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

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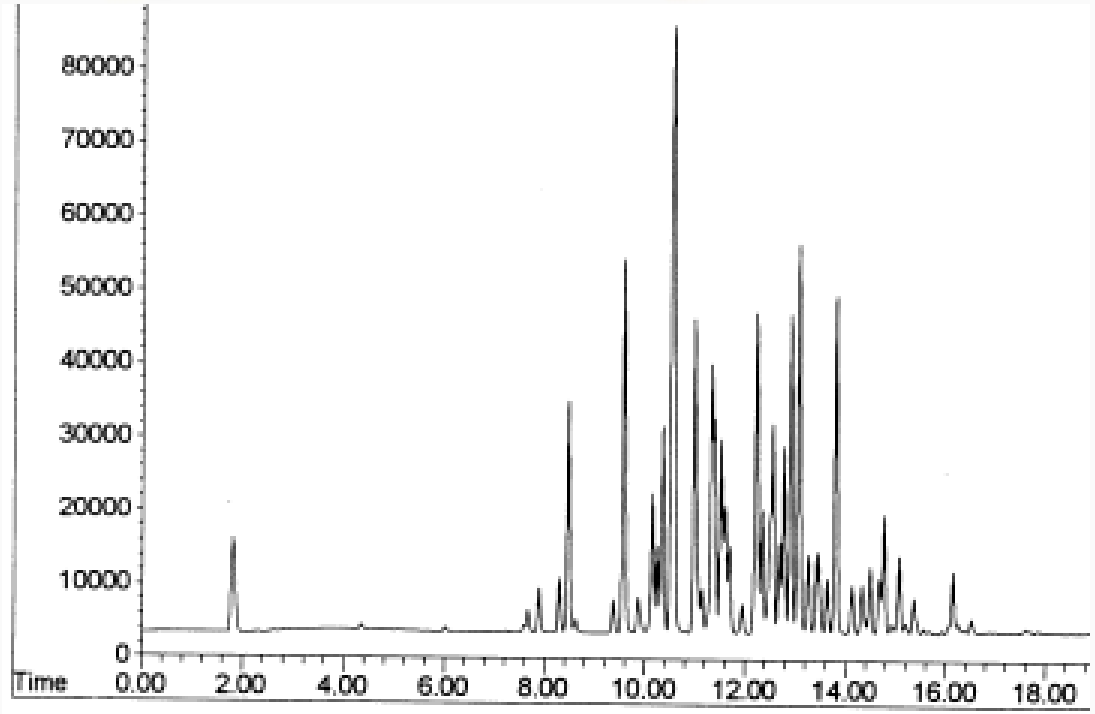
Goal

- 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



Aroclor 1242 Standard

- Only measures the 7 common Aroclor mixtures, not congeners
- Detection Limit: 65,000 pg/L
- Approximately $80-120 per sample

- Currently the only promulgated method for PCBs at 40 CFR 136; the only NPDES regulations are for Aroclors.

