Clean Water Act Methods

Overview of EPA's CWA Method Activities

August 2023, Adrian Hanley, U.S. EPA

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

Jesse Pritts – 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.)
- Full 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 stardardized 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)

CWA Microbiology Method Activities

Update EPA Microbial Methods in the 2022 Routine MUR

- Updated some of the older EPA Micro Methods
- Revisions include:
  - Update equipment (e.g., no mercury thermometers, add disposable culture dishes)
  - Standardize language between methods, e.g., QA, scope, legal disclaimer

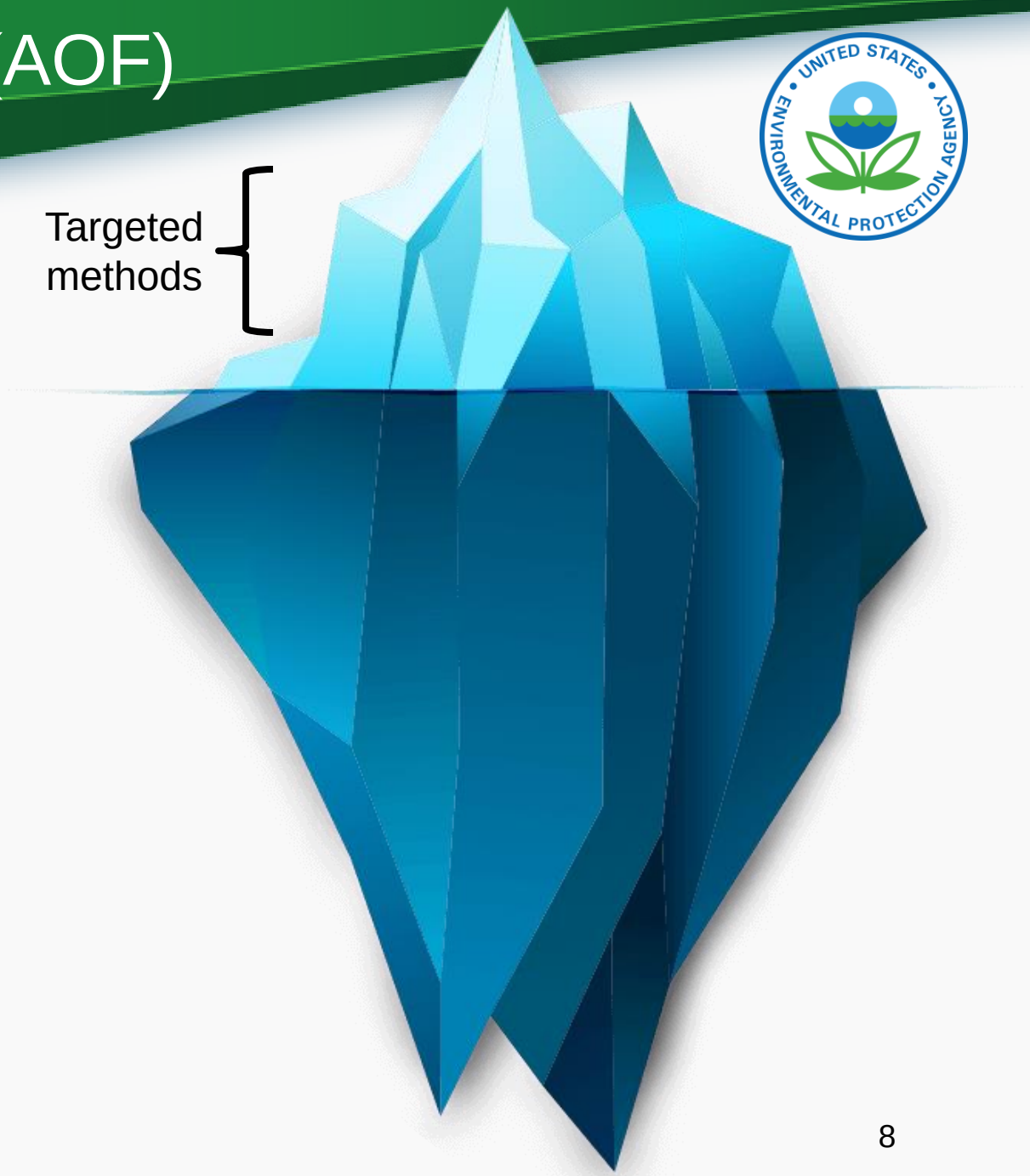
Revising the CWA Microbiology Alternate Test Procedure (ATP) Protocol

CWA Microbiology Method Activities

- Rapid methods for *E. coli* and enterococci by droplet digital PCR in ambient water
- Single-laboratory validation completed
  - Two laboratories participated
- Shortens response time for swimming advisories

Absorbable Organic Fluorine (AOF) Draft Method 1621

- Thousands of PFAS exist
- 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.)

