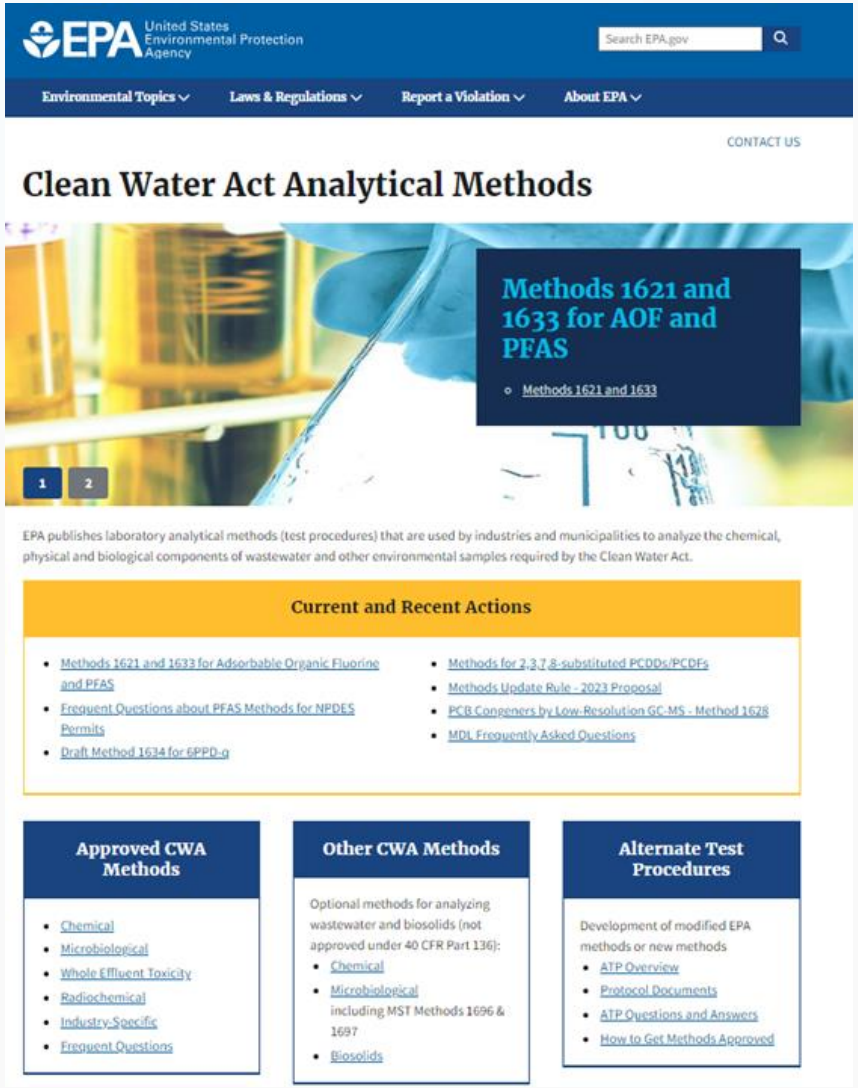
Clean Water Act Methods

Overview of EPA's CWA Method Activities

August 2024 Adrian Hanley U.S. EPA

Clean Water Act (CWA) Methods Program

- CWA Section 304(h) requires EPA, through rulemaking, to establish test procedures to measure pollutants for use under CWA programs
- Many industries and municipalities are permitted to discharge pollutants under the CWA NPDES Program
- They use analytical methods to analyze the chemical, physical, and biological components of wastewater and other environmental samples for compliance monitoring



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

What do we do?

1. Develop, validate, and publish EPA laboratory methods
2. Assist EPA's Effluent Guidelines Rulemakings and Studies with:
   - Sampling plans, selecting methods, laboratory procurement, and laboratory data review
3. Method Update Rules to 40 CFR Part 136 (approved methods for NPDES Permits):
   - EPA methods
   - Voluntary Consensus Standard Body methods
   - Alternate test procedures (ATPs)

Recent Method Projects

- *E. coli* and enterococci by droplet digital PCR in ambient water
- Absorbable Organic Fluorine (AOF) Method 1621 Validation
- PFAS Method 1633 Validation
- Gross Alpha Beta Method 900.0 Revision
- 6-PPDQ Draft Method 1634
- Review and approval of ATPs
- Many other collaborations