Measuring Aroclor Mixtures vs. Individual Congeners

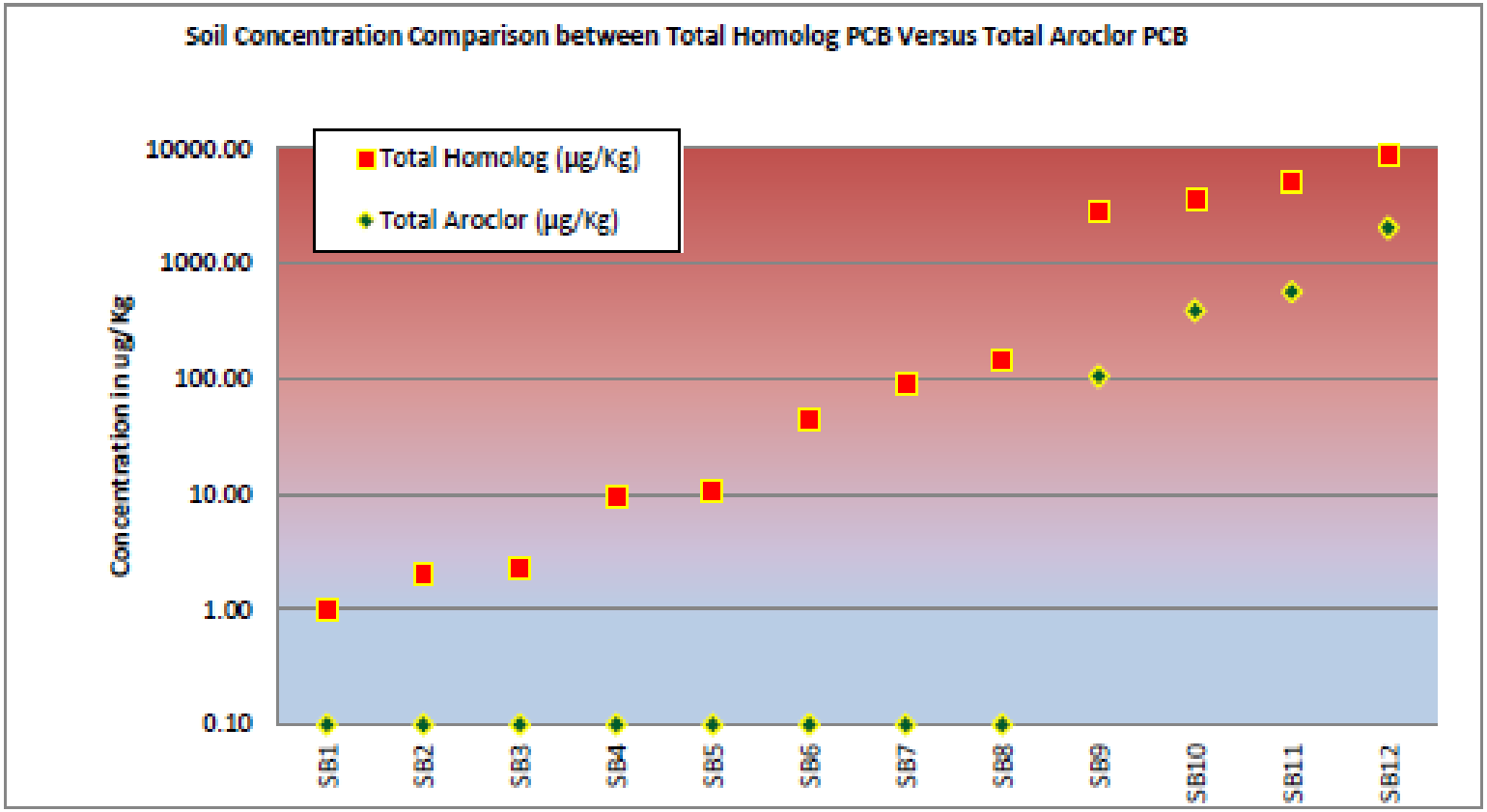


Figure 8: *Another comparison of Soil Total Homolog concentration versus Total Aroclor concentration.*

Taken from Wischkaemper et al, "U.S. EPA Region 4 Technical Services Section Issue Paper for Polychlorinated Biphenyl Characterization at Region 4 Superfund and RCRA Sites."

PCBs are Everywhere

Example Ambient Concentrations

- Arctic Ocean, 8 meters below the ice cap[1]: 0.54 to 1.96 pg/L (only 15 congeners measured)
- Mediterranean lagoon with no industrial history[2]: 138 to 708 pg/L (only 7 congeners measured)
- Houston, TX Urban Waterways[3]: 460 to 9,400 pg/L

  (all 209 congeners measured)
- Delaware River[4]: 1,000 to 7,000 pg/L

  (all 209 congeners measured)
- Delaware River Watershed air deposition[5]: from 0.26 to 76 ng/m^2 per day
  - The lowest reading was on a dry day at Lum's Pond State Park, DE
  - The highest reading was on a wet day in Camden, NJ

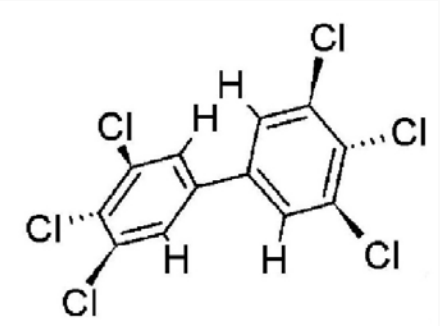
References are available in the notes section of this slide

Approach

Method focuses on specific congeners, but detects all

Focus:

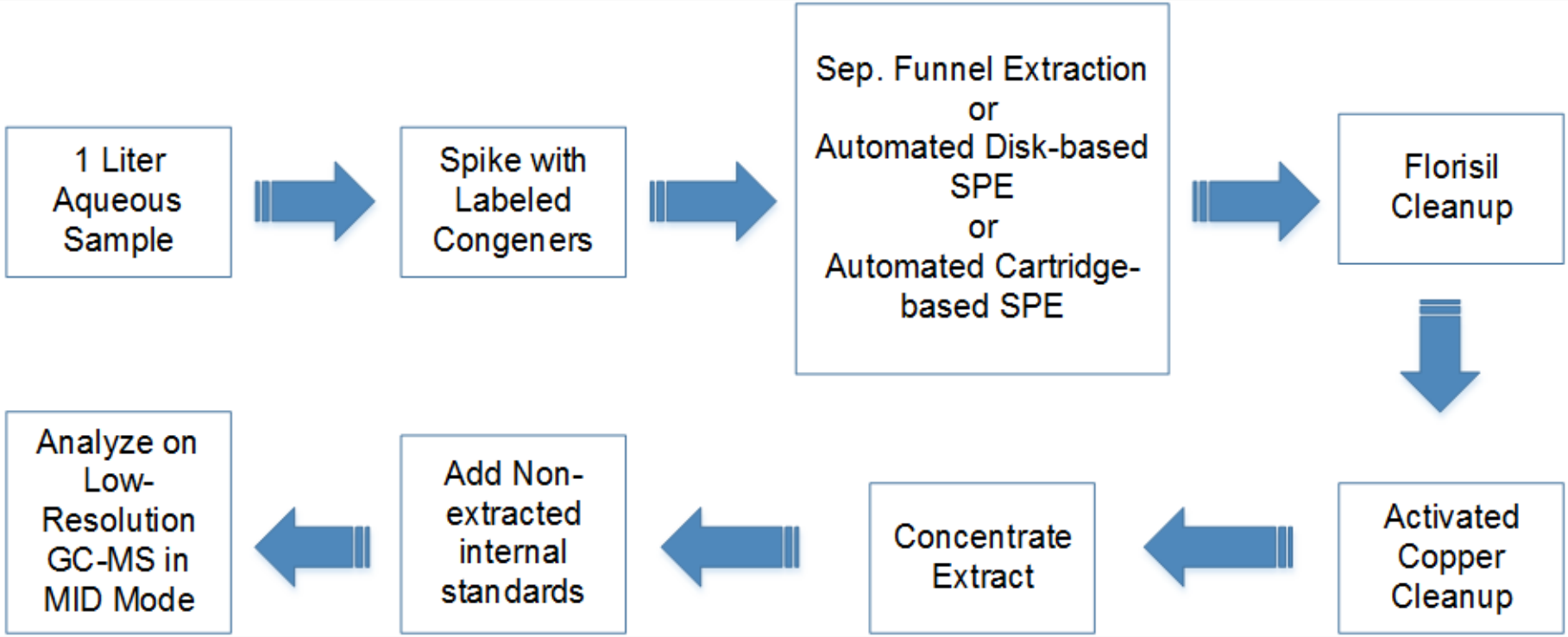
1. *First and last eluter of each homolog*
2. *Most common in environment*
3. *Prevalent in human tissue*
4. *Present in Aroclors in large quantities*
5. *WHO Toxic Congeners*



