Multi-Laboratory Validation of Low Resolution GC-MS SIM PCB Congener Method

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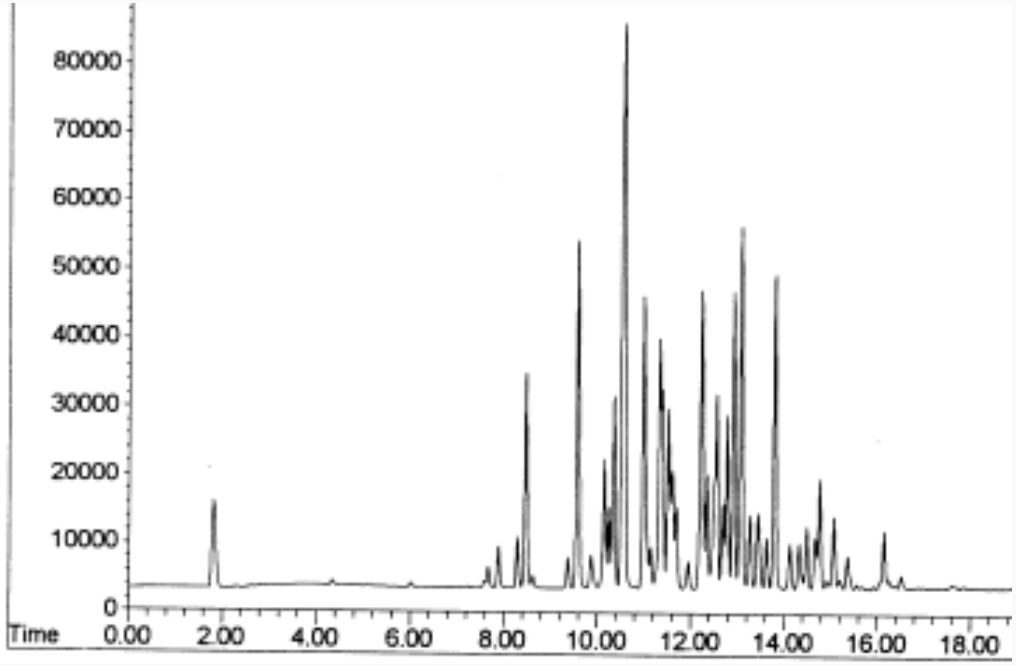
Goal

- Validate a low-resolution GC/MS method for PCB congeners in wastewater and other matrices
- Criteria to meet:
  1. *Identifies and quantifies PCBs using individual congeners, not Aroclors*
  2. *More sensitive than Method 608.3, but not too sensitive (i.e. background contamination issues)*
  3. *Can be implemented at a typical mid-sized full-service environmental laboratory*

Method 608.3



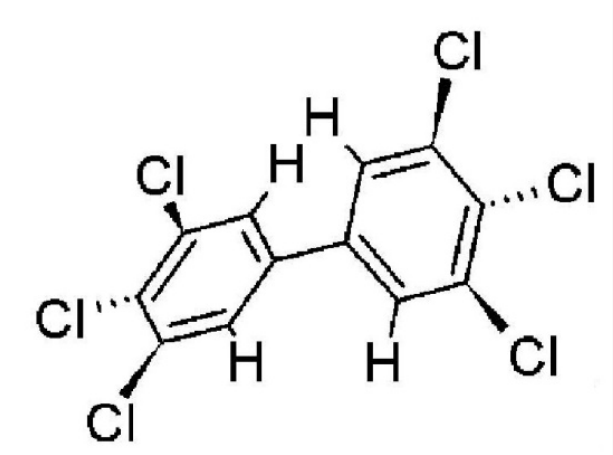
- Only measures the 7 common Aroclor mixtures, not congeners
- Detection Limit: 65 ng/L
- Approximately $80-120 per sample
- Currently the only promulgated method for PCBs at 40 CFR 136; the only NPDES regulations are for Aroclors.