Effluent Guideline Studies

- EPA Effluent Guidelines website is available at: https://www.epa.gov/eg
- Recently completed sampling and analysis:
  - Meat and Poultry Products
  - PFAS Manufacturers
- Upcoming Rulemakings and Studies
  - Metal Finishing Study
  - POTW Influent PFAS Study
  - Textiles Manufacturing Study
  - Landfills Rulemaking

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 items that are likely to illicit more comments (i.e., new methods) and be proposed separately and less frequently

2024 Routine MUR

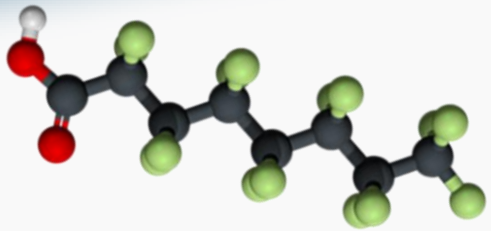
- Proposed in 2022
- Final promulgation on April 16, 2024! https://www.epa.gov/cwa-methods/methods-update-rules
  - 2 Alternate Test Procedures for Dioxins and Furans (EPA Method 1613B)
  - Included standardized language to revise the EPA membrane filtration Methods 1103.2, 1106.2, 1600.1, and 1603.1 found in Tables IA and IH
    - Update equipment (e.g., no mercury thermometers, add disposable culture dishes)
    - Standardize language between methods, e.g., QA, scope, legal disclaimer
  - 7 ASTM method revisions, 39 SM revisions
  - 5 New SM methods – same as previously approved technologies

Full MUR

- EPA will be proposing a Full MUR in the near future
- This rulemaking will propose new parameters and methods and the withdrawal of parameters and methods
- The timing on the MUR is uncertain
  - Awaiting response from the Office of Management and Budget
  - Either this year or early to mid next year

Note: The following slides detail EPAs current plans for the proposed Methods Update Rule. They may change. The rulemaking has not been proposed yet. It is not final until it undergoes public comment and final signature.

Full MUR – New Methods



- **Method 1633 - 40 PFAS compounds**
- Partnership with Department of Defense's (DoD) Strategic Environmental Research and Development Program
  - DoD funded and managed both single and multi-laboratory validation studies of the method, EPA OW and OLEM provided methodology and review
- Final EPA Method 1633 and the Multi-Laboratory Validation Study Report posted on the CWA analytical methods website on January 31, 2024 https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas
  - Validation included 10 participant laboratories, referee laboratory, data validators, and statisticians
  - Tested 8 environmental matrices: wastewater, surface water, groundwater, landfill leachate, soils, sediments, biosolids, and fish tissue
  - Minor edits and corrections will be included in the version that is proposed

Full MUR – New Methods (cont.)

- **Method 1621 – Adsorbable Organic Fluorine**
- Thousands of PFAS chemicals exist in the environment
  - Does not detect naturally occurring inorganic fluorine
- Naturally occurring organofluorines are very rare
- Most organic fluorine is man made
  - PFAS, fluorinated pesticides, some pharmaceuticals
- EPA Method 1621 yields a single part-per-billion aggregate concentration of all organofluorine compounds in a sample
- Final EPA Method 1621 and the Multi-Laboratory Validation Study Report posted on the CWA analytical methods website January 2024:

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

Full MUR – New Methods (Cont.)

- **EPA Method 1628 PCB Congeners**
- Measures all of the 209 distinct PCB chemicals (congeners)
- EPA Method 1628 finalized and posted on the CWA analytical methods website July 2021:

https://www.epa.gov/cwa-methods/pcb-congeners-low-resolution-gc-ms-method-1628-not-yet-approved

- EPA Method 1628 uses widely available affordable equipment
  - Low-resolution gas chromatograph mass spectrometer
- Quantifies using Carbon-13 isotope dilution standards
  - The gold standard of quantification

Withdrawals

- Withdraw the seven Aroclors (commercial PCB mixtures) from 40 CFR Part 136 Table IC
  - Aroclor methods are prone to false non-detects and are a poor surrogate for analyzing PCB contamination
  - Replace these parameters with EPA Method 1628 which measures all the PCBs congeners
  - If the rule is finalized, it will initiate a ~5-year phase out of Aroclor analysis from NPDES permits
- Withdrawing old colorimetric methods for individual metals that have long been supplanted by newer techniques
  - NELAC has no accredited labs for these methods
  - Several more reliable methods are currently approved

Withdrawals (cont.)

