SW-846 updates 2024

TNI Environmental Measurements Symposium
August 8, 2024

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

Disclaimer

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Presentation Overview

- Primer on OLEM, RCRA, SW-846
- ASTM-EPA collaboration on flash point testing
- SW-846 updates in progress:
  - Organic methods
  - Inorganic methods
  - Aqueous leaching methods
- Other requests
- Alternatives to methylene chlorided
- Plans for web updates, communications:
  - FAQs
  - Newsletter

Recent OLEM Rulemakings, Guidance:

- **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
- **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)
- **TSCA:**
  - §761 Alternate PCB Extraction Methods and Amendments to PCB Cleanup and Disposal Regulations (88 FR 59662, final rule published 8/29/2023)
  - Not OLEM, but notable: Methylene chloride regulation under TSCA (89 FR 39254, final rule published 5/8/2024)

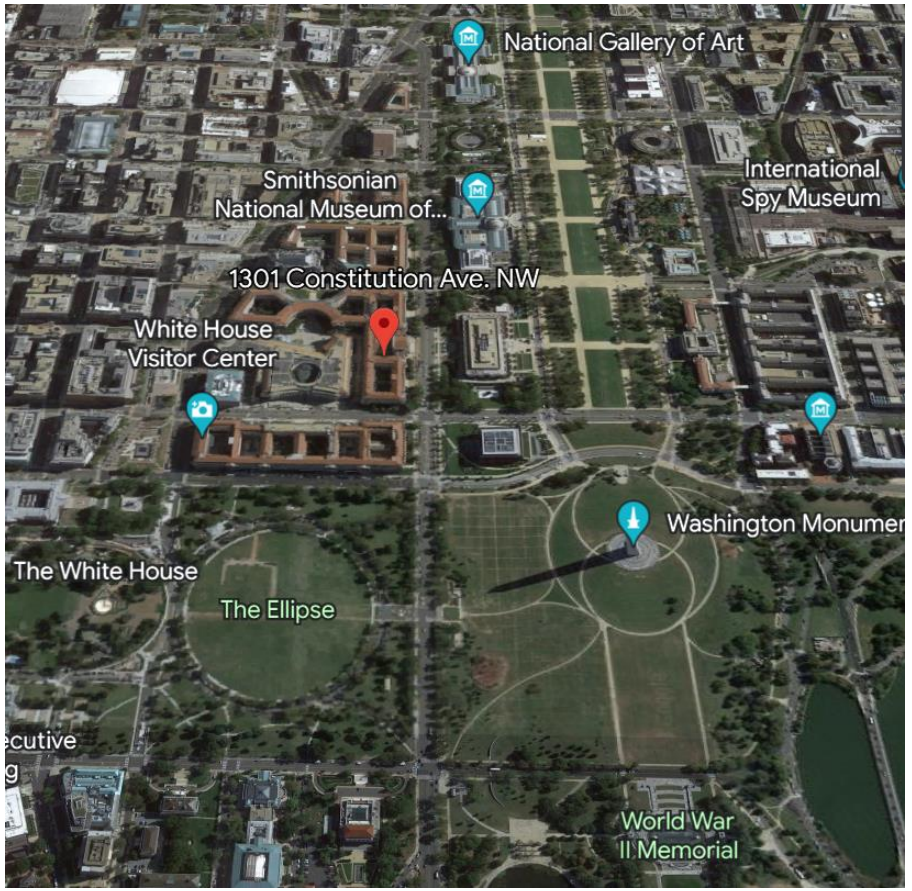
Program offices under Office of Land and Emergency Management (OLEM)

OLEM program offices include:

- Office of Resource Conservation and Recovery (**ORCR**)
- 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**)
- **OMS, PARMS**, etc…

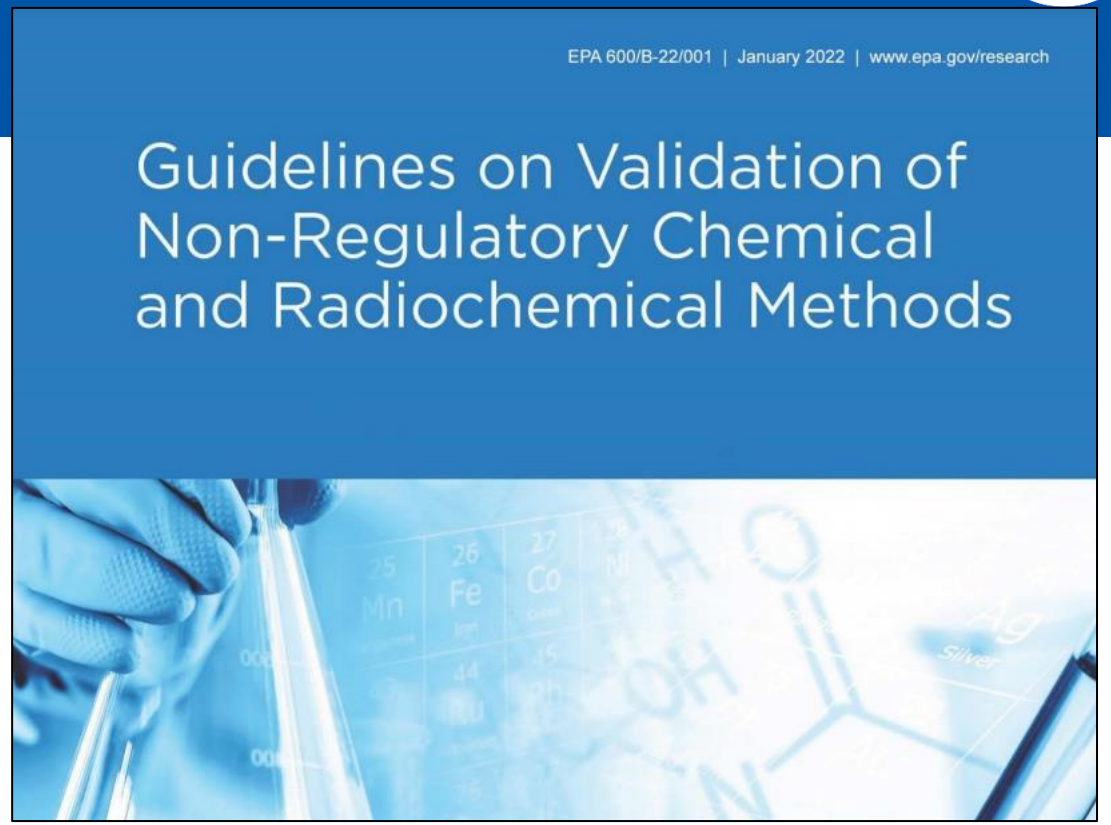
Waste Characterization Branch, Office of Resource Conservation and Recovery

Hazardous waste listings, §261	Narendra Chaudhari
Hazardous waste characteristics, §261	Dan Lowrey
Land disposal restrictions, §268	Sharon Oxendine, Bethany Russell
Homeland security, disaster debris	Melissa Kaps
SW-846 Compendium	Troy Strock
Branch Manager	Jocelyn Hospital



What is a method?