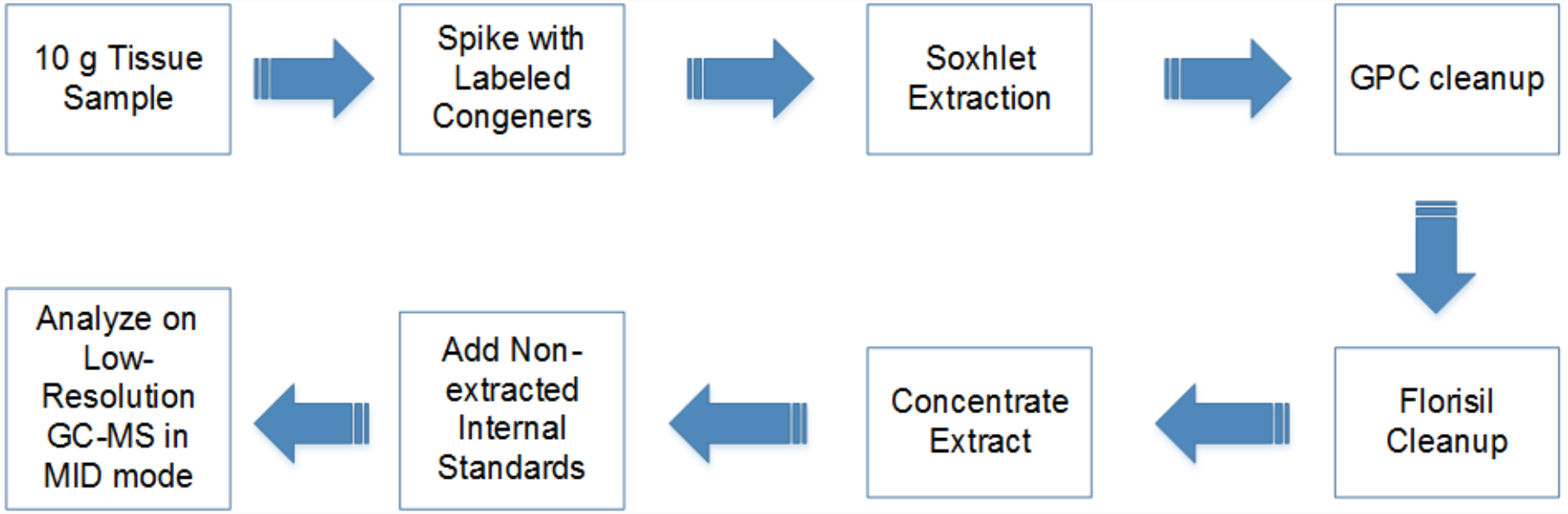
Summary of Method Steps

- *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*

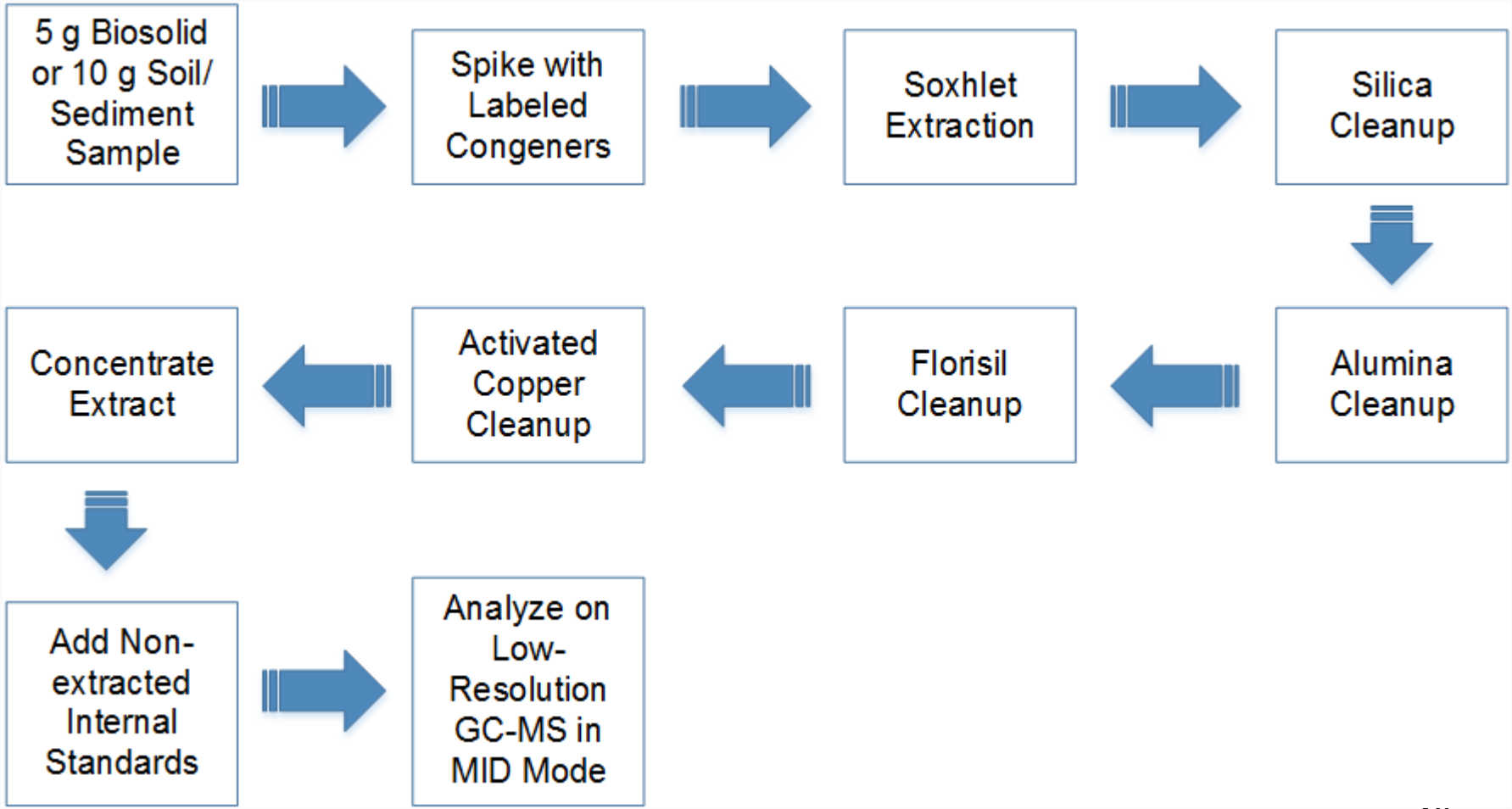
Aqueous Samples



Tissue Samples



Solid Samples



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

Quantification (cont.)

Quantitation Scheme	Congeners
Isotope dilution	1, 3, 11, 15, 19, 28, 37, 54, 70, 77, 104, 126, 153, 155, 169, 180, 188, 189, 202, 205, 206, 208, 209