- Withdraw Oil and Grease Method 1664A
  - Method 1664, Revision B, was approved by EPA in an earlier 2012 rulemaking, 77 FR 29758
  - The 2012 rule strongly recommended laboratories and permits replace Method 1664, Revision A with Method 1664, Revision B
  - The 2012 rule said EPA may revisit withdrawing Method 1664, Revision A in a future rulemaking

  https://www.federalregister.gov/d/2012-10210/p-171
  - Laboratories and regulatory entities have had more than 12 years to make this adjustment

New VCSB Methods

- **PFAS measured using ASTM Method D8421**
- ASTM Submitted a multi-lab validation (MLV) Report, method, and full data packages supporting the validation of ASTM D8421
- Same 40 analytes as EPA Method 1633, with a few additions
- Only applies to aqueous samples
- Less sensitive than EPA Method 1633
- Uses a small sample size (5 mL), EAD recommends including a small sample sampling guidance with the method
  - Small samples are prone to higher variability

New VCSB Methods (cont.)

- **Peracetic acid and hydrogen peroxide measured using Standard Methods (SM) 4500-PAA and 4500-H2O2**
- Peracetic acid is a green substitute for chlorine disinfection
  - Breaks down into hydrogen peroxide and acetic acid
- Methods: chemical reaction followed by photometric analysis
- Similar to the most common residual chlorine field analysis
- EPA/EAD reviewed the study plan and study report in 2019 and considers the results valid and supportive of adopting the method

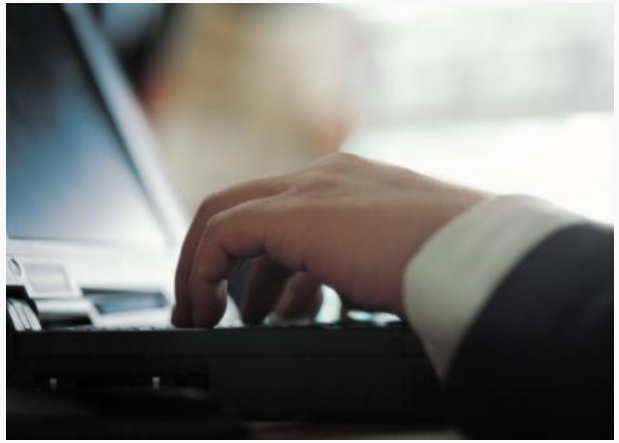
Simplify VOC Analysis

- The Environmental Monitoring Coalition provided data showing acrolein and acrylonitrile can be collected in the same bottle and preserved at the same pH as the other volatile organic compounds (VOCs)
- Revised sampling requirement in 136.3 Table II by removing the separate preservation requirement

Parameter number/name	Container [1]	Preservation [2 3]	Maximum holding time [4]
Purgeable Halocarbons and aromatic hydrocarbons	G, FP-lined septum	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$ [5], HCl to pH 2 [9]	14 days.[9]
~~Acrolein and acrylonitrile~~	~~G, FP-lined septum~~	~~Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$, pH to 4-5 [10]~~	~~14 days.[10]~~

Contact Information

For more information or additional feedback, please contact:



Adrian Hanley, US EPA
CWA Methods Team Leader
Office of Science and Technology
Office of Water
Phone: 202-564-1564
E-Mail: hanley.adrian@epa.gov