- Optimized process
- Appropriate types, frequency of quality controls
- Characterized performance:
  - Bias/Trueness
  - Detection and Quantification Capability
  - Instrument Calibration/Verification
  - Measurement Uncertainty
  - Precision
  - Range
  - Ruggedness
  - Selectivity



EPA 600/B-22/001, published January 2022
https://www.epa.gov/system/files/documents/2022-12/GUIDELINES%20ON%20VALIDATION%20NRCRM%20EPA%20600B-22-001.PDF
https://www.epa.gov/labs/national-program-manager-regional-laboratories-activities

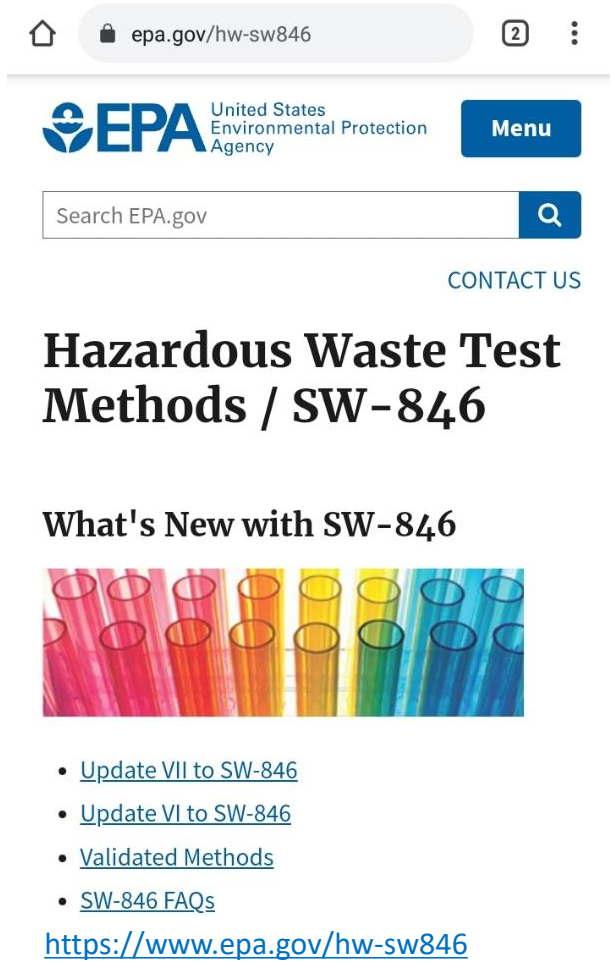
What is a method?

- 4.7 Ruggedness: the extent to which an analytical method remains unaffected by minor variations in operating conditions.

Ruggedness testing involves experimental designs for examining method performance when minor changes are made in operating or environmental conditions. The changes should reflect expected, reasonable variations that are likely to be encountered in different laboratories.

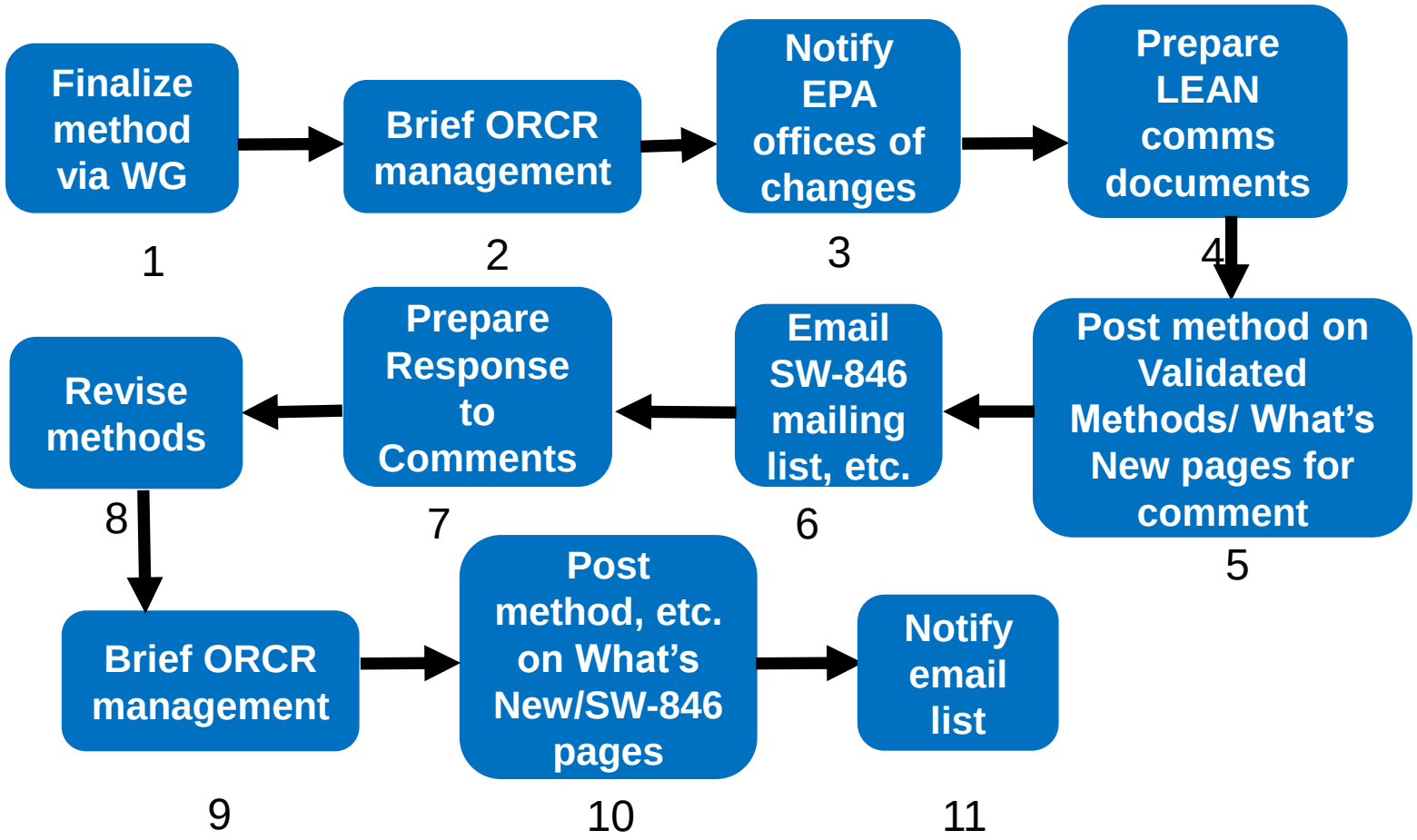
The SW-846 Compendium

- 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"
  - Appropriate modifications are permitted
  - Other reliable, published methods may be used
  - Regulated entity is responsible for ensuring results are appropriate, decisions are accurate



