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VAMWA/VMA Study
EPA Method 1668 Reliability and Data Variability Associated with Ambient Monitoring

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Topics

- Background
  - PCB's
  - Virginia TMDL for PCBs & Department of Environmental Quality (DEQ) Guidance
  - EPA Method 1668
- Virginia Association of Municipal Wastewater Agencies/ Virginia Manufacturer Association (VAMWA/VMA) Study
  - Purpose
  - Study Design
  - Results
- Recommendations
- Future Studies

Background –PCB's

- PCB 's are
  - Bioaccumulative
  - Stable and do not readily decompose
  - Persistent in the environment due to ubiquitous nature
- PCB's have been the subject of numerous environmental investigations and studies for several decades
- 209 PCB Congeners
  - 12 designated as toxic by the WHO

Background Va DEQ TMDL Guidance

VA DEQ. Guidance Memo No. 09-2001, March 2009

- An established guidance procedure for implementing point source monitoring of PCBs
- Monitoring data will be used to prepare TMDL for each water segment and assign waste load allocation to various sources of PCBs.
- Prescriptive monitoring, sample collection, analyses by EPA Method 1668 and data reporting criteria
- Applies to point source dischargers into PCB impaired waters
  - Implemented by letter requests and permit conditions
  - Major and minor municipal wastewater facilities
  - Industrial wastewater facilities and storm water dischargers
  - Dry and wet weather sample collection

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EPA Method 1668

Chlorinated Biphenyl Congeners in Water, Soil, Sediments, Biosolids and Tissue by HRGC/HRMS

- High resolution GC/MS method using isotope dilution and internal standard technique
- 209 Congeners
  - not all determined discretely
  - approximately 70 determined as mixtures due to co-elution
- Labor intensive method requiring multiple qualitative handling of the sample and extract before final analysis
- Analytical cost - $700 - $1300/sample
- Method provides several extract cleanup options depending on sample type to minimize interferences.
  - GPC – remove high MW interferences
  - Silica Gel, Florisil - remove polar and non polar interferences
  - Carbopak/Celite, HPLC, and Anthropogenic isolation column

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EPA Method 1668

- Detection limit is limited by level of interference, matrix background – rather than by instrumental limitations
- Estimated Minimum level (EML/Report Limit)
  - limited by several factors including lowest calibration point, linearity, volume of sample extracted, and final extract volume.
  - EML can be different for every sample
- Multiple Versions
  - EPA Method 1668B performed poorly in EPA's inter-lab study – 2003/2004
  - Not validated according to EPA's own procedures/directive
  - Not currently promulgated and is continuing to evolve, as demonstrated by the fact that EPA has published and proposed a new version-1668C, in recent method update rule

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VAMWA/VMA Concerns

- Method Issues
- Low WQ Standard
  - 640 parts per quadrillion (ppq), 3-6 orders of magnitude lower than most other water quality standards.
  - The low standard, coupled with the ubiquitous nature of PCBs, makes it likely that PCBs will be detected in every sample.
- End Use of Data
- Potential for Contamination
  - Analytical and Field
- Data Reporting/ Qualification of Data

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Purpose of the Study

- To evaluate consistency among laboratory data generated using Method 1668B
- To Identify necessary qualifications that should accompany data before it is used for any regulatory purpose
- To evaluate method performance and lab variability specific to wastewater matrices.
- Evaluate variability, probability and magnitude of sample contamination for low level PCBs
  - Relative to the water quality standard for total PCBs
  - Evaluation of blank composite samples since NPDES permittees often collect composite samples to ensure sample representativeness

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Study Design

Phase I

- Laboratory Survey and Evaluation

Phase II

- Evaluate HRSD reagent water and equipment cleaning procedures

Phase III

- Inter-lab study

Phase I, Laboratory Survey Study Design

- Laboratories were invited to participate in a survey
  - includes list of labs from VA DEQ and DRBC websites
- Nine laboratories responded
- Labs were evaluated based on:
  - experience with EPA Method 1668
  - adherence to the method
  - laboratory capabilities: personnel, equipment, capacity, accreditation
  - fulfillment of initial demonstration of capability
  - separate sample extraction room
  - degree of historical method blank contamination
  - responsiveness to the survey
- Identified top three labs based on responses
  - Does not imply that other 6 labs were not capable of performing analysis by EPA Method 1668

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Phase I, Laboratory Survey Results