- Single-Laboratory Validation Included:
  - 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
  - Method detection limit of 3 ppb
  - Ten wastewater and surface water matrices were tested at two spike concentrations
- Draft method and single laboratory validation report:

https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

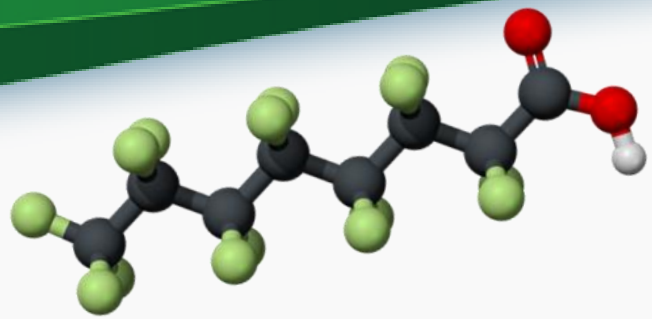
Multi-Laboratory Validation

- Study Plan/QAPP finalized
- Recruited 6 contract laboratories and 5 volunteer laboratories
- 9 Laboratories have successfully completed calibration and initial demonstration of capability
- Analysis of 9 wastewater and surface water matrices currently underway
- Anticipate finalizing the method in 2023

PFAS Method 1633 Validation

- Solid-phase extraction isotope dilution method
  - Based on an SOP originally developed by SGS AXYS
  - DoD is funding and managing both single- and multi-laboratory validation studies of the method, in consultation with EPA OW and OLEM
  - The goal is to provide EPA OW with the documentation needed to consider promulgation of this method at 40 CFR 136. OLEM plans to leverage the validation data to support an SW-846 method.
  - Test matrices include: wastewater, surface water, groundwater, landfill leachate, soil, sediment, biosolid, and fish tissue (includes shellfish)
- 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

PFAS Method 1633 Validation (cont.)



- Multi-Laboratory Validation
  - Includes 10 participant laboratories, referee laboratory, data validators, and statisticians
  - All laboratory analyses have been completed, and data packages have been received and reviewed
  - MLV Report for aqueous samples (WW, SW, GW) published on EPA and DoD websites July 2023
  - Currently reviewing data, performing statistical analysis, and writing the multi-laboratory report for remaining matrices
- Method Revisions
  - Draft 4 released July 2023 contains final aqueous QC criteria
  - Final method anticipated in late 2023

Method 1633 Aqueous MLV

- Method Detection Limit – Blank Calculation (MDL_b)
  - 400 individually calculated MDL values
    - 40 analytes X 10 laboratories = 400 individual MDLs
  - 4 MDL_b values above ND, from 2 laboratories
  - 1 MDL_b value above the MDL_s
- Pooled Method Detection Limit (MDL)
  - 27 of 40 below 1 ng/L
  - 6 between 1 and 2 ng/L
  - 3 between 2 and 3 ng/L (6:2 FTS, 8:2 FTS, and 3:3 FTCA)
  - 4 between 3 and 10 ng/L (NMeFOSE - 3.8, NEtFOSE - 4.8, 7:3FTCA - 8.7, and 5:3FTCA - 9.6)

Method 1633 Aqueous MLV (cont.)