Modified isotope dilution	4 + 10, 52 + 73, 85 + 120, 89 + 90 + 101, 106 + 118, 138 + 163 + 164
Extracted internal standard	5 + 8, 18, 31, 41 + 64, 44, 66 + 80, 61 + 74, 93 + 95, 99, 105 + 127, 110, 132 + 168, 147, 139 + 149, 156, 166, 177, 182 + 187, 199
Indirectly, via another congener	All 144 remaining congeners

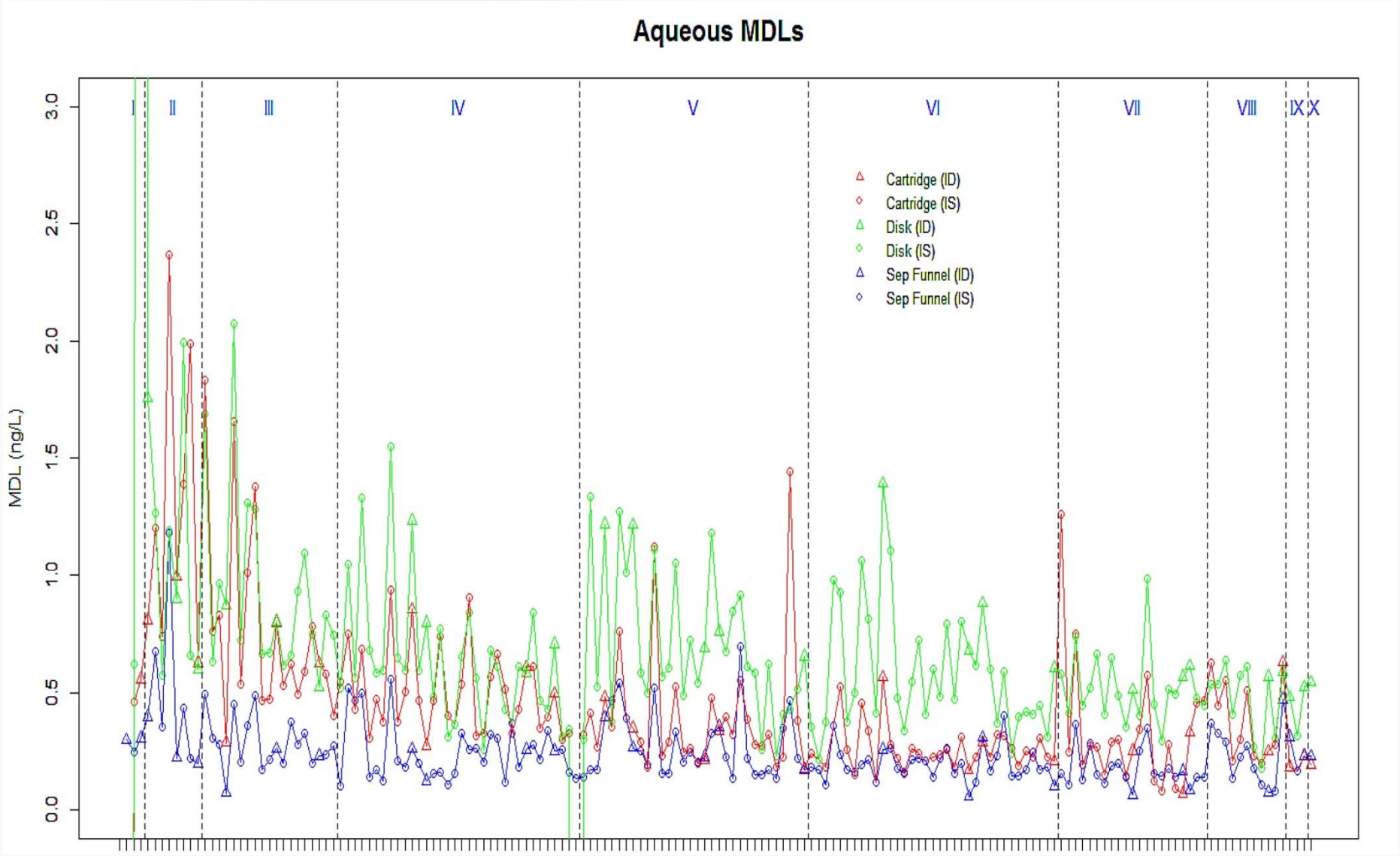
Target congener with an exact labeled analog (coeluting congener without an exact label)

