EPA Method 1668ABC Status and Use in TMDLs

22nd Annual Environment Virginia Symposium

Session I – 10:30-11:45 AM: Addressing PCBs: Regulatory Approaches to Developing TMDLs

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Overview

1. What is EPA Method 1668?
2. What is a PCB?
3. History of EPA Method 1668.
4. Status of Method 1668C.
5. Concerns with Method 1668C.
6. Recommendations for Method 1668C.
7. Use of Method 1668 on the Delaware Estuary PCB TMDL.

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What is EPA Method 1668?

- Method 1668 is an High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) method to analyze Polychlorinated Biphenyls (PCBs). Isotope dilution.
- Can measure “209” PCB congeners as ~184 chromatographic peaks. Sensitive to ~ 5 pg/L.
- In contrast:
  - Other common PCB methods are designed to determine PCBs as Aroclors.
  - Aroclors – Monsanto trade name for a mixture of PCBs.

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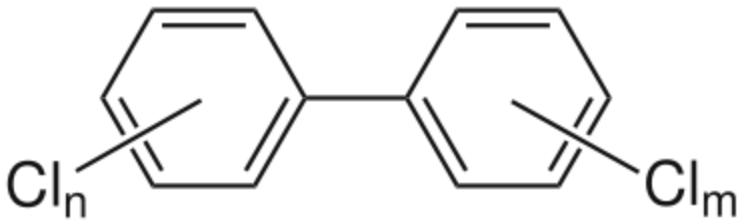
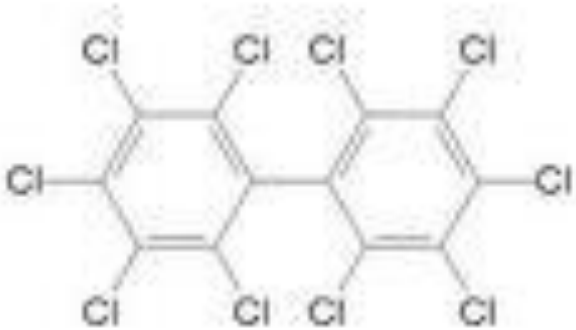
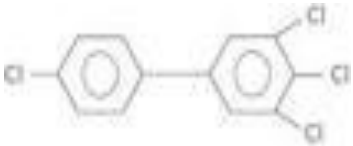
What is a PCB?



Biphenyl with 1 to 10 Chlorine Atoms



Decachlorobiphenyl or PCB 209



PCB 81; a tetrachlorobiphenyl

PCB Congener

Table of PCB Species by Congener Number

Descriptor*	CASRN	Congener Number	IUPAC Name	Type
	1336-36-3		Polychlorinated biphenyl (PCB)	Category
CP1_---_--_-	2051-60-7	1	2-Chlorobiphenyl	Congener
CP0_---_--_-	2051-61-8	2	3-Chlorobiphenyl	Congener
CP0_---_--_-	2051-62-9	3	4-Chlorobiphenyl	Congener
---_---_--_-	13029-08-8	4	2,2'-Dichlorobiphenyl	Congener
CP1_---_--_-	16605-91-7	5	2,3-Dichlorobiphenyl	Congener
CP1_---_--_-	25569-80-6	6	2,3'-Dichlorobiphenyl	Congener
CP1_---_--_-	33284-50-3	7	2,4-Dichlorobiphenyl	Congener
CP1_---_--_-	34883-43-7	8	2,4'-Dichlorobiphenyl	Congener
CP1_---_--_-	34883-39-1	9	2,5-Dichlorobiphenyl	Congener
---_---_--_-	33146-45-1	10	2,6-Dichlorobiphenyl	Congener
CP0_---_--_2M	2050-67-1	11	3,3'-Dichlorobiphenyl	Congener

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PCB Homolog

Table of PCB Homologs

CASRN	IUPAC Name	No. of Congeners
27323-18-8	Monochlorobiphenyl	3
25512-42-9	Dichlorobiphenyl	12
25323-68-6	Trichlorobiphenyl	24
26914-33-0	Tetrachlorobiphenyl	42
25429-29-2	Pentachlorobiphenyl	46
26601-64-9	Hexachlorobiphenyl	42
28655-71-2	Heptachlorobiphenyl	24
55722-26-4	Octachlorobiphenyl	12
53742-07-7	Nonachlorobiphenyl	3

Homolog – a group of PCB congeners with the same number of chlorine atoms.