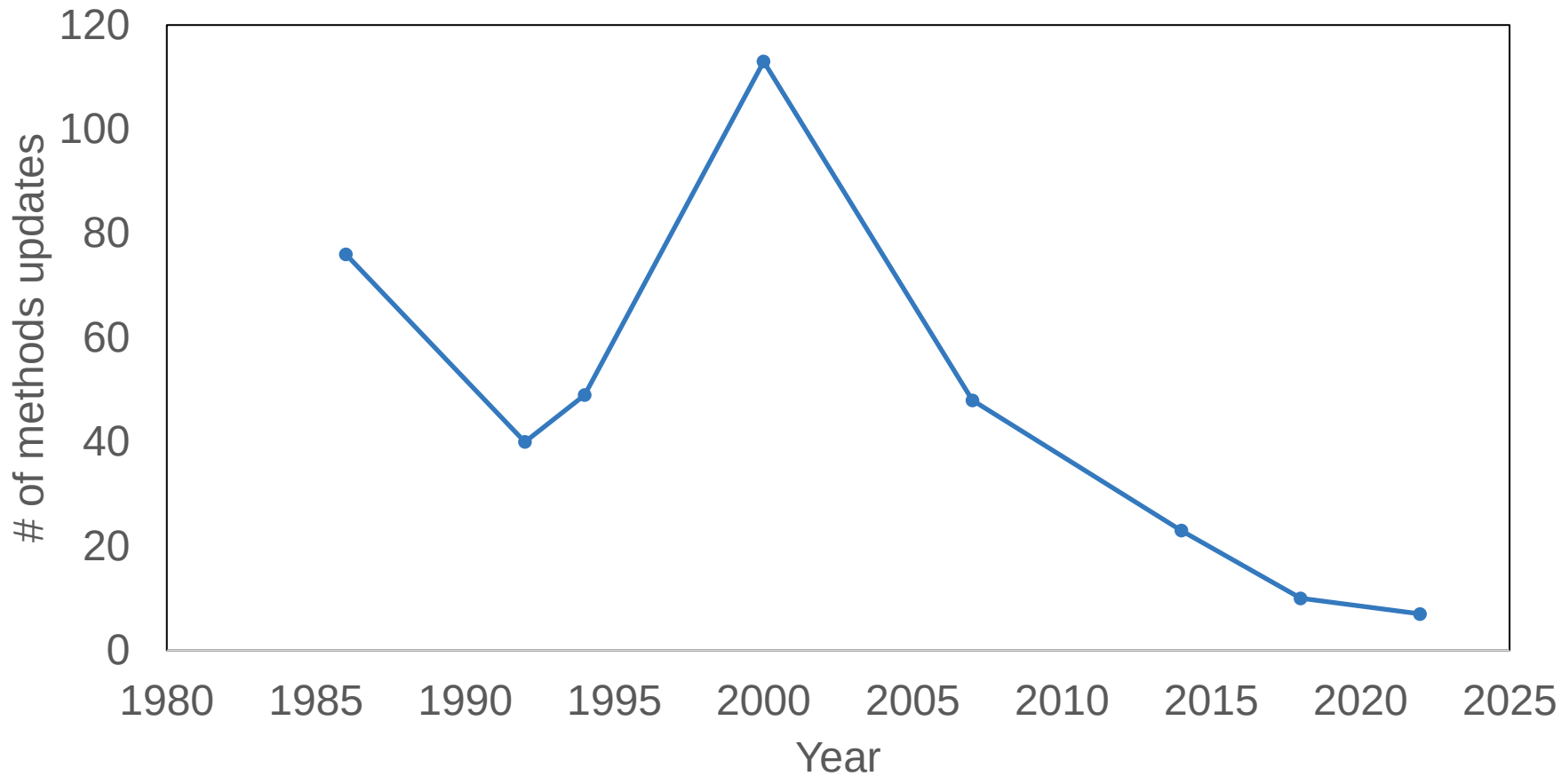
Streamlined Publication Process for Non-Regulatory SW-846 Methods

- Shorter process than publishing proposed and final Federal Register notices
- Provide public notice and request comments through SW-846 mailing list
- Publish a response to comments document in the final docket along with any revised documents



https://www.epa.gov/hw-sw846/streamlined-procedure-publishing-non-regulatory-sw-846-methods

The SW-846 Compendium: Methods updates since 3rd edition



ASTM/EPA Collaboration: Flash Point Standards

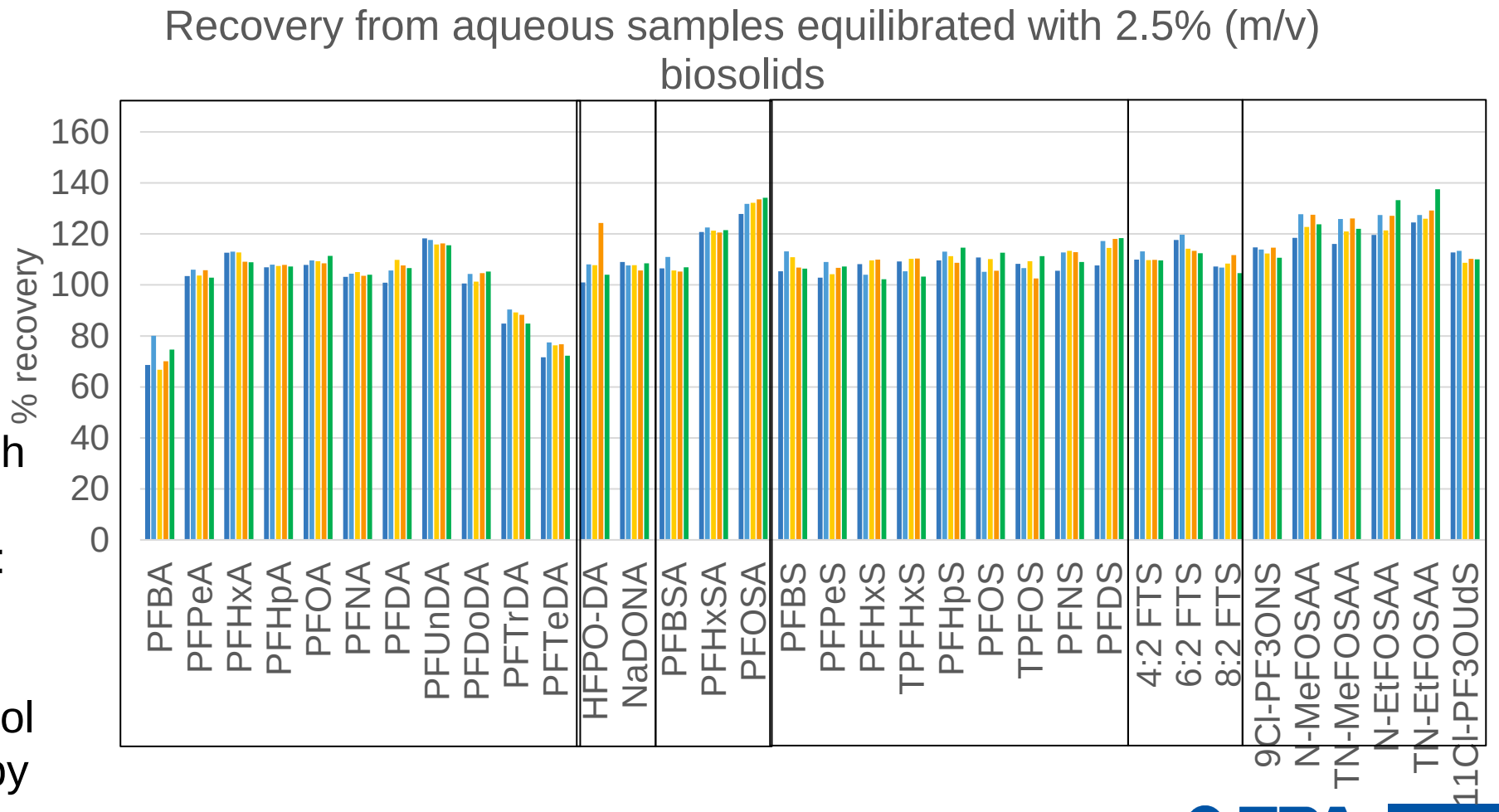
- ORCR published final Modernizing Ignitable Liquids Determinations rule in June 2020, incorporated ASTM **D8174-18** and **D8175-18** by reference at 40 CFR Part 261.21(a)
  - **D8174-18**: Small scale closed cup
    - 2 mL sample size, Applicable flash point range: -20 to 70°C
  - **D8175-18**: Pensky-Martens
    - 75 mL sample size, Applicable flash point range: 20 to 70°C
  - Maintained method-defined aspects of ASTM **D93-79/D93-80**, **D3278-78**
  - State adoption was optional
- Next steps: Interlaboratory validation study
- We need at least 10 participating laboratories - Please contact me if your laboratory has experience, interest

Organic methods updates: PFAS analytical methods

- Completed validation studies:
  - US Department of Defense collaborating with EPA Office of Water to validate Method **1633**
  - ASTM International collaborating with EPA Region 5 lab on interlaboratory study for **D8421-22**
- Next steps: Incorporate data, references into SW-846 updates
  - **3512A, 8327A**: Add target analytes, include extracted internal standard/isotope dilution calibration
  - **3536, 3551, 3670**(?): New sample preparation and cleanup methods

