day^{-1}
- Fractions: L/S 0.2-10





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SW-846 methods program contacts:

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Opportunities for involvement:

- Participate in an upcoming validation study
- Sign-up for SW-846 mailing list, submit a technical question about SW-846 methods: https://www.epa.gov/hw-sw846/forms/contact-us-about-hazardous-waste-test-methods