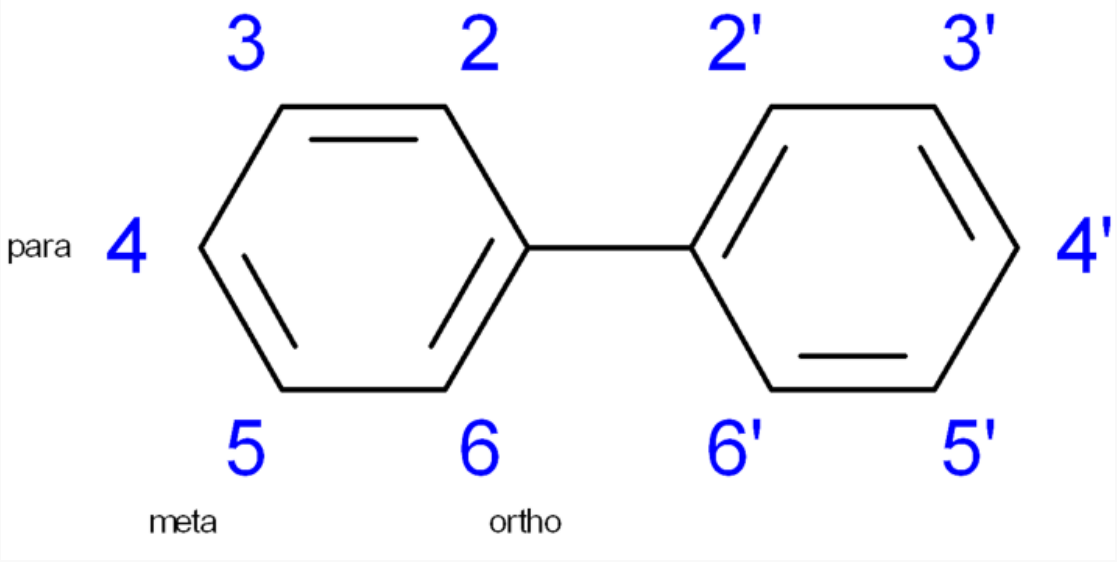
Overtime - Side Topic

- What is the difference between a draft method, final method, promulgated/approved method?
- The Clean Water Act (CWA) Methods Program has not always been perfectly consistent, but here are some general definitions for CWA methods
- Draft Method: not done yet, usually published after it has been single-laboratory validated – essentially guidance
- Final Method: 2 categories
  - Most common: a method that has undergone multi-lab validation and is complete
  - Less common: a single-lab validated method which EPA has no plans for a multi-lab validation study or to propose for rulemaking (e.g., Method 1699)
- Approved/promulgated method: a method that been approved at 40 CFR Part 136 through rulemaking for use in NPDES permits

Background PCB Slides

PCB Primer

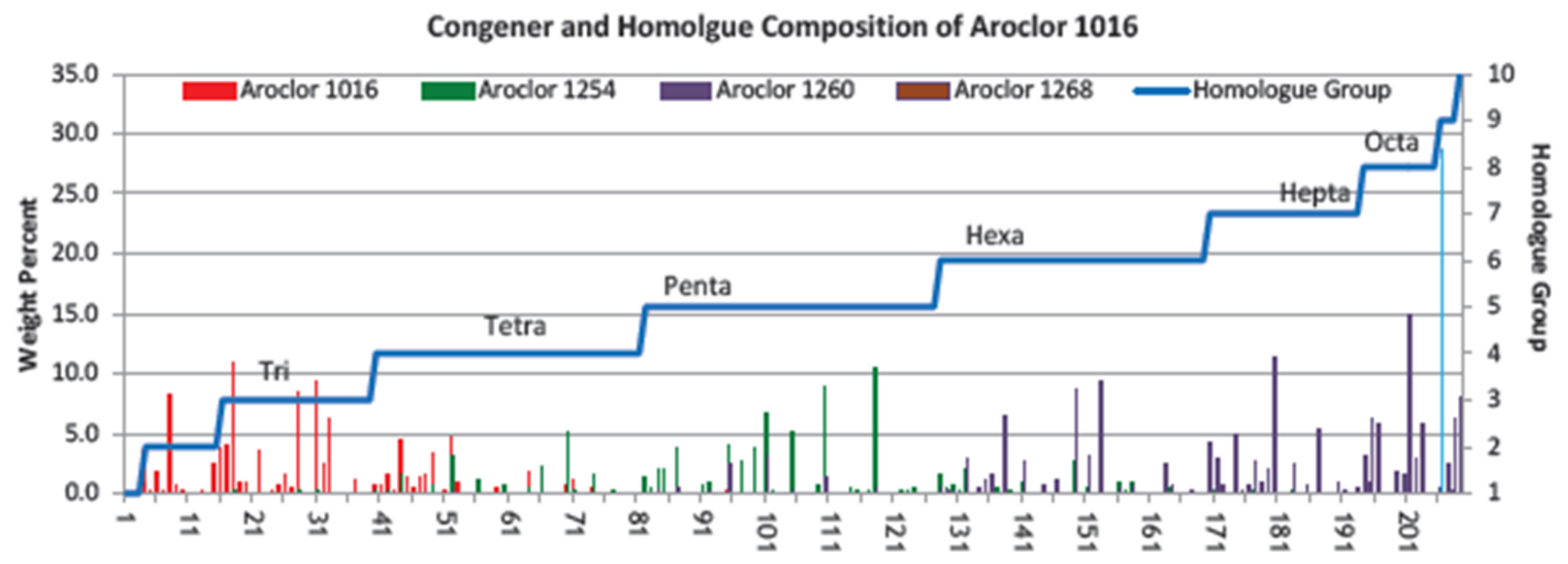
There are 209 Chlorinated Biphenyl Congeners, each with its own unique molecular structure.