ORD 3512/8327 R&D Experiments: Effect of particulates on recovery

- 5 mL replicate aqueous samples
- Added 125 mg NIST biosolids SRM
- Spiked with PFAS target analytes (PFBA had some background)
- Mixed end-over-end for 48h
- Refrigerated for 48 h
- Prepared by Method **3512**:
  - Spike with labeled analogs
  - Dilute 1:1 with methanol
  - Vortex, filter, analyze by LC/MS/MS



Organic 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
Maintain high redox potential	• Pretreatment for DOC, as needed • Surrogate to monitor oxidation process
Improve fluorine mass balance	• Monitor for ultra-short chain transformation products
Minimize volatile loss	• Closed system
Processes for solids	• Heat-activated vs UV-activated • Extraction followed by oxidation vs direct oxidation

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

SW-846 Organic Updates: VOC methods, Chapter 4 sample preservation and holding times

- Validated methods to propose for publication:
  - **5035A**: Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
    - Incorporate reference to frozen holding time study for sealable coring devices from ASTM D6418 research report
    - Move Appendix A into chapters, methods, as appropriate
  - **8015D**: Non-halogenated organics using gas chromatography/flame ionization detection (GC/FID)
    - Add light hydrocarbons
- **Chapter 4**: Include pH ≤ 2 preservation option for acrolein and acrylonitrile in aqueous samples

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Related Topics: Hazardous Waste Test Methods / SW-846

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Validated Test Methods Recommended for Waste Testing

EPA and independent laboratories validated the following methods, which are recommended for use as the most up-to-date methods available. However, these methods have not been formally incorporated into the SW-846 Compendium through the public comment process. While many of the following methods may be added to SW-846 in the future, authorized states may have regulatory restrictions regarding which version of a method can be used.

Therefore, EPA recommends checking with your state or EPA regional office before using the following methods.

Method Number	Method Title	Publication Date
3542A	Extraction of Semivolatile Analytes Collected using Method 0010 (Modified Method 5 Sampling Train)	2005-05
3570	Microscale Solvent Extraction (MSE)	2002-11
3571	Extraction of Solid and Aqueous Samples for Chemical Agents	2007-07
5030C	Purge-and-Trap for Aqueous Samples	2003-05
5035A	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples	2002-07

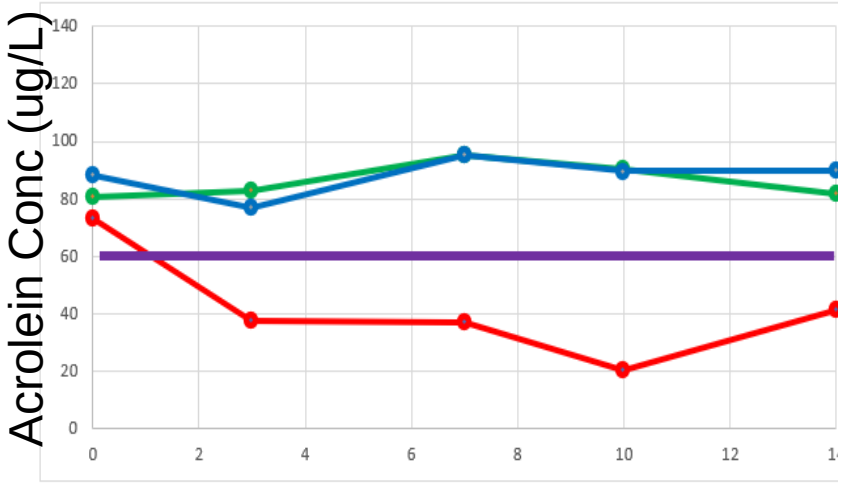
https://www.epa.gov/hw-sw846/validated-test-methods-recommended-waste-testing

Acrolein and Acrylonitrile aqueous stability study

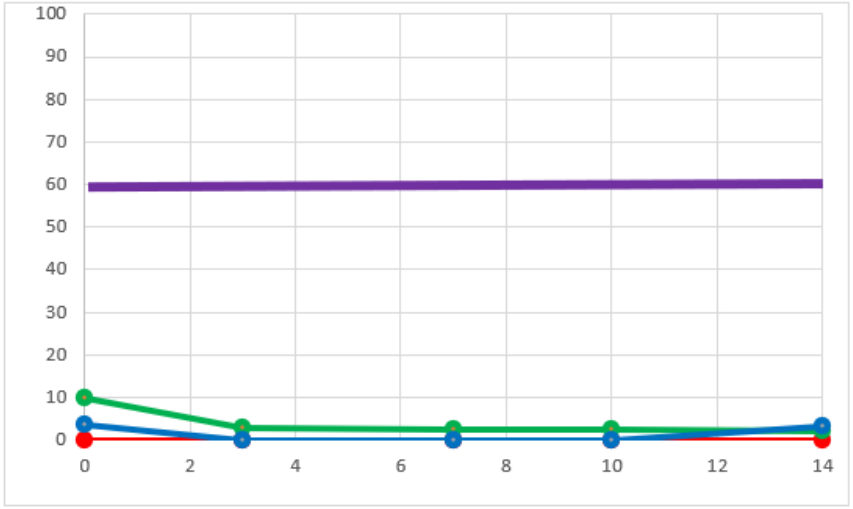
- Multiple commercial labs participated in a 14 day stability study
- Samples preserved at pH 2, pH 4-5, no pH adjustment
- Conclusions: pH 2 preservation worked as well or better than pH 4-5
- Acrolein was not as stable as acrylonitrile

pH 2; pH 4 – 5; No preservative Lower Control Limit

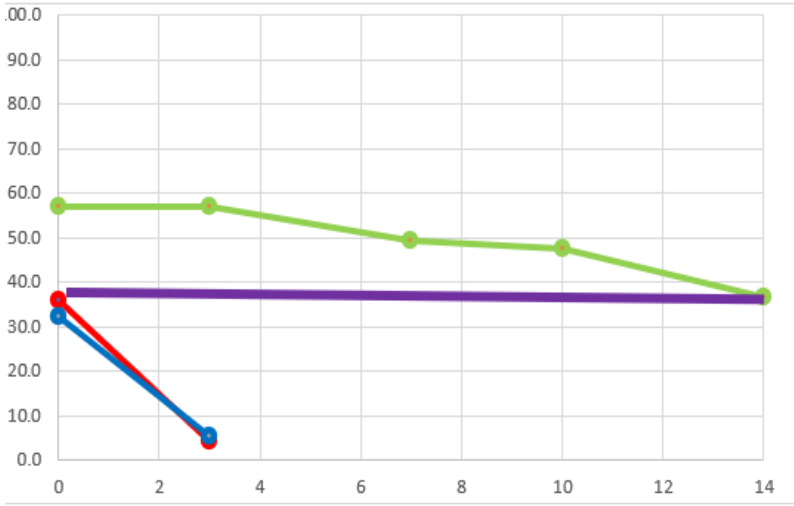
POTW effluent



Industrial wastewater



Landfill leachate



Days in refrigerated storage

Inorganic Methods Update: 3050C

- **3050C**, “Acid Digestion of Sediments, Sludges and Soils”
- Motivation for update:
  - **3050B (**1996) Used different digestion procedures for ICP-OES and ICP-MS
    - Only nitric acid for ICP-MS to minimize polyatomic interferences from chlorine
  - Modern ICP-MS instruments use polyatomic interference correction technologies (e.g., collision/reaction cell, triple quadrupole)
  - Same digestate can be analyzed by ICP-OES and ICP-MS