- Labs referencing 1668A, 1668B or both
- Dedicated sample prep area and multiple instruments
- HRGC/HRMS Analyst experience range: 5-18 years
- Sample volume extracted: 1-4L
- Final extract volume: 20 – 100 uL
- All labs certified/accredited
- 8/10 had completed IPR and DOC
- Deviations from approved method -10/10
- Contamination control procedures
- Variable EML procedures
- Costs $600-$1300 w/ various additional charges
- Laboratory Method Blanks
  - ***Total PCB data ranged from non-detect to 5660 ppq***

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Phase II - Reagent Water and Equipment Evaluation

- Evaluate HRSD's reagent water
- Evaluate Sampling Equipment Cleaning Procedure
  - Section 4.2 of EPA Method 1668B
  - Equipment assembly performed in HRSD's clean room
- 4 reagent water and 6 equipment blanks, 3 days
- Reagent water collected from one location
  - Collected into 2 liter containers provided by the laboratory
- Equipment Blanks
  - Water collected into a 10 liter glass carboy, pumped into a second 10 liter carboy through the cleaned sampling equipment and transferred into 2L sample containers
- All reagent water and equipment blank samples were sent to one laboratory for analysis

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Reagent Water and Equipment Blank Data

Sample Description	Collection Date	Total PCB, ppq
HRSD Reagent Water	03/17/10	105
HRSD Reagent Water Duplicate	03/17/10	47.4
HRSD Reagent Water	03/22/10	55.5
HRSD Reagent Water Duplicate	03/22/10	57.3
AVERAGE Reagent Water Total PCB		66.3
HRSD Equipment Blank	03/17/10	72.0
HRSD Equipment Blank, Duplicate	03/17/10	48.2
HRSD Equipment Blank	03/18/10	34.6
HRSD Equipment Blank, Duplicate	03/18/10	132
HRSD Equipment Blank	03/22/10	89.0
HRSD Equipment Blank, Duplicate	03/22/10	60.6
AVERAGE Equip. Blank Total PCB		72.7
Contract Laboratory Method Blank		61.1

Phase II Data Evaluation

- Results indicate HRSD reagent water and equipment cleaning procedure do not add significant PCB contamination
- Laboratory method blank results suggest that most PCB concentrations observed in blank samples may be associated with analysis

Phase III, Inter-laboratory Study Design

- 28 Field samples were collected using HRSD's closed loop automated samplers:
  - equipment blanks
  - field equipment rinsate blanks
  - 24 hour composite blanks
  - 24 hour composite sample and sample replicates
  - samples for matrix spike and matrix spike duplicates
- Additional method blank analysis requested
- Split samples sent to 3 pre-qualified laboratories
- Labs instructed to adhere to EPA Method 1668B
- Level IV data report packages
- Analytical TAT 30-35 days after sample receipt

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Phase III - Data Review and Analysis

- Data reviewed for strict adherence to the method requirements
- Narratives and raw data provided by laboratories were reviewed
- All labs provided proof of adherence to method
- Blank data, matrix spike, matrix spike duplicate, and OPR data reviewed and evaluated to assess data quality

Phase III - Laboratory QC Data Analysis – OPR Results

OPR Data		# of Congeners Spiked	Obtained % Recovery (Range)	Contract Lab Acceptance Limits (%)	# of Recovery outside of Limits
OPR Lab A	Native Compounds	27	81-122	50-150	0
	C13 Labeled Compounds	31	59-99	30-140	0
OPR Lab B	Native Compounds	27	95-110	50-150	0
	C13 Labeled Compounds	30	52-92	50-150	0
OPR Lab C	Native Compounds	32	82-184	50-150	3 – biased high
	C13 Labeled Compounds	31	49-161	30-150	12 – biased high

Phase III Laboratory QC Data Analysis – MS/MSD Results

MS/MSD Data		# of Congeners Spiked	Obtained % Recovery (Range)	Contract Lab Acceptance Limits (%)	# of Recovery outside of Limits
MS/MSD Lab A	Native Compounds	28	92-144	50-150	0
	C13 Labeled Compounds	31	36-101	30-140	0
				40-125	
MS/ MSD Lab B	Native Compounds	26	94-179	50-150	1 biased high
	C13 Labeled Compounds	29	20-111	25-150	0
				15-150	
MS/MSD Lab C	Native Compounds	32	82-119	51-150	0
	C13 Labeled Compounds	31	63-170	40-125	20 biased high
				30-140	
				15-140	