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History of Method 1668

A B C – What does it all mean?

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History of Method 1668

- Long development history back to mid-90's.
- EPA's Health Effects Research Laboratory (HERL) requested a method to determine the "dirty dozen" congeners to support risk assessments.
- Method 1668 was developed by the EPA Offices of Science and Technology to specifically determine the 12 PCB congeners designated as toxic by the World Health Organization (WHO) commonly referred to as the WHO-list PCB congeners.

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History of Method 1668

- The initial Method 1668 development work was carried out by Pacific Analytical, Inc. (PAI) in 1995 and was largely based on EPA Method 1613 (dioxins/furans).
- Method 1668 underwent a single-laboratory validation between February and September 1995 at PAI and the first draft of the method was released in October 1995. The method was ultimately published in March 1997 (EPA-821-R-97-001).

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History of Method 1668

- In mid-1997, EPA began expanding the method for analysis of all 209 CB congeners. AXYS Analytical Services, Ltd. (AXYS) conducted the method development under contract to EPA and the expanded method was published in December 1999 as revision "A" (Method 1668A, EPA-821-R-00-002).
- Method 1668A was validated in a single laboratory (AXYS) and as a result, EPA Method 1668 was validated in two laboratories (AXYS and PAI).

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History of Method 1668

- The method validation study to support the expanded Draft Method 1668A underwent peer review in September to November of 1999 and comments were incorporated by EPA into the method prior to the revised method being published.
- The method validation study was published in February 2000.

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History of Method 1668

- EPA expressed an interest soon after release of Method 1668A in promulgating the method for use in Clean Water Act (CWA) programs.
- Between 1999 and approximately 2003, only a very small number of laboratories claimed they could perform Method 1668A and many laboratories indicated it could not be performed as written.

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History of Method 1668

- EPA received significant criticism from the public and private sector that the method had not undergone any interlaboratory validation studies demonstrating performance of the method.
- Validation of the method had only occurred at a single laboratory location (AXYS).

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History of Method 1668

- EPA embarked on an interlaboratory study of Method 1668A in 2003.
- EPA identified the study objectives were to:

1. characterize method performance in multiple laboratories using multiple sample matrices (wastewater, biosolids and fish tissues),
2. revise the method to reflect study results, and
3. evaluate and, if necessary, revise the QC acceptance criteria.

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History of Method 1668

- Laboratories participating in the study were provided a version of the method referred to as "Method 1668A with corrections and changes through August 20, 2003," (EPA-821-R-07-004).
- Was not available to the public until approximately late 2007.
- The changes identified by EPA for Method 1668A (August 20, 2003) were primarily to correct typographical errors in the method and make minor technical clarifications.

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History of Method 1668

- EPA conducted the interlaboratory study of Method 1668A in 2003-2004 and published the study report "Method 1668A Interlaboratory Validation Study Report," (November 2008, EPA-821-R-08-021); the report was released to the public in February 2009.
- EPA additionally released the revision "B" of the method to the public in February 2009.

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History of Method 1668

- According to EPA, Method 1668B "revises EPA Method 1668A to replace single-lab quality control (QC) acceptance criteria with interlaboratory criteria, and make other changes" as described in EPA Method 1668B.

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History of Method 1668

- EPA issued a proposed rule on September 23, 2010, (Federal Register, Vol. 75, No. 184, pages 58023-58076) to approve several new or revised analytical methods.
- “2010 Methods Update Rule” (MUR).

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History of Method 1668

- In this rule, EPA is proposing to promulgate EPA Method 1668C.
- The 2010 MUR identifies that the proposed method version, Method 1668C, is based on an interlaboratory study, peer reviews and user experiences.

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History of Method 1668

- Included in the docket for the 2010 MUR was a new version of the above interlaboratory study titled "Method 1668A Interlaboratory Validation Study Report," (March 2010, EPA-821-R-10-004, hereinafter the "Study Report"), an addendum to the Study Report titled "Addendum to the Method 1668A Interlaboratory Study Report," (March 2010, EPA-820-R-10-003, hereinafter "the Addendum"), and a peer review of the Study Report titled "Peer Review of the Method 1668A Interlaboratory Validation Study," (April 2010, EPA-820-R-10-007).

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History of Method 1668

- The primary revisions of Method 1668B to create the "C" revision includes update of the QC acceptance criteria in Table 6 of the method based on the Addendum and revision of the estimated method detection limits (EMDLs) and estimated minimum levels of quantitation (EMLs) to method detection limits (MDLs) and minimum levels (MLs).
- The MDLs and MLs were developed by EPA by pooling data from three laboratories.