Approach

Method focuses on specific congeners, but detects all

Focus:

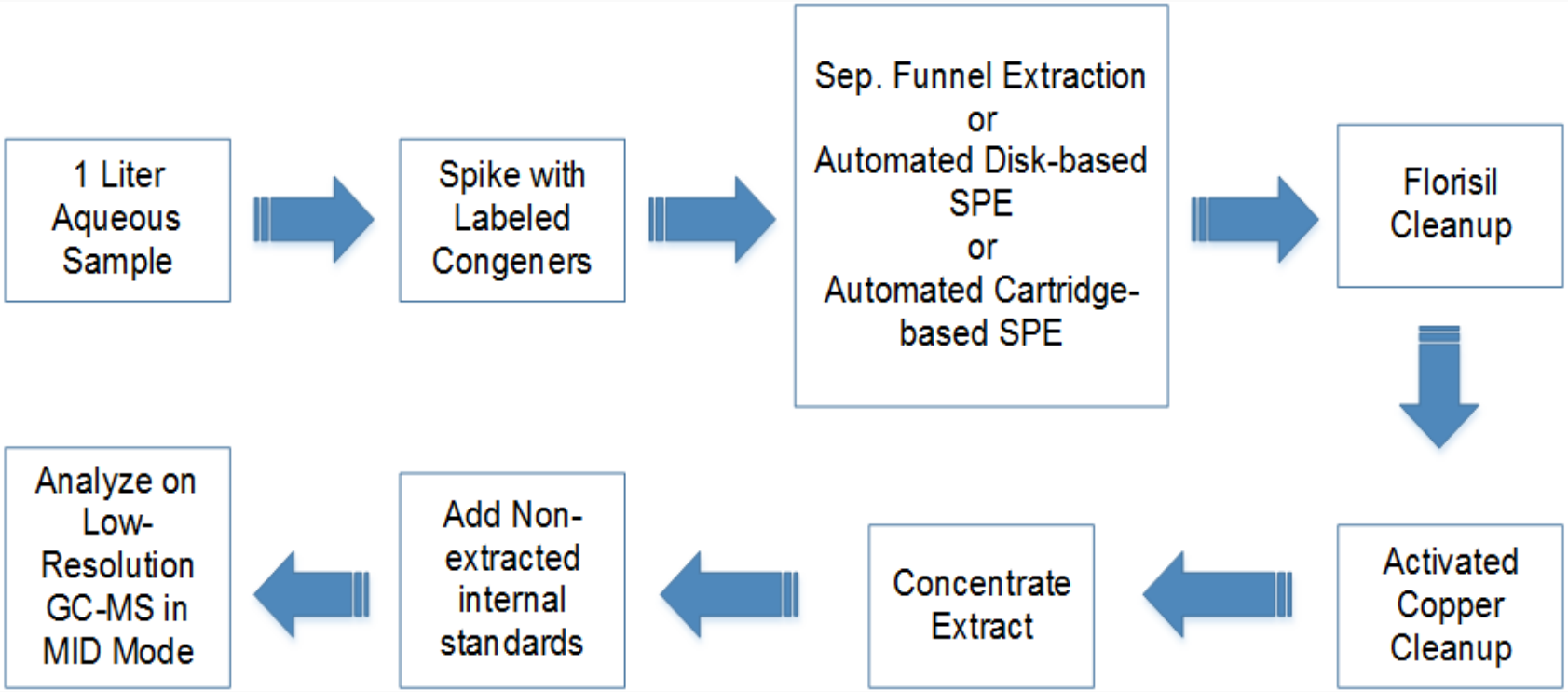
1. First and last eluter of each homolog
2. Most common in environment
3. Prevalent in human tissue
4. Present in Aroclors in large quantities
5. WHO Toxic Congeners



Summary of Method Steps

- Measure sample aliquot
- Spike sample (including QC) with labeled congeners
- Extract
- Cleanup
- Concentrate
- Add non-extracted internal standards
- Analyze by low-resolution GC/MS with SIM

Aqueous Samples



Other Matrices

- Solids samples (soils, sediments, and biosolids) are spiked with the labeled compounds, extracted by Soxhlet, and extracts cleaned with:
  - Silica gel
  - Alumina
  - Florisil
  - Activated copper
- Tissue samples are spiked with the labeled compounds, extracted by Soxhlet, and extracts cleaned with:
  - GPC (Gel Permeation Chromatography)
  - Florisil

Quantification

Analysis

- DB-5 column
- EI using SIM detection (2 ions per congener)
- 167 peaks for 209 congeners

Quantification

- 48 congeners are calibrated
  - 23 congeners by true isotope dilution
  - 6 congeners by isotope dilution with 8 co-eluters
  - 19 congeners by extracted internal standard (EIS) quantification with 9 coeluters
- Remaining 144 congeners quantified indirectly

Single-Lab Study Summary

Single-laboratory validation study met EPA's goals

1. Method identifies and quantifies PCB contamination using individual congeners, not an estimated quantity based off patterns generated from Aroclor mixtures
2. Method is more sensitive than currently approved Method 608.3, but not so sensitive to be adversely affected by typical laboratory background contamination
3. Can be implemented at a typical mid-sized full-service environmental laboratory