Phase III - Results

Lab A	Total PCB, pg/L	Total PCB w/ “J” flag	Total PCB w/o “J” Flag	% Data w/ “J” Flag
Method Blank	170.0	132.3	37.7	78%
Equip. Blank 1	102.4	65.7	36.7	64%
Equip. Blank 2	3213	94.8	3118	3%
Equip. Blank 3	149.6	91.5	58.0	61%
Equip. Blank 4	105.9	74.2	31.7	70%
Rinsate Blank	180.7	71.2	109.6	39%
24 Hr. Comp. Blk	167.9	85.6	82.3	51%
Sample 1	2326	90.9	2235	4%
Sample 1 dup.	11044	64.0	10980	1%
Sample 1 Tripl.	3274	93.3	3181	3%
Sample 2	2235	104.7	2130	5%

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Laboratory A – Data Analysis

- Equipment Blank 2 – amount detected of 3213 ppq indicates possible contamination
- Sample 1 duplicate – amount detected of 11044 ppq indicates severe contamination, amount detected in all other samples were well below this amount of contamination
- In both cases, contamination data obtained were above the ML (less percentage “J” Flag)

Phase III Results

Lab B	Total PCB, pg/L	Total PCB w/ "J" flag	Total PCB w/o "J" Flag	% Data w/ "J" Flag
Method Blank	268.5	81.9	186.6	31%
Method Blank dup.	137.9	78.2	59.7	57%
Rinsate Blank	221.7	111.7	110.1	50%
24 Hr. Comp. Blk	236.9	93.0	143.9	39%
Sample 1	1669	79.0	1590	5%
Sample 1 dup.	1338	65.8	1271	5%
Sample 1 Tripl.	1552	57.3	1495	4%
Sample 2	1057	123.2	933.4	12%

Phase III Results

Lab C	Total PCB, pg/L	Total PCB w/ "J" flag	Total PCB w/o "J" Flag	% Data w/ "J" Flag
Method Blank	179.3	179.3	0.0	100%
Method Blank dup.	73.6	73.6	0.0	100%
Rinsate Blank	368.4	368.4	0.0	100%
24 Hr. Comp. Blk	311.9	211.9	100.0	68%
Sample 1	2410	2230	180.0	93%
Sample 1 dup.	2304	2114	190.0	92%
Sample 1 Tripl.	2680	2360	320.0	88%
Sample 2	1627	1427	200.0	88%

Blank Comparison Between Laboratories

Blank Results	Method Blank	Method Blank, dup.	Rinsate Blank	24 Hr. Comp. Blank
Lab **A**	170.0	No data	180.7	167.9
Lab **B**	268.5	137.9	221.7	236.9
Lab **C**	179.3	73.6	368.4	311.9
Average	**205.9**	**105.8**	**256.9**	**238.6**