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Status of Method 1668C

- Comments to the 2010 MUR closed 12/22/2010.
- 307 public comments to the 2010 MUR received by 12/22/2010.
- 27 public comments were received on EPA Method 1668C.
- Significant representation by hundreds of industrial and municipal stakeholders.

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Status of Method 1668C

Environmental Standards Inc. Report, “Review and Evaluation of EPA 1668”, Dec 21, 2010. This effort was conducted on behalf of the following sponsors:

- Utility Water Act Group
- The Federal Water Quality Coalition
- General Electric Company
- ALCOA, Inc
- Georgia Pacific LLC
- The Delaware Estuary TMDL Coalition
- E.I. du Pont de Nemours and Company
- National Association of Clean Water Agencies

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Comment Themes

- Illinois EPA, TCEQ, NYSDEC, NMED, and the commercial environmental laboratory testing community provided a blanket endorsement of EPA 1668C.
- Industries, Utility/Energy, State and Federal Water Coalitions, Municipalities all voiced various technical concerns over promulgation of EPA 1668C.
- ELAB (Environmental Laboratory Advisory Board) – EPA's Federal Advisory Committee on issues related to laboratory measurement and accreditation also expressed "serious flaws" with the method and stated these "should be corrected before promulgation."

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Concerns with Method 1668C

- A COMPLEX METHOD.
- EPA has made no real substantial changes to address technical issues or ambiguities in the method since Method 1668A or to incorporate the technical advancements that have been made since 1999.
- No beneficial information derived on how to improve the method based on the EPA Interlaboratory Study.
- Of the 11 laboratories that submitted data to EPA, only six laboratories submitted data deemed usable by EPA for wastewater, six laboratories submitted data deemed usable for tissue, and four laboratories submitted data sets deemed usable for biosolids. Only four laboratories submitted data deemed usable by EPA for all three matrices.
- REALLY?

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Concerns with Method 1668C

- Interlaboratory Study data – many method deviations by labs that were not addressed by EPA.
- Performance Based Method can result in significant lab to lab variation. Better definition of PBMS is needed.
- PCBs are ubiquitous in the environment. Background levels of PCBs in laboratory method blanks and field quality control blanks indicates wide spread contamination levels in blanks that are not well addressed in the method.
- Numerous technical and quality control issues exist in the method.
- MDL procedure by 40 CFR Part 136 FLAWED. Pooled evaluation procedure used for Method 1668C biased and flawed.

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Recommendations for Method 1668C

1. Propose and promulgate new detection and quantitation procedures for methods under the CWA as recommended by the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in the Clean Water Act Programs.
2. Address the Method 1668C technical issues identified by other data users and by the laboratories that employ the method. EPA should include stakeholders to form an independent expert methods committee to review and update the method.
3. Design and conduct an interlaboratory study of the revised consensus method produced above. Absent a successful method validation study and interlaboratory validation study, the regulated community cannot have confidence in the accuracy, precision and reliability of this method for regulatory or remedial purposes.

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Use of Method 1668 on the Delaware Estuary PCB TMDL

- Method 1668A was specified for PCB data collection by the Delaware River Basin Commission (DRBC) to support the Stage 2 PCB TMDL.
- DRBC used this method to better characterize the PCB loadings to the estuary and to develop and calibrate the model.
- Environmental Standards developed the analytical protocols and many of the collection and data reporting protocols as part of the Data Quality Subcommittee to the Technical Advisory Committee.
  - http://www.state.nj.us/drbc/PCB_info.htm
- Method 1668A with DRBC modifications was used for collection of Point Source samples – both wet and dry weather events.
- Sample collection was REQUIRED, not VOLUNTARY.

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Use of Method 1668 on the Delaware Estuary PCB TMDL

- Significant sources that contributed to the majority of the PCB load were required to implement PCB Pollutant Minimization Plans (PMPs).
- PMPs were used to identify PCBs and reduce load to the Estuary to the extent practical.
- States in the Estuary including Pennsylvania, Delaware and New Jersey identified PCB monitoring programs and PMP implementation in NPDES permits.
- Method 1668 is required for these monitoring activities. DRBC requires monitoring load reduction biennually as a PMP requirement.

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Thank You

"Setting the Standards for Innovative Environmental Solutions"

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