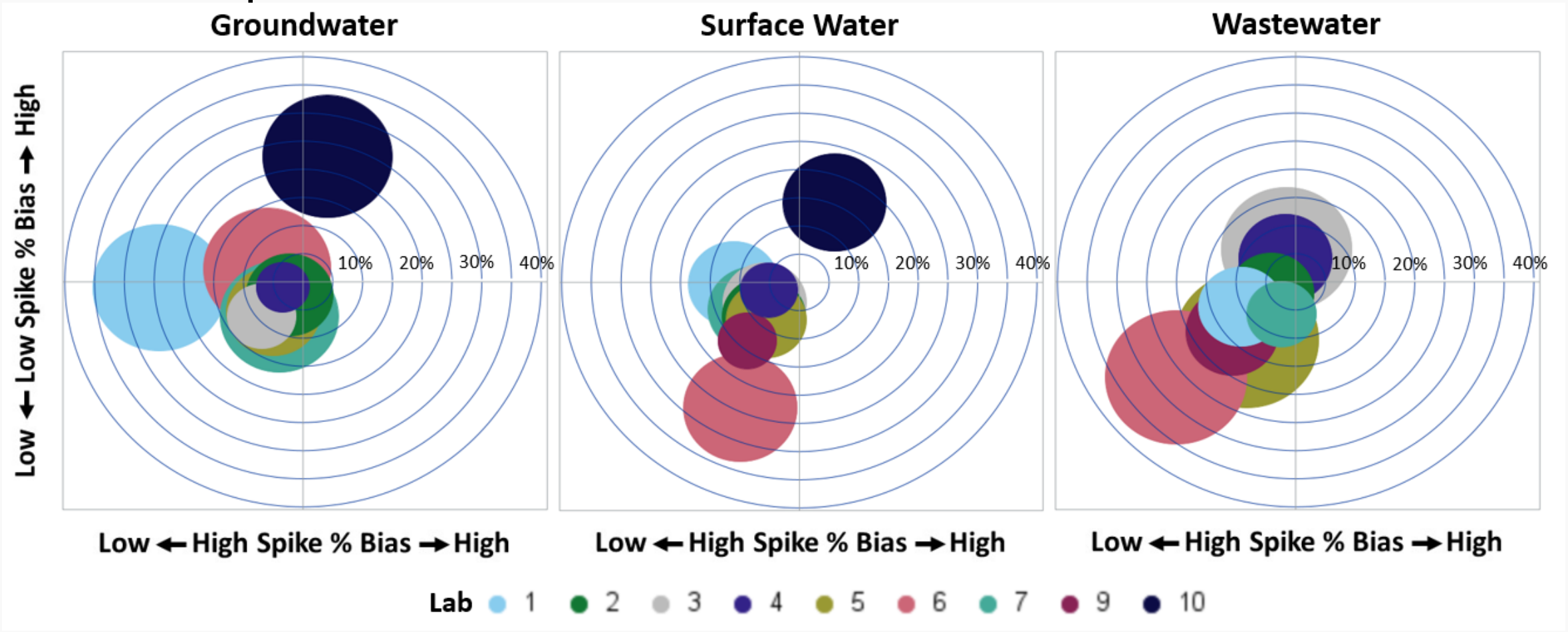
- Ongoing Precision and Recovery (OPR) Low-Level OPR (LLOPR)
  - The performance was about the same for the OPR and LLOPR, so the data were combined and used to develop a single set of criteria
  - Most criteria are inclusive of the highest and lowest observed data point from all 10 laboratories
  - No criteria are more stringent than 70-130%
  - Lowest lower acceptance limit was 50%, highest upper acceptance limit was 160%

Method 1633 Aqueous MLV (cont.)

- 24 Extracted Internal Standards (EIS)
  - Single set of EIS criteria made from only matrix samples (no blank spikes)
  - Roughly 700 sample results per EIS, from 10 laboratories
  - 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 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 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)

Method 1633 Aqueous MLV (cont.)

- Matrix Spike Results



608.3, 624.1, 625.1 QC Criteria Update

- TNI, ACIL, APHL, and WEF have volunteered to provide data to update QC criteria
  - Initial calibration, MDLs, calibration verification, ongoing precision and recovery, surrogate recovery, MS/MSDs
- Secondary Data Collection
  - Use existing data anonymously
  - Volunteer laboratories
    - Perform NPDES compliance monitoring
    - Have an SOP and formal quality system
  - Coordinate with laboratory associations