Structure of PCB molecule

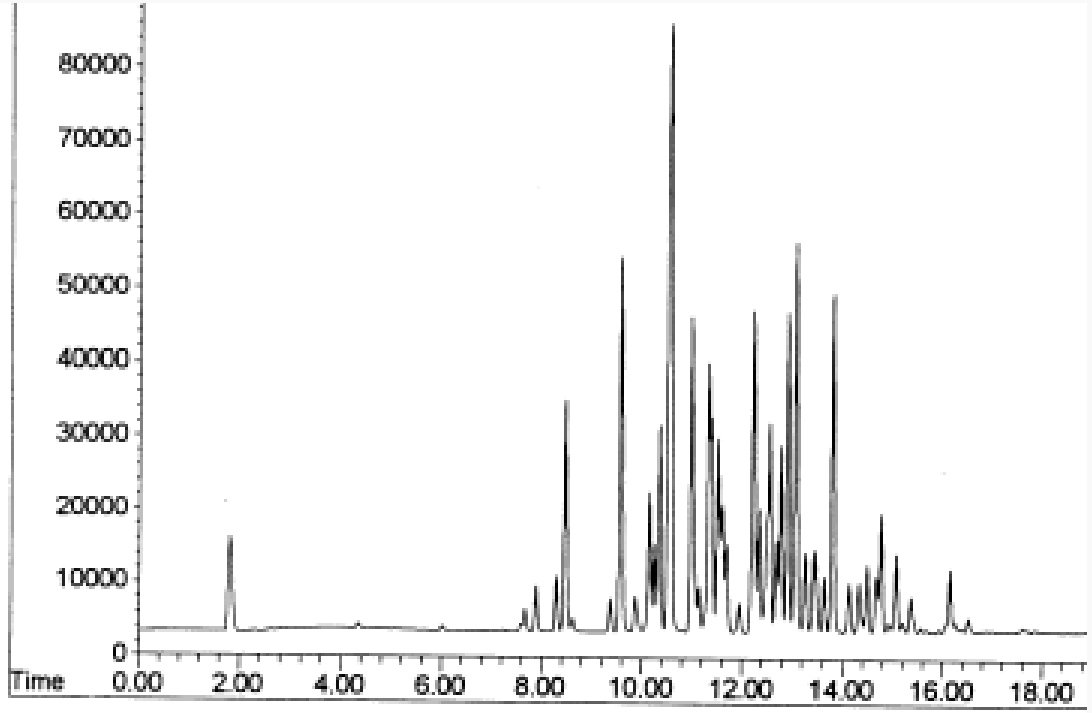
# of Chlorine Atoms	# of Congeners	Congener Numbers
1 – Monochloro	3	1-3
2 – Dichloro	12	4-15
3 – Trichloro	24	16-39
4 – Tetrachloro	42	40-81
5 – Pentachloro	46	82-127
6 – Hexachloro	42	128-169
7 – Heptachloro	24	170-193
8 – Octachloro	12	194-205
9 – Nonachloro	3	206-208
10 – Decachloro	1	209

What is an Aroclor mixture?



- It is a commercial mixture of PCB congeners
- There are other Aroclor mixtures besides 7 regulated mixtures
- Some PCBs were manufactured that were not Aroclor mixtures

Weaknesses of Aroclor Methods



Aroclor 1242 Standard

- Weathered Aroclors have different patterns and will often create a false non-detect
- Non-aroclor PCB contamination is not detected
- Non-targeted Aroclors are likely not detected
- If more than one Aroclor is present, results may be reported as a non-detect because no pattern may be apparent

PCBs in CWA regulations/criteria

- Aroclors are not specifically mentioned in any effluent guideline, but they are on the Priority Pollutant List
- Steam Electric effluent guideline states: “There shall be no discharge of polychlorinated biphenyl compounds such as those commonly used for transformer fluid.”
  - This non-numeric criterion is used because PCBs are removed from wastewater by filtration
- Water quality criteria use “PCBs”