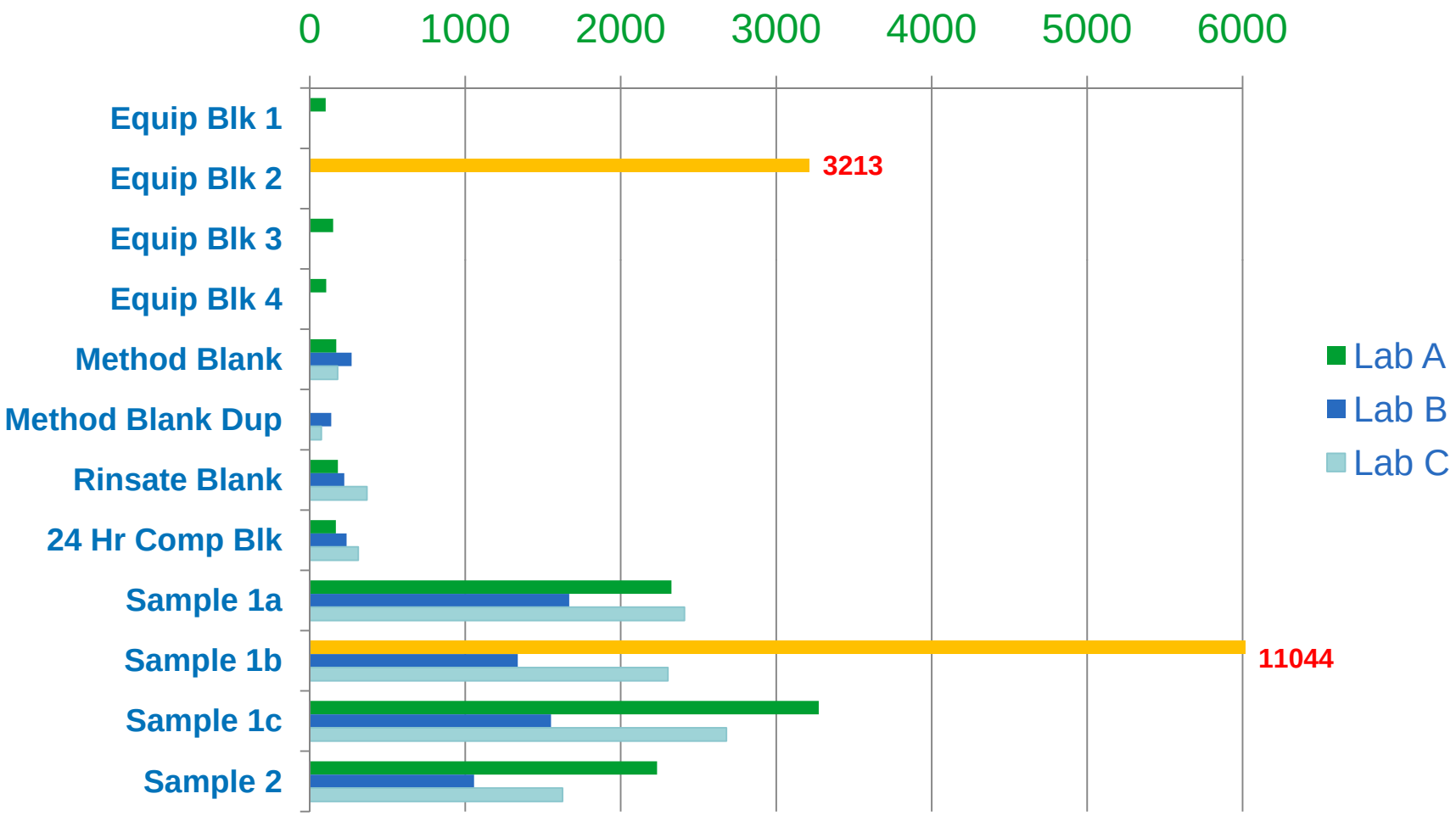
Result Comparison Between Laboratories

Sample Results	Sample 1a	Sample 1b	Sample 1c	Sample 1- avg.	Sample 2
Lab **A**	2326	**11044**	3274	**5548**	2234
Lab **B**	1669	1338	1552	1520	1057
Lab **C**	2410	2304	2680	2464	1626

Summary of Total PCBs in Each Sample Type

	Avg PCBs, ppq	STD, ppq	Mean +2S
Method Blanks	165.9	70.8	
Equipment Blanks	892.7	1547	
Method and Equip. Blanks (excluding outliers)	148.4	60.3	269.0
Rinsate Blank	256.9	98.6	
24 Hr. Composite Blank	238.9	72.0	
Rinsate and 24 Hr Comp. Blanks	247.9	77.9	403.7
All Blanks	392.5	784.4	1961.3
All Blanks (excl. outliers)	191.0	83.1	357.2
Sample 1	3177.5	3010.9	
Sample 2	1639.4	589.2	

Result Summary



Discussion of Results - Outliers

- There were 2 apparent outliers in the data set
- One equipment blank was reported@3213 ppq which was ~20X higher than the average for all other blanks
- Sample 1 was reported by Lab A @11044 ppq which was ~5X higher than the average for all other samples
- The Laboratory was not able to explain the variability although it is suspected that the contamination may be due to laboratory issues

VA DEQ Guidance Blank Criteria for TMDL Data Collection

- Method Blank – flowchart instructs permittees to take actions when individual congener and/or total PCB level exceeds 300 ppq
- Field Equipment Rinsate Blanks – flowchart instructs permittees to take actions when individual congener exceeds 40 ppq or if the total PCB level exceeds 600 ppq
- Possible re-sampling and analysis if blank criteria is exceeded unless the total congener in the sample does not exceed the limit (WQ Criteria – 640 ppq) or congener is not found in samples

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PCB Congener Exceeding 20 ppq