Multi-laboratory Validation Study

- Participants
  - 8 contracted laboratories
  - 4 volunteer laboratories
- Real-world Matrices
  - Wastewater (9)
  - Biosolids (3)
  - Sediment (3)
  - Fish tissue (3)

Custom Standards Provided

- 209 congener mix
  - Commercially available 9-standard set
- Initial calibration standards (6)
  - 48 Natives, 32 ^{13}C labels
- Labeled compound standards
  - 29 ^{13}C labels
- Native standards – 48 congeners
- Internal standards – 3 ^{13}C labels

Required Analyses

- Retention time determination for all 209 congeners
- Initial calibration of 48 congeners
- Method detection limits for all 209 congeners
- Initial precision and recovery for 48 congeners
- Unspiked sample analyses for all 209 congeners
- Matrix spikes and matrix spike duplicates on all samples, using 57 congeners (48 calibrated congeners and 9 additional congeners commonly detected)

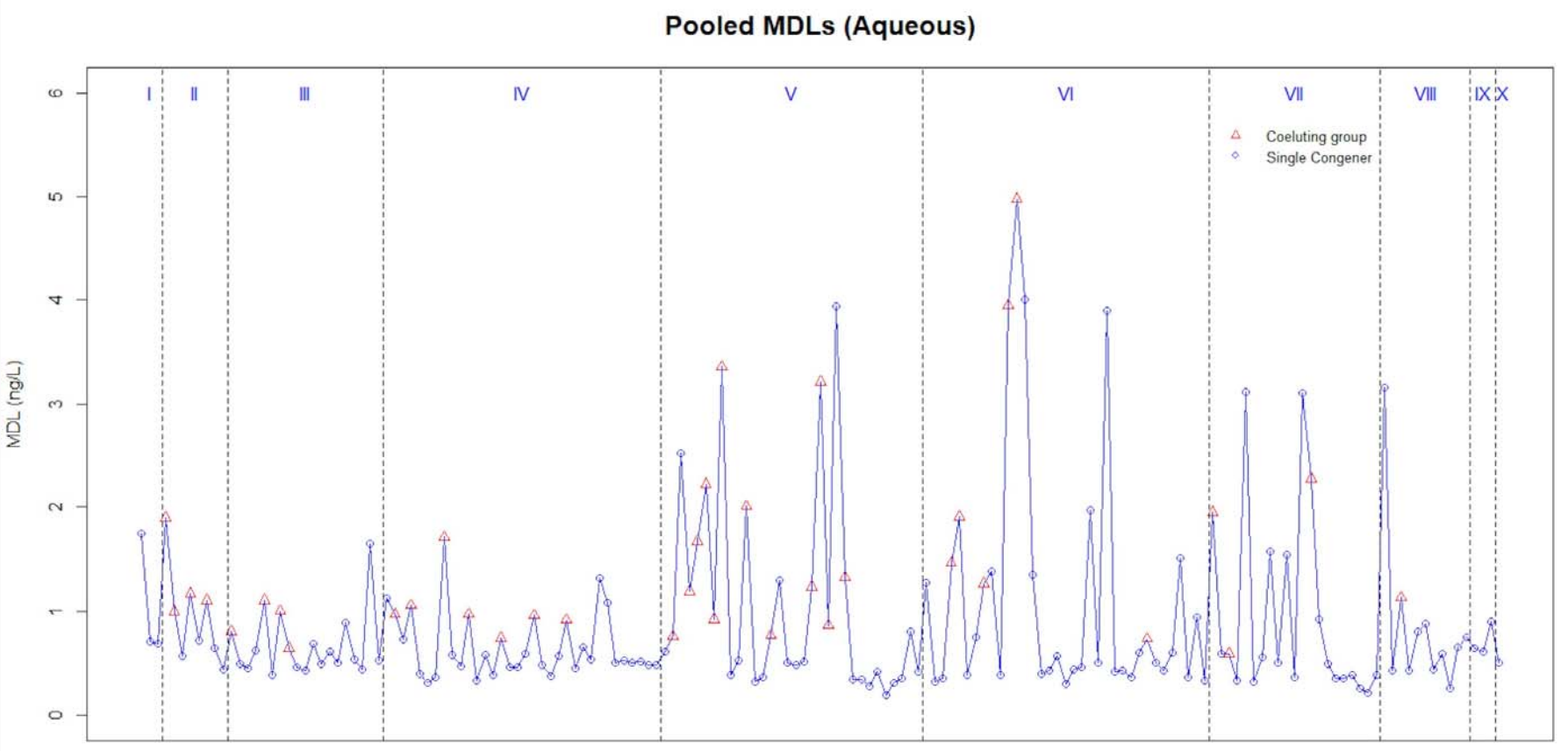
Study Results Received

- 7 of the initial 12 laboratories completed all aspects of the wastewater portion of the study
  - The labs that dropped out cited time and resource issues, not capability
- Fewer laboratories had agreed to the analyze the other matrices
  - 6 laboratories completed the soil/sediment portion of the study
  - 4 laboratories completed the biosolids portion of the study
  - 4 laboratories completed the fish tissue portion of the study
- Obtained enough data to develop pooled MDLs and to evaluate the use of statistically based QC criteria for IPR and OPR analyses
- Obtained enough data to meet the study design for all of the matrices

Wastewater Results Summary

- IPRs
  - Mean recoveries ranged from 81 to 104% across the 48 calibrated congeners
  - RSDs ranged from 7 to 27%
- Pooled MDLs ranged from roughly 0.2 to 5 ng/L across 167 analytes (congeners and groups of coeluting congeners)
- MS/MSD mean recoveries ranged from 48 to 125% for 56 of the 57 spiked congeners

Wastewater Pooled MDLs



Solid Results Summary

- IPRs
  - Mean recoveries ranged from 83 to 110% across the 48 calibrated congeners
  - RSDs ranged from 14 to 27% for 47 of the 48 congeners
- Pooled MDLs ranged from roughly 0.05 to 0.95 ng/g across 167 analytes and 0.05 to 0.4 ng/g for 165 of those 167
- MS/MSD mean recoveries ranged from 34 to 150% for 45 of the 57 spiked congeners

Tissue Results Summary

- IPRs
  - Mean recoveries ranged from 84 to 104% for 47 of the 48 calibrated congeners
  - RSDs ranged from 12 to 29% for 46 of the 48 congeners
- Pooled MDLs ranged from roughly 0.04 to 0.23 ng/g across 167 analytes
- MS/MSD mean recoveries ranged from 43 to 117% for 54 of the 57 spiked congeners

Biosolids Results Summary

- IPRs and MDLs specific to biosolids were not part of the study design, because the same reference matrix is used for sediment (Ottawa Sand)
- Results from the other solid samples will be used for these tests in biosolids