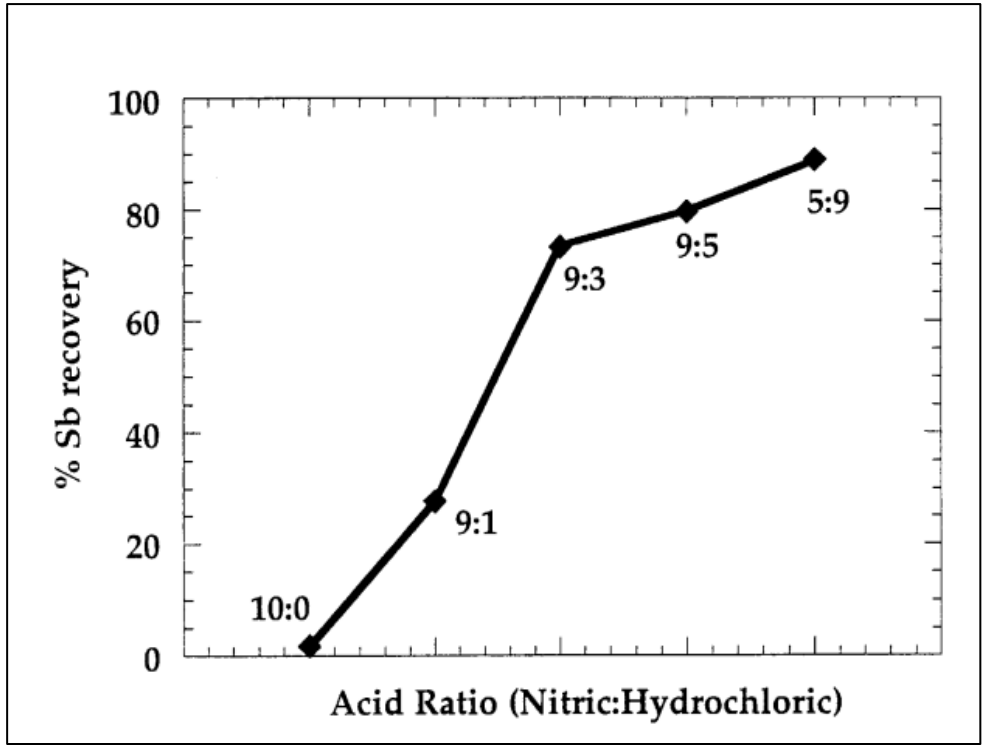


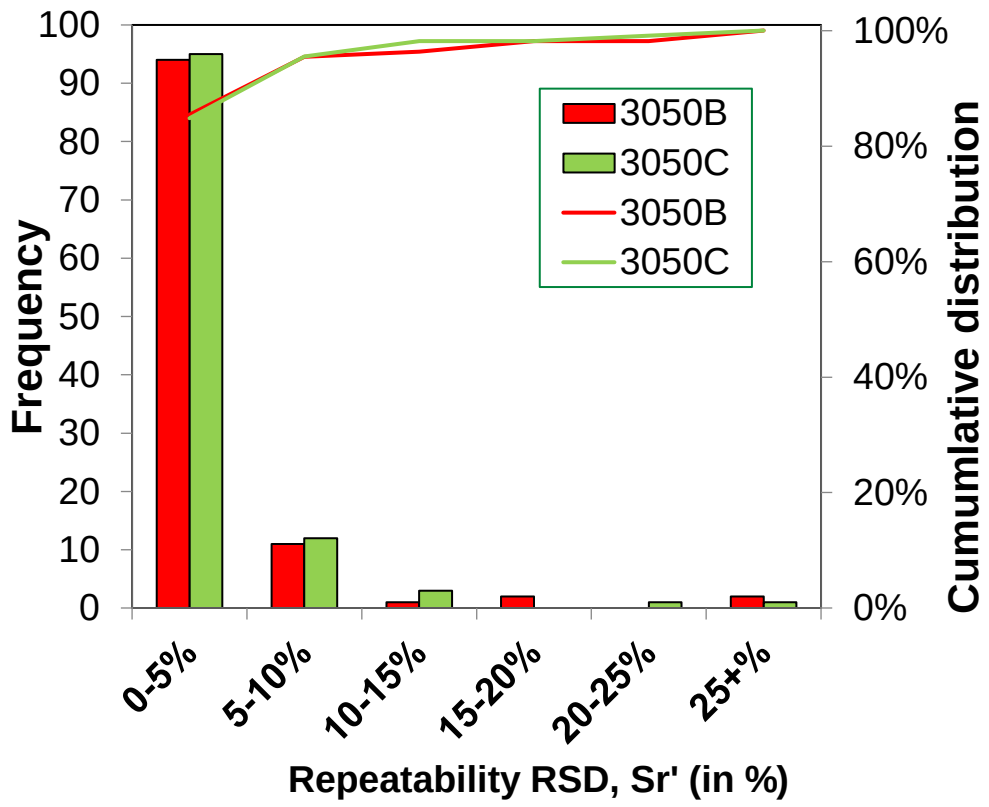
Figure from **3051A**, microwave digestion method for solids

Inorganic Methods Update: 3050C

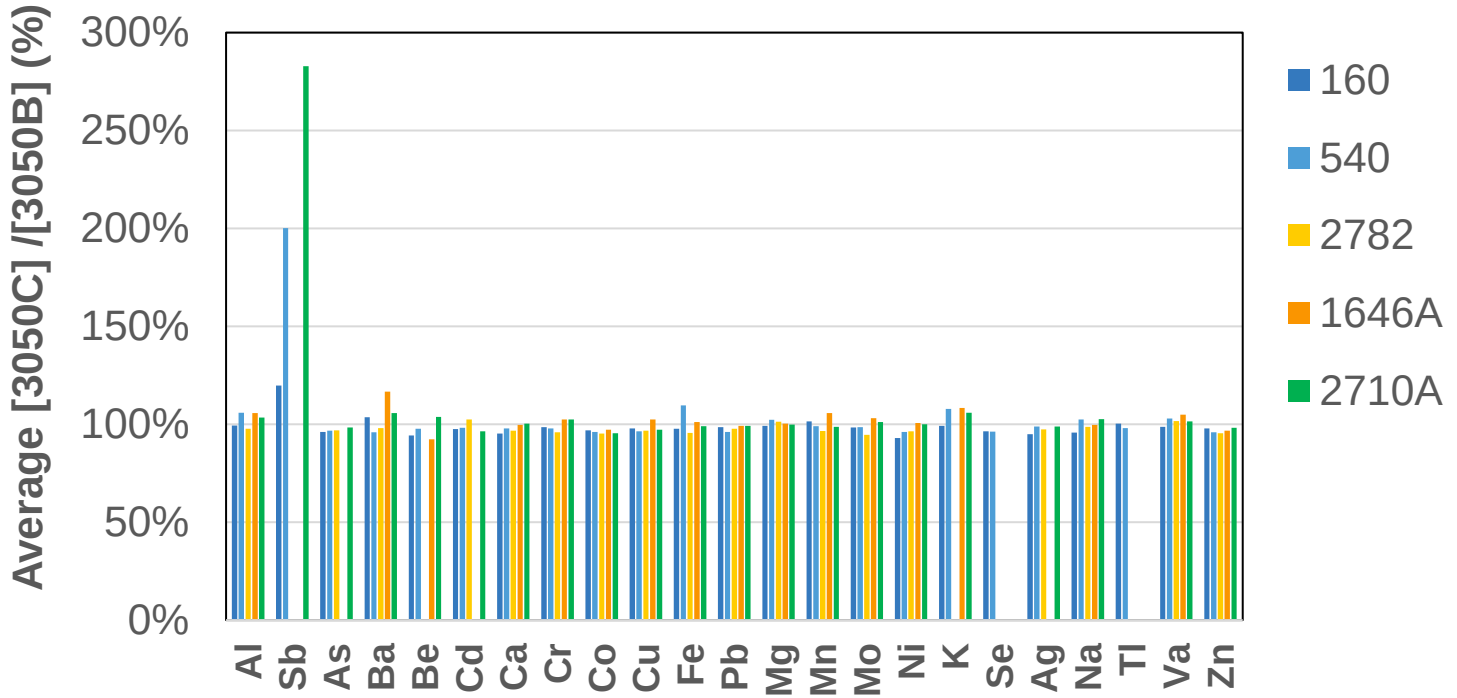
- **3050C**, “Acid Digestion of Sediments, Sludges and Soils”
  - Updated digestion process - same for ICP-OES and ICP-MS:
    - Initial reflux with HNO_3 and HCl
    - Treatment with hydrogen peroxide
    - Final reflux with HCl
- Anticipated Release: Fall 2024 propose for public comment
- Update will include technical corrections to **3500**-series organic extraction methods (2010 spiking memo), **8000D** (fix equation)