- Over 20 laboratories recruited, currently beta testing electronic deliverable

Gross Alpha Beta Method 900.0 Revision

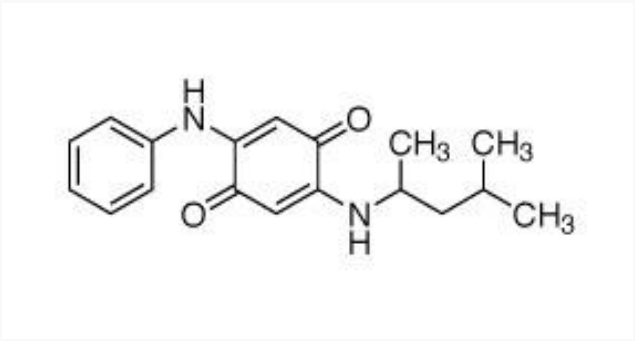
- Clean Water Act approved the original version of EPA Method 900.0 for Gross Alpha Beta in 1980
- In 2018, EPA's OGWDW approved Revision 1 to EPA Method 900.0 for use in drinking water at 40 CFR 141.66(c)
- Plan is to evaluate the performance of the revised method in wastewaters with high total dissolved solids (TDS)
- Study plan finalized
- Laboratory testing ongoing

Continuous Monitoring Collaboration

- Total residual chlorine pilot study
- Based on EPA Drinking Water Method 334.0
- Hampton Roads Sanitation District's (HRSD) SOP for Online Total Residual Chlorine Analysis approved as a limited use ATP by VA DEQ for compliance analysis of total residual chlorine (TRC) in the contact tank to meet VPDES permit requirements.
- Collaborating with a new Standard Methods Joint Task Group to develop an approach for validating the calibration and measurements resulting from online analyzer technology

6-PPDQ Single Laboratory Validation

- University Washington Publication (Science, December 2020)
  - Widespread occurrence of 6-PPDQ at concentrations toxic to salmon
- Method Team: EPA OW, EPA R10, and Eurofins Sacramento
- Eurofins Sacramento SOP: Strata XL cartridge, acetonitrile elution, LC/MS/MS analysis with extracted and non-extracted internal standard ($^{13}C_{12}$-6PPDQ and D_5-6PPD-Q)
- Validation Study
  - Calibration Study
  - Stability/holding time study
  - Initial Demonstration of Capability
  - Testing of 3 stormwaters and 3 surface waters (low and high spike)



EMC Acrylonitrile and Acrolein Holding Time Study

- At 40 CFR Part 134.3(e) Table II, acrolein and acrylonitrile have a different preservative requirement than the rest of the analytes in Method 624.1 (pH of 4-5 instead of a pH of ≤ 2)
- The Environmental Monitoring Coalition (EMC) led a holding time study determine how long these 2 analytes would remain stable if they were preserved at pH ≤ 2
- EPA reviewed and agreed to the study plan and then reviewed the resulting data and study report
- EPA OW plans to propose a change to the preservation requirement at 40 CFR Part 136.3 for acrylonitrile and acrolein to a pH of ≤ 2 during the next Full MUR

ATP Reviews

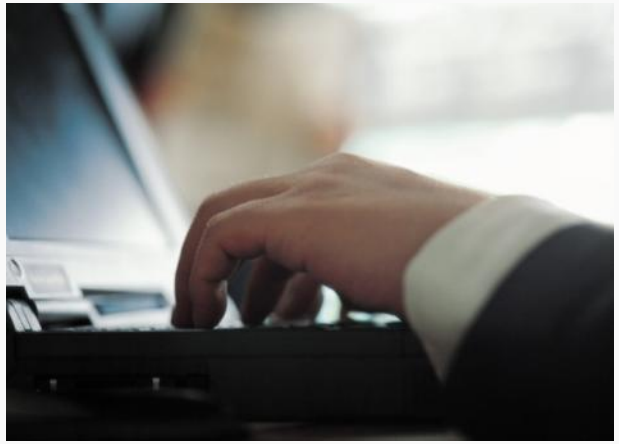
- Alternate test procedures (ATPs) for nationwide use are submitted to EPA HQ for review
  - Codified at 40 CFR 136.4 and 136.5

- Protocols for EPA review of ATPs and new methods are available at:

https://www.epa.gov/cwa-methods/alternate-test-procedures

Contact Information

For more information or additional feedback, please contact:



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