Method Blank	**Lab C**	**PCB 129 @21.5**	**PCB 129 @21.5**	
Rinsate Blank	**Lab C**			**PCB 11 @97.2**
24 hr Comp. Blk.	**Lab C**			**PCB 11 @100**
Method Blank	**Lab B**	**PCB 5 @103**	**PCB 9 @41.4**	**PCB 11@22.8**
Method Blank Dup	**Lab B**		**PCB 9 @21.6**	
Rinsate Blank	**Lab B**	**PCB 5 @23.7**		**PCB 11 @23.3**
24 hr Comp. Blank	**Lab B**	**PCB 5 @41.8**		**PCB 11 @34.8**
Method Blank	**Lab A**			**PCB 11 @27**
Equip. Blank 1	**Lab A**			**PCB 11 @25.3**
Equip. Blank 3	**Lab A**			**PCB 11 @30.3**
Equip. Blank 4	**Lab A**			**PCB 11 @25.7**
Rinsate Blank	**Lab A**			**PCB 11 @46)**
24 hr Comp. Blank	**Lab A**		**PCB 44 @23.7**	**PCB 11 @43.4**

PCB Congener Exceeding 20 ppq

- Most commonly found is PCB 11
  - Reported widespread in the environment
  - Non-arochlor congener
  - byproduct of certain yellow pigment manufacturing
- Although congeners exceeding 20 ppq is limited to a few congeners, a significant number of congeners in blanks and samples were flagged with a “J”
  - value is below the calculated minimum reporting level but above the EDL

Study Conclusions-Contamination

- There is a high probability of laboratory contamination at levels above the water quality standard.
  - Study results demonstrated that contamination of laboratory method blanks can be 25%-6000% of the water quality standard concentration.
  - Accordingly, it is difficult to differentiate lab contamination from actual sample concentration.
- It may not be possible to avoid contamination given the limitations of EPA Method 1668, the nature of PCBs and presence of PCBs in the environment

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Study Conclusions-Contamination

- A wide range of contamination can occur between labs without conclusive explanation
- 60%of contamination occurred in the lab and 40% in the field when collecting samples
- It is possible to collect 24 hour composite samples with contamination not exceeding what is found in the laboratory.
- Total PCBs in the equipment rinsate and 24 hour composite field blanks were comparable

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Study Conclusions – Interlab Variability

- The choice of laboratories used to perform the analytical method will affect the results.
  - An order of magnitude of variability can occur between labs analyzing split samples.
  - Variability between labs and split samples can be without known sources
- Despite certification, not all labs consistently met method 1668 requirements
- Sample volume, final extract volume and calibration range will affect data variability and uncertainty in data

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Study Conclusions – Interlab Variability

- Results that qualify as outliers are likely.
  - Although this study used three laboratories, there are several results that would likely qualify as outliers.
  - The likely presence of outliers has a significant impact on the variability - and reliability - of the data produced.
  - Regulated entities typically use only one laboratory and will not know if their results include outliers.

Study Outcomes –Recommendations to DEQ

- Updates to Guidance Memo No. 09-2001 to reduce inaccuracies in data generated associated with Method 1668, to address contamination issues with regard to qualification and reporting data and suggestions to minimize inter-lab variability
- Application of data generated by Method 1668 should be non-regulatory
- Study impact of air deposition for TMDL

Study Outcome- Recommendations to VAMWA/VMA Members

- Selection of Laboratories
- Collection of split samples to save for future analysis in case sampling and/or analysis of the original sample is unacceptable.
- Collection of a field equipment rinsate blank. However, collection of a 24-hr composite field blank may be unnecessary.
- PCB data generated using Method 1668B and submitted to DEQ should include language highlighting the limitations of data

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Study Outcome- Recommendations to VAMWA/VMA Members

- Calculations
  - Calculate total PCBs after first excluding congener data that was flagged with a “J” or “EMPC” and then excluding congeners flagged with a “B” when contamination is greater than 10% of the sample concentration.
  - Submitted reports should not include any alternate calculation by the commercial laboratory
- Submit raw data to DEQ to the extent required by VPDES permit condition or in response to a specific DEQ request.
- Emphasize to data users (including regulatory officials) that only properly adjusted results are a reliable representation of the true sample concentration.

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Future Studies

- Conduct a similar PCB contamination study by collecting samples and blanks during wet weather conditions.
- Evaluate the spatial contamination risk to collecting PCB-free samples and blanks by conducting sampling events in various urban and rural areas.
- Determine the significance of PCB 11 contamination in laboratory and sample handling equipment.
- Review sample congeners for trends across samples.
- Investigate the possibility of using one or a small group of congeners as indicators for total PCBs.
- Calculate a MDL for total PCBs within and between labs.

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