Inorganic Methods Update: 3050C

Distribution of repeatability RSDs for elements in reference materials, 6020B



Comparison of 3050C and 3050B grand mean concentrations by reference material, 6010D



Aqueous leaching methods: SW-846 LEAF Methods

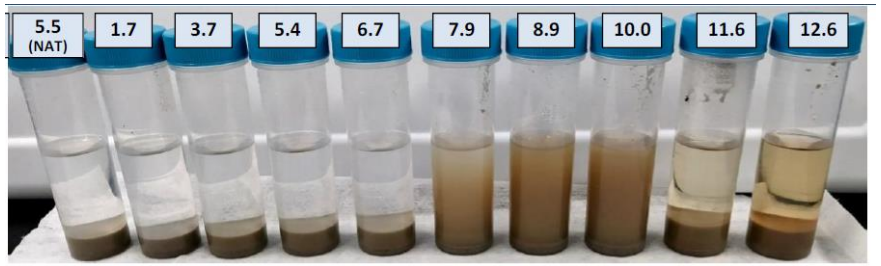
- Methods 1313, 1316: Batch equilibrium leaching tests
  - *Method 1313: Varies solution pH (range: 2 to 13)*
  - *Method 1316: Varies liquid-solid ratio (L/S range 0.5 to 10)*
  - *Granular solids*
- Methods 1314, 1315: Dynamic leaching tests
  - *Method 1314: Up-flow column percolation test – granular 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

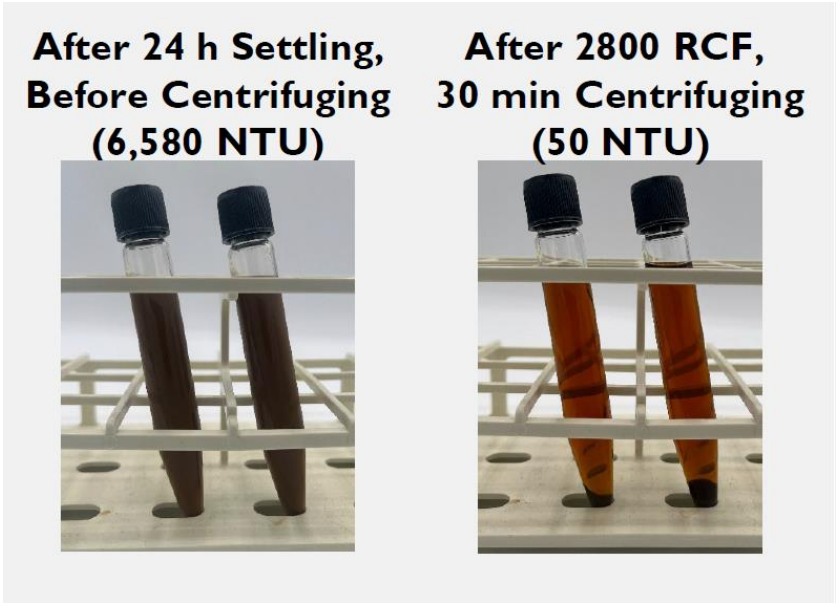
Aqueous Leaching: Adapting LEAF methods to SVOCs and PFAS

- 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 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 1313 and 1316

- 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
  - No filtration avoids sorption-related losses
  - Alum addition resulted in inconsistent separations, increasing TSS during storage
- Solution: Centrifuge