Target congener quantified by extracted internal standard (congener without a congener-specific response factor)

Summary of Some Single Laboratory Validation Results

Performed by SGS AXYS Analytical

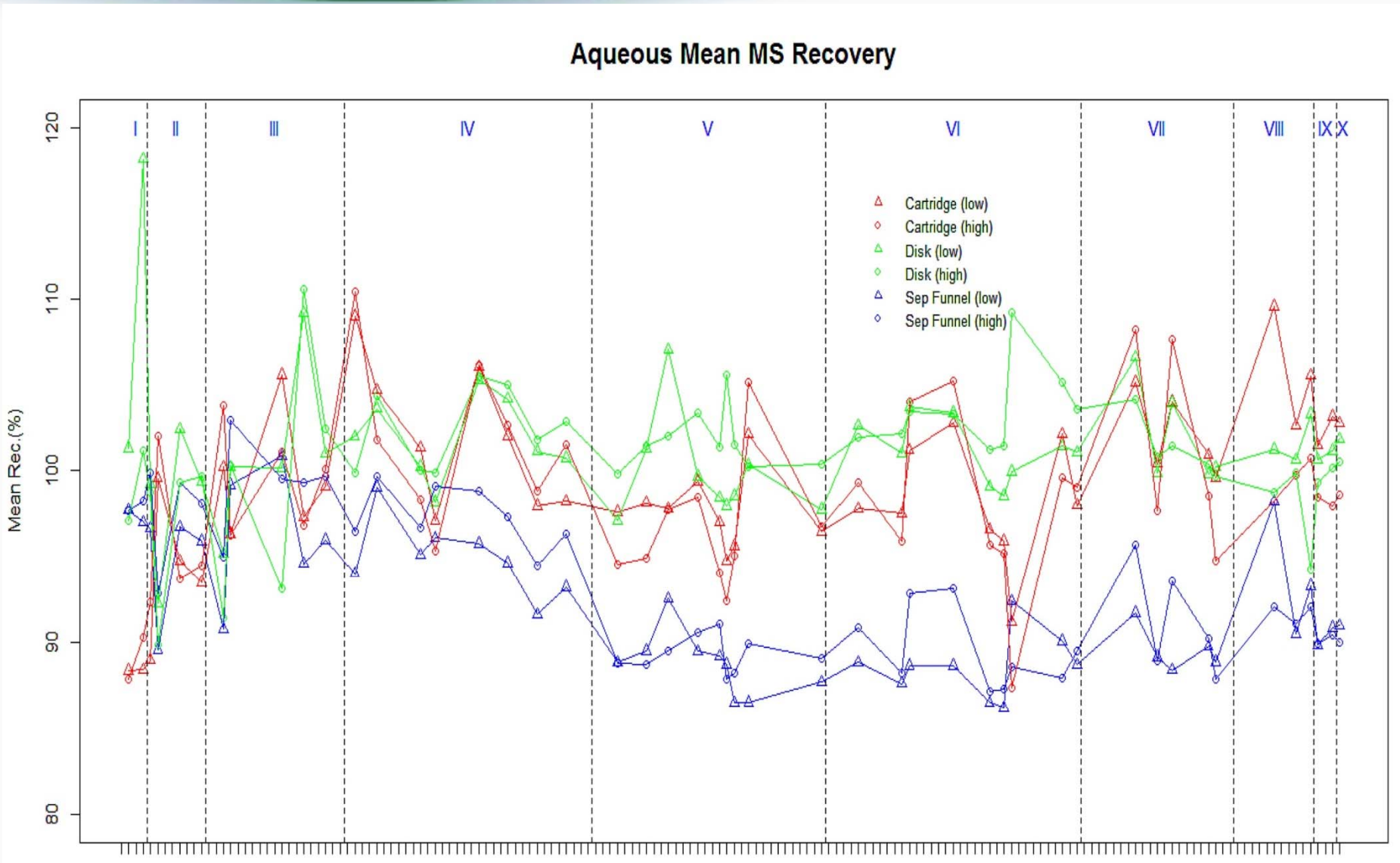
Method Detection Limit Study
Aqueous Samples