- MS/MSD analyses were run on biosolids and mean recoveries ranged from 54 to 224% for all 57 spiked congeners, with mean recoveries over 150% largely limited to three mono- and di-chloro congeners in two of the three study samples

QC Acceptance Criteria Development

- Matrix-specific QC acceptance criteria for IPRs were calculated by constructing a prediction interval around the mean recovery, using the Student's *t* value with the degree of freedom determined using the Satterthwaite estimation procedure and the between- and within-lab variance for the congener, assuming four replicate analyses
- Maximum RSD limits for the IPRs were calculated as an upper confidence limit around the observed RSD values for all labs.
- Acceptance criteria for the OPRs were calculated in a fashion similar to that used for the IPRs, but assuming only a single replicate analysis

QC Criteria (cont.)

- The statistical calculations also allowed for the fact that multiple analytes are being tested simultaneously.
- This resulted in calculated acceptance criteria that were very wide in many cases, and some lower limits that were negative numbers
- Obviously, such negative numbers have no physical meaning
- The challenge is to balance the desire for practical acceptance criteria tat can be applied across all labs against the time and expense required to collect much larger amounts of data and to give laboratories much more time to practice the method before the study actually starts.

QC Criteria (cont.)

- Our solution was to employ the statistically calculated limits where those limits appear reasonable to most analysts, and rely on simpler “consensus-style” round number limits in place of any calculated limits that include negative lower limits and/or exceptionally high upper limits.
- As shown in the study report and the method, we incorporated statistically derived limits for the target analytes for IPRs and OPRs in aqueous and solid samples, and consensus-style limits for the target analytes in tissues, and for the labeled compounds in all matrices
- We also provided guidance in the method on the application of these limits

Internal and External Reviews

- Both the multi-lab study report and the draft method were submitted for review by the EPA workgroup (which included a one commercial laboratory and a wastewater utility laboratory manager), internal peer reviewers, EPA management, and four of the labs that participated in the study
- No unfavorable comments were received, but minor revisions were made to both documents to clarify points raised by the reviewers

It's now live!

- Both the study report and the draft method have been posted on the EPA web site:

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

Or

https://www.epa.gov/cwa-methods

Contact Information

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