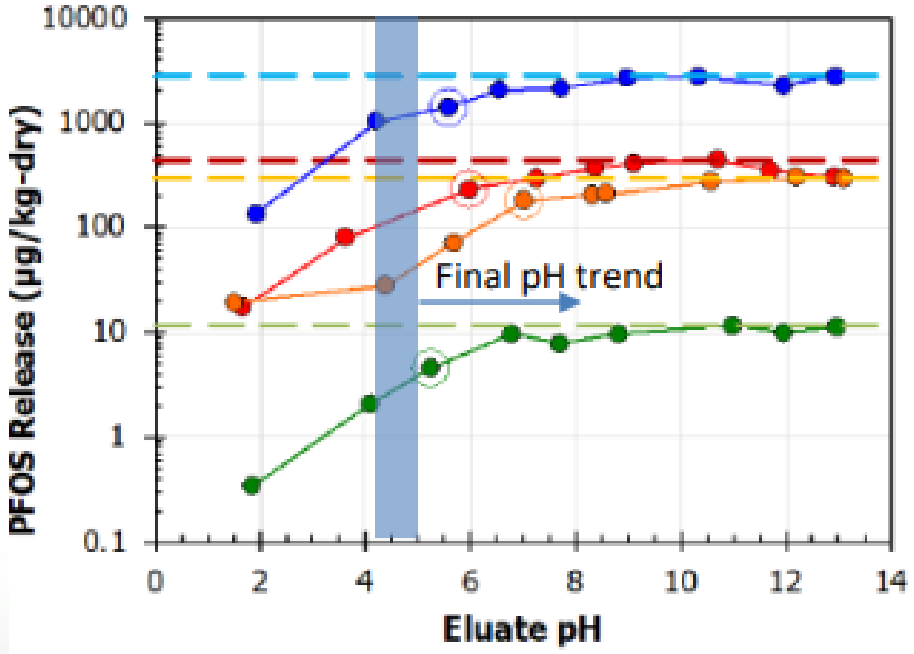


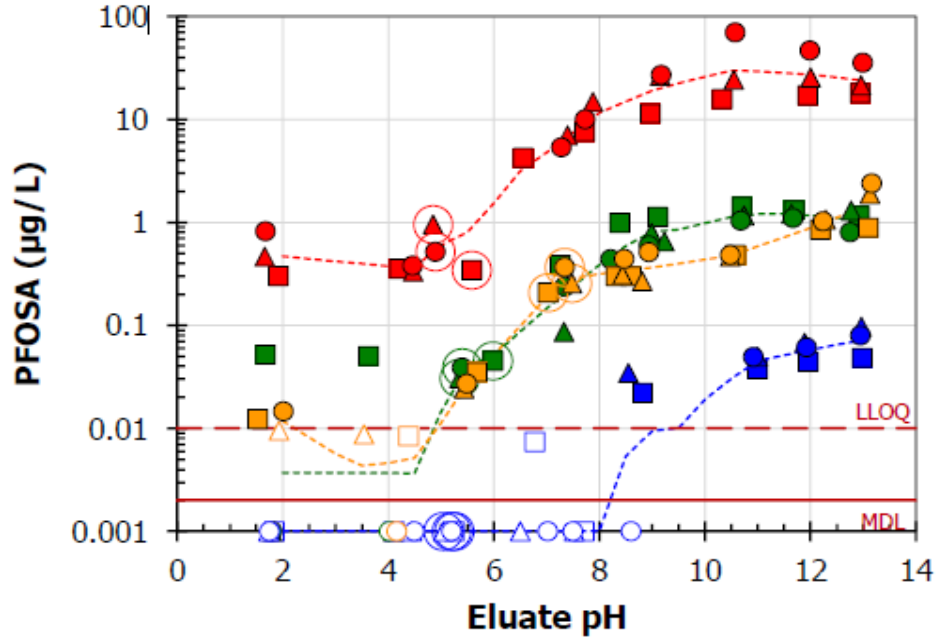


Preliminary info from draft document entitled "Development of Equilibrium Leaching Tests for Materials Containing SVOCs and PFAS Background Information Document", authored by Andrew Garrabrants, Fangfei Liu, Kaelyn Warne, Rosanne DeLapp, Zhiliang Chen, Darlington Yawson, David Kosson (Vanderbilt University), 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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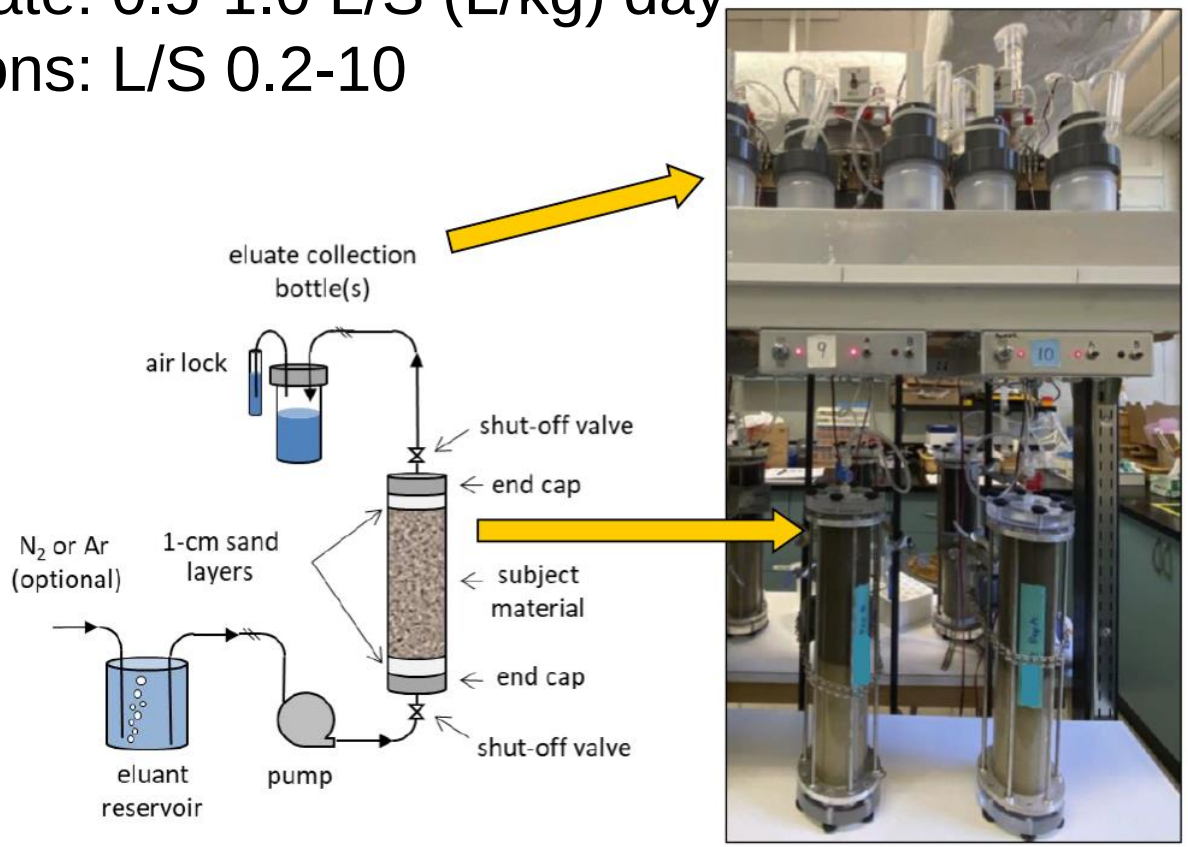
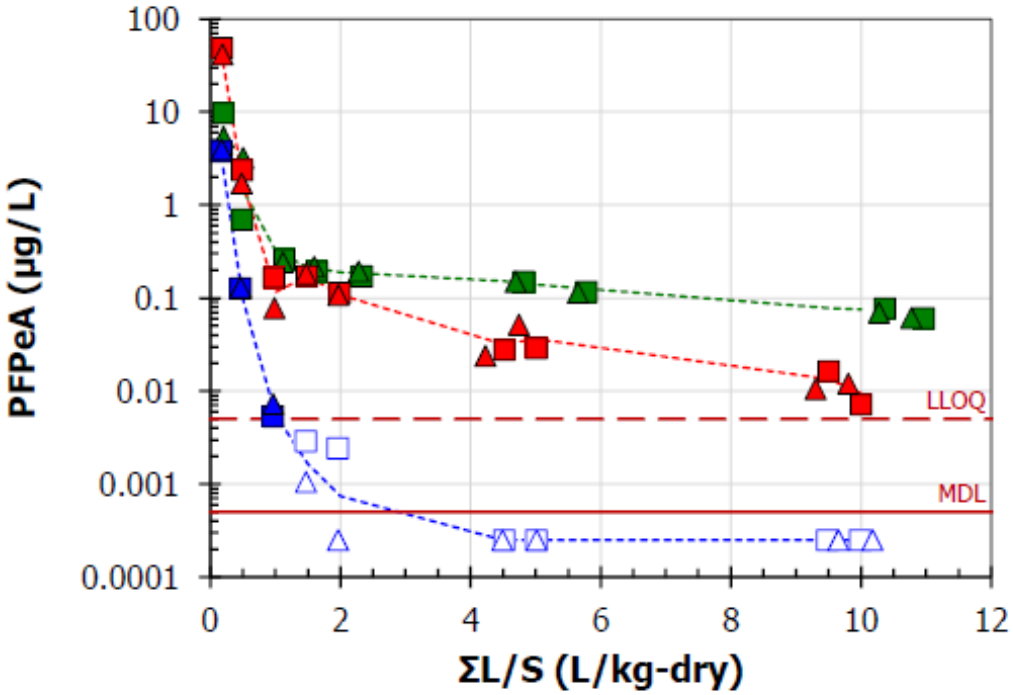
Method 1314A example: Saturated column leaching profile, AFFF-contaminated soil

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





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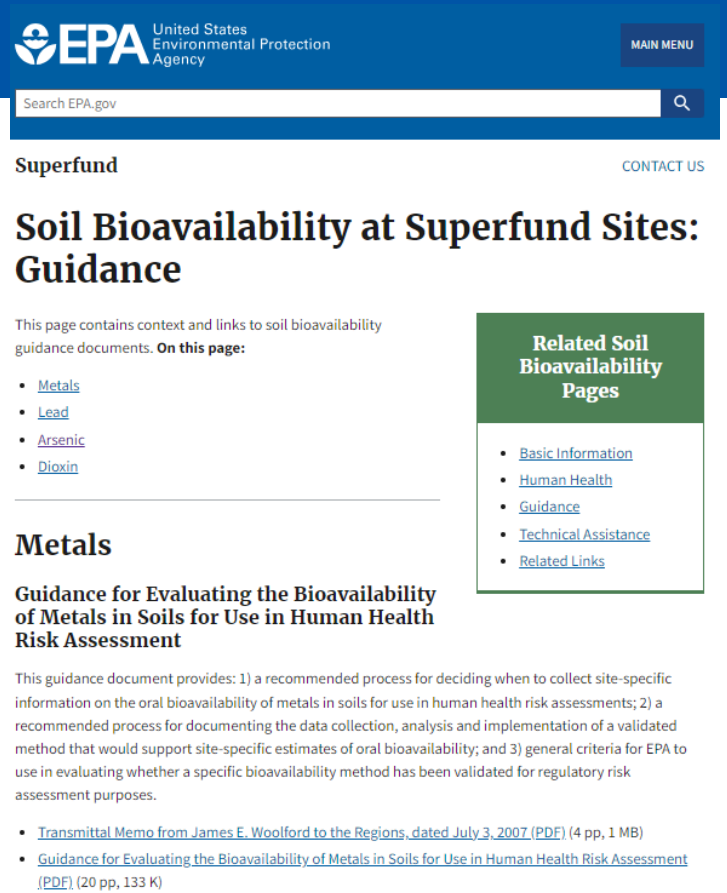
Aqueous leaching methods: Include Arsenic in Method 1340A

