Agenda

• Welcome and Introductions
• EPA Method 1633 – Adrian Hanley, EPA
• Minnesota Landfill Study – Laura Marti, MPCA
• Conclusions & Next Steps
USEPA Draft Method 1633 for Per- and Polyfluorinated Alkyl Substances (PFAS) and the NPDES Method Approval Process

The 10,000-foot view
• If you don’t know, and you work in the environmental sector, you’ve been hiding under a rock for the last few years. I won’t bore everyone else who has seen hundreds of “What is PFAS” slides.

• Below are two points one needs to keep in mind when discussing how to analyze environmental samples for PFAS compounds:
  – Thousands of PFAS compounds have been used in industry and released into the environment
  – Many PFAS compounds are known to degrade and form new compounds

What is PFAS?
Because of the multiple Federal and State players in investigation and remediation activities, DoD sought a unified approach to a PFAS analysis method and approached the Administrator for the Office of Water in 2019 to start a collaborative effort to develop, validate, and give formal EPA approval to a PFAS method that would be useful for DoD and various EPA Programs.

DoD agreed to pay for the method validation effort, and follow direction provided through EPA review of each step of the validation process.

EPA is responsible for drafting and revising Method 1633 and drafting portions of the validation study reports.

OLEM is using the data for a parallel SW-846 method validation.
OW’s CWA Method Validation Process

• Methods are approved by EPA for nationwide NPDES use via a process that includes:
  – Identifying a promising technique or procedure based on internal (EPA) or external development efforts (e.g., literature review, lab SOPs, or Voluntary Consensus Standard Body procedures)
  – Formal study planning documentation (e.g., QAPP and/or study plan)
  – Drafting an actual method in EPA format
  – Single-laboratory validation with at least 9 different water and wastewater matrices
  – Refinement of any issues identified in the single-laboratory validation study
  – Multi-laboratory validation targeting 9 laboratories running 9 wastewater matrices
  – Development of QC acceptance criteria that reflect the real-world performance of the method in the multi-laboratory validation study
The method and all the supporting documentation are included in a rulemaking docket, typically for proposal at 40 CFR Part 136.

Following the proposal, EPA:
- Reviews and responds to all public comments received
- Makes any needed revisions to the method based on the comments

The method gains final approval through a final rule that promulgates the method for use in Clean Water Act NPDES compliance monitoring.

No method is formally approved until that rulemaking process is complete, but unapproved methods may still be useful to EPA and other organizations.
Generic OW/Wastewater Method Schedule

• Method validation
  – Single-laboratory validation: 1-2 years
  – Multi-laboratory validation: 1 year

• Rulemaking
  – Proposal: 6 months to 1 year
  – Comment response and finalization: 1-2 years

Note: Once a method has been multi-lab validated, we usually post it on our website. Many states will immediately start using these methods in permits, which is their right if they operate their own NPDES program.

Due to high demand from stakeholders, Method 1633 was posted after single lab validation.
The draft method uses liquid chromatography (LC) with tandem mass spectrometry detection (MS/MS) to target 40 specific PFAS analytes representing:

- Perfluoroalkyl carboxylic acids (11 analytes, including PFOA)
- Perfluoroalkyl sulfonic acids (8 analytes, including PFOS)
- Fluorotelomer sulfonic acids (3 analytes)
- Perfluorooctane sulfonamides (3 analytes)
- Perfluorooctane sulfonamidoacetic acids (2 analytes)
- Perfluorooctane sulfonamide ethanols (2 analytes)
- Per- and Polyfluoroether carboxylic acids (5 analytes, including ADONA)
- Ether sulfonic acids (3 analytes)
- Fluorotelomer carboxylic acids (3 analytes)

- The draft method employs 24 isotopically labeled standards to quantify the 40 analytes by isotope dilution.
Single-laboratory Validation

- DoD selected a procedure developed by SGS-Axys Analytical in British Columbia.
- DoD developed a formal study plan for a single-laboratory validation study.
- OW and OLEM reviewed the study plan and offered recommendations to DoD for steps and matrices of interest to EPA.
- SGS-Axys performed the single-laboratory validation study under the direction of DoD.
- DoD provided OW and OLEM with all the results for our review.
- OW agreed to draft some materials for the DoD study report.
Summary of Single-laboratory Validation

- The DoD single-laboratory study tested:
  - 3 groundwaters
  - 3 surface waters
  - 3 landfill leachates
  - 7 wastewaters from different industries
  - 3 sediments
  - 3 tissues (fish and clams)
  - 3 biosolids
  - 7 soils

- Results were generally good, with some issues related to the landfill leachates, which are very complicated samples.
The reported MDLs from the single-laboratory study varied by analyte and matrix, as summarized below:

- Aqueous sample MDLs ranged from about 0.12 to 5.94 ng/L, with all but 4 of the 40 analytes having MDLs between 0.12 and 1.5 ng/L.
- Soil sample MDLs ranged from about 0.014 to 0.348 ng/g (dry weight).
- Tissue sample MDLs ranged from about 0.032 to 9.98 ng/g (wet weight), with all but 1 of the 40 analytes having MDLs between 0.032 and 1.5 ng/g.