Method Detection Limit Study
Solid and Tissue

- *MDL_s (solid) ranged between 3 – 91 ng/kg*
- *MDL_s (tissue) ranged between 97 – 2,100 ng/kg*
- *No MDL_s for PCB-1 and -81 in solids and tissues*
- *MDL_b result for PCB-11 in solids (16 ng/kg)*

Matrix Spike Analyses
Aqueous Samples (cont.)



Matrix Spike Analyses
Solid and Tissue (cont.)

Matrix	Low Spike Mean Recovery Range	Medium Spike Mean Recovery Range	High Spike Mean Recovery Range
Soil/Sediment	44 to 128%	53 to 117%	NA
Biosolid	97 to 130%	58 to 216%	52 to 125%
Fish Tissue	89 to 114%	88 to 113%	93 to 116%

Single-Lab 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

Participants and Matrices

- Participants
  - 8 contracted laboratories
  - 4 volunteer laboratories
- Matrices
  - Wastewater
  - Biosolids
  - Sediment
  - Fish tissue

Custom Standards Provided

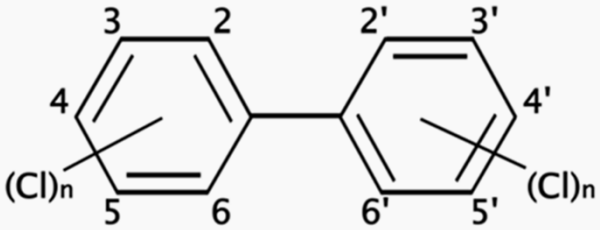
- 209 congener mix
  - From a catalog, 9 standard set
- Initial calibration standards (6)
  - 48 Natives, 32 ^{13}C labels
- Labeled compound standards
  - 29 ^{13}C labels
- Native standards – 48 congeners
- Internal standards – 3 ^{13}C labels

Required Analyses

- One initial calibration
- Initial Demonstration of Capability (IDC)
  - Required for each matrix type using reference matrix
  - Method Detection Limit (MDL) Study: 7 blanks and 7 low spikes minimum (3 different analytical batches and dates)
  - Initial Precision and Recovery (IPR) Determination: 4 medium level spiked samples minimum

Required Analyses (cont.)

- Matrix testing
  - Include routine sample QA/QC
    - Method blanks, fortified blanks, CCVs, etc.
  - Wastewater matrix testing
    - Nationwide use: 9 wastewater matrices
    - 1 unspiked sample and 1 MS and MSD per matrix
  - Biosolids, sediment/soil, and fish tissue
    - 3 sources for each matrix type
    - 1 unspiked sample and 1 MS and MSD per matrix



Initial Calibration Results

- Summary of preliminary results from 9 laboratories
  - 48 congeners are calibrated
  - Most response factors are above 0.7
  - Most RSD values are below 10%

Note: Further data review for coelutions and statistical analysis may improve this data set. More data will also be received.

Initial Calibration (9 Labs)