- SW-846 Method **1340**, “In Vitro Bioaccessibility Assay for Lead in Soil” published in 2017
- Used to estimate relative bioavailability in ingested soil
- Validation study for lead and arsenic is complete, round-robin study report written
- Current status: ORD and OSRTI workgroup that led validation study are reviewing updated method
- Next steps:
  - SW-846 methods workgroup review, management review, propose for public comment



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Superfund

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Soil Bioavailability at Superfund Sites: Guidance

This page contains context and links to soil bioavailability guidance documents. **On this page:**

- Metals
- Lead
- Arsenic
- Dioxin

Related Soil Bioavailability Pages

- Basic Information
- Human Health
- Guidance
- Technical Assistance
- Related Links

Metals

Guidance for Evaluating the Bioavailability of Metals in Soils for Use in Human Health Risk Assessment

This guidance document provides: 1) a recommended process for deciding when to collect site-specific information on the oral bioavailability of metals in soils for use in human health risk assessments; 2) a recommended process for documenting the data collection, analysis and implementation of a validated method that would support site-specific estimates of oral bioavailability; and 3) general criteria for EPA to use in evaluating whether a specific bioavailability method has been validated for regulatory risk assessment purposes.

- Transmittal Memo from James E. Woolford to the Regions, dated July 3, 2007 (PDF) (4 pp, 1 MB)
- Guidance for Evaluating the Bioavailability of Metals in Soils for Use in Human Health Risk Assessment (PDF) (20 pp, 133 K)

https://www.epa.gov/superfund/soil-bioavailability-superfund-sites-guidance#arsenic

TSCA methylene chloride rule

- Regulation:
  - Prohibited uses of methylene chloride
  - Made an exception for laboratory testing, but reduced workplace exposure limits by 10-fold
  - Implementation timeframe is relatively short
- Implications:
  - Methylene chloride cost likely to increase
  - Available laboratory testing capacity could decrease
- Potential solutions:
  - Reduce sample size, extraction volume (e.g., SPE, micro-extraction)
  - Alternative solvents (e.g., Ethyl acetate)
  - Alternative determinative techniques (e.g., LC/MS)

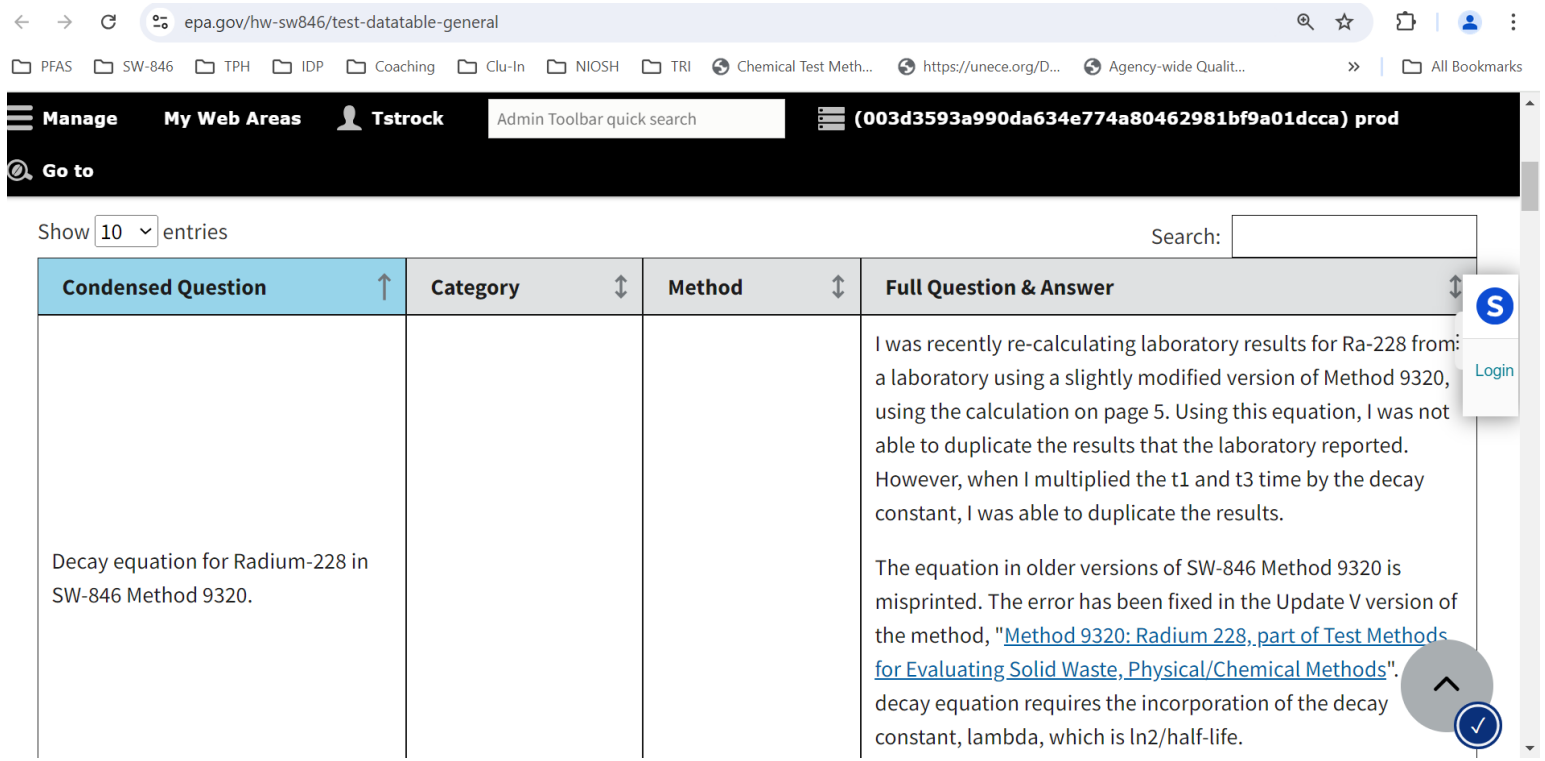
https://www.federalregister.gov/documents/2024/05/08/2024-09606/methylene-chloride-regulation-under-the-toxic-substances-control-act-tsca

Other SW-846 projects, method publications

- Representative sample collection methods for different classes of chemicals in soils
- Passive sampling for PAHs and PCBs in sediment porewater
- Automated extractions for PFAS in solids, e.g., microwave, pressurized fluid extraction
- Alternative technologies for acid digestions of solid samples, e.g., infra-red
- Alternative analytical methods for petroleum hydrocarbons, e.g., UV fluorescence
- Alternatives to organofluorine testing, e.g., reductive dehalogenation/ion selective electrode
- etc.

Web updates in progress: Revamp Frequently Asked Questions

- Move FAQs to searchable table, more user-friendly
- Revise some outdated FAQs
- Add more commonly asked questions from inquiries database



Improving communications: Newsletter

- Establish more regular, consistent communications with community of method users
- Provide notifications about current events, including more than just SW-846 updates
- Enable people to subscribe/unsubscribe to mailing list

Special thanks to **Melissa Beedle** in EPA Region 8 for putting it together!

SW-846 methods program contacts:

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Jocelyn Hospital, Waste Characterization Branch manager

- *Phone: (202) 566-2233*
- *E-mail: hospital.jocelyn@epa.gov*

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