The MDLs for the 40 analytes were often MDL\textsubscript{b} values, driven by background levels of those analytes in the laboratory and in various supplies and reagents used in the procedure.
As with the MDLs, recoveries of the 29 labeled compounds varied by analyte and matrix.

The average recoveries of most of the labels were between:
- 46 and 148% in wastewater samples
- 48 and 90% in surface water samples
- 65 and 111% in groundwater samples
- 42 and 131% in landfill leachates

The $^{13}$C-labels generally exhibited higher minimum recoveries than the deuterium-labeled compounds in the aqueous samples, likely due to the potential exchange of deuterium with hydrogen from water.

Recoveries in the solid samples were generally higher than in aqueous samples.
Next Steps

- DoD is completing the report on the single-laboratory study.
- EPA will review the draft report and provide comments to DoD before the report is widely released.
- DoD is starting the multi-laboratory validation study using at least 9 laboratories and multiple matrices.
  - DoD’s study will validate the draft method as currently written, without an option for the labs to make any modifications.
  - This will provide a baseline of method performance.
  - Expected to be complete in 2022
- OW will use the study results to develop formal multi-laboratory performance specifications for the final method and prepare the method for proposal.
• Adsorbable organic fluorine (AOF) by combustion ion chromatography (CIC)
  – Adsorbs sample onto activated carbon or other sorbent and wash out inorganic halides (including inorganic Fluorine)
  – Combust in a furnace
  – Exhaust is bubbled through a basic solution that captures fluorine as the fluoride ion ($F^-$)
  – Analyze the solution by ion chromatography to detect the fluoride ion
  – Detects the fluoride from any organofluorine compounds (including any PFAS, but also some pharmaceuticals and pesticides)
  – Does not detect inorganic fluorine

• OW is currently working with ORD and a commercial laboratory to flesh out and test a draft procedure from ASTM.
AOF Considerations

• Similar to EPA Method 1650 for adsorbable organic halides (AOX) that was used in the pulp and paper effluent guideline

• Different PFAS compounds have different affinities for the activated carbon sorbent, making the use of spiked samples for QC purposes more challenging.
  – Which spike compounds should you use? The “good” ones or the poorer performers?

• Because AOF is not a specific compound, but an aggregate measure of organic fluorine content, it may be most useful as a screening procedure or for range-finding efforts.
For more information or additional feedback, please contact:

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Managing PFAS in Minnesota Closed Landfills
Closed Landfill Program - CLP

• 1994 Landfill Cleanup Act

• Created CLP – manage mixed municipal waste LFs

• Landfill responsibility transferred to state

• 110 landfills throughout Minnesota

• Funding sources: tax dollars, CLIF

• Total program cost: ~ $480 million through FY20
  • Estimated need: $309 million over next 30 years

• Link to CLP website
97% of assessed closed landfills have PFAS contamination

- 60 landfills exceed state guidelines, with 80% located outside the metro area
- 15 sites with PFAS found at 10x the health-based guidance values
- Highest level of PFAS in groundwater is at Gofer Landfill in SW Minnesota
MDH health-based guidance values evolve over time as additional research becomes available

- Surrogate values used when widespread detection of chemical in drinking water, but insufficient toxicological data to set an HBV
  - Dec 2021 – HBV for PFHxA
  - 0.2 ug/L

### Values noted in parts per billion (ppb)

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Blue = HRL; Red = HBV; Green = Surrogate
Priorities for managing PFAS at landfills

- Drinking water wells
- Determine extent of contamination
- Leachate and groundwater treatment
- Fund rapid emergency response
Gofer Landfill

- Highest PFAS detections in monitoring wells
  - PFOA = 47 µg/L
  - PFOS = 20 µg/L
- No remediation system
- Thick clay unit protecting aquifer below
- Discharging to surface water
- Delineation Investigation
Large PFAS plume mixed with other disposal site plumes = over 150 sq. mi.
Affected:
• 4 major aquifers
• 14 East Metro communities
• 1000s of private wells
Source - 3M Waste
2009 – 2M yd³ waste excavated, placed in containment cells
2018 - $850M settlement with 3M
Still finding contamination in monitoring wells
  - continue to monitor

https://www.pca.state.mn.us/waste/pfas-waste-sites
Winona County Landfill

- Leachate collection
- Sent to WWTP
- PFAS is higher in the leachate than groundwater
  - PFOS: 0.93 ug/L
  - PFOA: 0.58 ug/L
Communication tools

• [Groundwater Contamination Atlas](#)
• PFAS media event in March 2021
• Sign up for Gov Delivery emails
• Public meetings (virtual & in person)
Minnesota's PFAS Blueprint

- Released in February 2021
- Provides information about PFAS toxicity and their occurrence in Minnesota
- Identifies the state’s approach to managing and addressing PFAS in our environment
- Proposes strategic path forward
  - Full Blueprint
  - Blueprint Summary

Monitoring Plan

- Planned release in 2022
- Lays out a path forward for PFAS monitoring at sites
- Systematic approach to monitoring
Closed Landfill Program

Next Steps

• Receptor monitoring
• Drinking water treatment
• Delineation investigations
• Leachate feasibility study
DNR Updates, Conclusions & Next Steps