Congener	Mean RR or RF Range	RSD Range	Congener	Mean RR or RF Range	RSD Range	Congener	Mean RR or RF Range	RSD Range
PCB-1	0.995 - 1.216	0.7 - 6.4	PCB-70	0.959 - 1.190	0.7 - 3.3	PCB-153	0.937 - 1.115	0.9 - 7.3
PCB-3	1.001 - 1.223	0.6 - 5.0	PCB-74/61	0.880 - 1.139	1.2 - 7.1	PCB-155	0.861 - 1.060	0.4 - 3.0
PCB-4/10	1.007 - 1.208	0.3 - 7.0	PCB-77	0.911 - 1.206	0.3 - 5.2	PCB-156	0.938 - 1.326	3.9 - 19.2
PCB-8/5	1.012 - 1.217	2.3 - 5.9	PCB-85/120	0.774 - 1.092	0.4 - 3.8	PCB-166	0.956 - 1.223	2.5 - 13.5
PCB-11	0.990 - 1.230	0.3 - 5.0	PCB-95/93	0.798 - 1.037	1.2 - 7.1	PCB-169	0.892 - 1.116	1.0 - 4.7
PCB-15	0.991 - 1.203	0.3 - 3.6	PCB-99	0.940 - 1.174	1.1 - 5.9	PCB-177	0.755 - 0.894	2.4 - 9.7
PCB-18	0.597 - 0.695	1.0 - 4.1	PCB-101/89/90	0.910 - 1.134	0.6 - 5.1	PCB-180	0.956 - 1.101	0.4 - 5.9
PCB-19	1.011 - 1.223	0.7 - 2.5	PCB-104	0.894 - 1.139	0.6 - 3.8	PCB-187/182	0.917 - 1.200	2.8 - 8.3
PCB-28	0.535 - 1.222	1.0 - 14.4	PCB-105/127	0.869 - 1.558	1.4 - 7.5	PCB-188	0.923 - 1.076	0.3 - 5.4
PCB-31	0.910 - 1.396	0.8 - 8.3	PCB-110	0.86 - 1.508	1.0 - 5.9	PCB-189	0.898 - 1.200	0.5 - 4.7
PCB-37	1.016 - 1.234	0.8 - 3.7	PCB-118/106	0.909 - 1.624	0.7 - 5.8	PCB-199	0.535 - 0.815	1.6 - 13.0
PCB-44	0.811 - 1.008	1.0 - 6.3	PCB-126	0.869 - 1.133	0.9 - 3.0	PCB-202	0.856 - 1.137	0.7 - 7.3
PCB-52/73	0.937 - 1.178	0.5 - 3.7	PCB-132/168	0.498 - 0.869	1.1 - 16.2	PCB-205	0.916 - 1.155	0.8 - 13.4
PCB-54	1.024 - 1.245	0.3 - 2.6	PCB-138/163/164	0.840 - 1.049	0.6 - 5.6	PCB-206	0.736 - 1.052	0.5 - 28.4
PCB-41/64	0.935 - 1.074	0.4 - 8.5	PCB-147	0.729 - 0.876	2.4 - 10.9	PCB-208	0.739 - 1.087	0.6 - 6.5
PCB-66/80	0.953 - 1.165	0.6 - 4.4	PCB-149/139	0.753 - 0.938	1.8 - 12.1	PCB-209	0.567 - 1.030	0.8 - 9.8

IDC Results

- Summary of preliminary results from 4 laboratories
  - Almost all mean recoveries were above 80 percent
  - Most RSD values are below 6%

Note: Further data review for coelutions and statistical analysis may improve this data set. More data has and will be received.

IDC Results

Congener	Mean % Rec.	Mean RSD	Congener	Mean % Rec.	Mean RSD	Congener	Mean % Rec.	Mean RSD
PCB-1	104.4	4.4	PCB-70	85.9	1.4	PCB-153	87.0	1.9
PCB-3	93.7	3.9	PCB-74	88.1	2.5	PCB-155	86.4	2.0
PCB-4	94.9	4.6	PCB-77	84.4	1.0	PCB-156	94.9	1.7
PCB-8	76.6	6.2	PCB-85	84.4	1.2	PCB-166	89.9	1.4
PCB-11	89.7	2.4	PCB-95	82.8	1.1	PCB-169	82.8	2.2
PCB-15	88.8	2.5	PCB-99	86.8	2.1	PCB-177	85.1	2.3
PCB-18	78.4	4.9	PCB-101	85.9	1.5	PCB-180	83.3	2.3
PCB-19	90.8	3.8	PCB-104	87.1	1.8	PCB-187	80.2	2.6
PCB-28	91.5	3.0	PCB-105	90.0	1.2	PCB-188	86.2	2.3
PCB-31	88.9	3.2	PCB-110	83.3	0.7	PCB-189	82.9	2.9
PCB-37	86.6	0.9	PCB-118	86.1	0.7	PCB-199	99.5	3.4
PCB-44	91.9	2.2	PCB-126	84.8	0.7	PCB-202	86.5	3.6
PCB-52	86.4	2.3	PCB-132	85.1	1.3	PCB-205	81.1	4.3
PCB-54	89.9	3.1	PCB-138	84.8	1.0	PCB-206	80.2	4.8
PCB-64	81.3	2.5	PCB-147	86.1	1.7	PCB-208	81.0	4.8
PCB-66	87.3	1.9	PCB-149	86.7	1.6	PCB-209	72.5	6.5

All of the study data should be received in the next few months

All laboratories that submit complete data packages will be acknowledged in the study report

Contact Information

For more information or additional feedback, please contact:

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