COMMONWEALTH OF VIRGINIA
DEPARTMENT OF ENVIRONMENTAL QUALITY
WATER DIVISION

P.O.BOX 1105 **Richmond, VA 23218**

Subject: TMDL Guidance Memo **No. 14-2004**
Procedures for reviewing and deriving total PCB concentrations from samples analyzed using low-level PCB method 1668 to be used in the development and implementation of TMDLs

To: Regional Directors

From: Melanie D. Davenport, Director

Date: April 4, 2014

Copies: Deputy Regional Directors, Regional Water Permit Managers, Rick Weeks, James Golden, Fred Cunningham and Watershed Staff

Summary:
Low-level Polychlorinated Biphenyl (PCB) data generated by the Virginia Pollutant Discharge Elimination System (VPDES) point source dischargers using EPA Method 1668 support development of Total Maximum Daily Loads (TMDL) and the implementation of completed PCB TMDLs. This guidance outlines steps for 1) ensuring a standardized procedure to review data and 2) calculating Total PCB concentrations.

Electronic Copy:
An electronic copy of this guidance in PDF format is available for staff internally on DEQNET.

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Procedures for reviewing and deriving total PCB concentrations from samples analyzed using low-level PCB method 1668 to be used in the development and implementation of TMDLs

I. Background

In 2004, the Virginia Department of Health lowered the trigger value for fish consumption advisories due to polychlorinated biphenyls (PCBs) levels in fish tissue from 600 parts per billion (ppb) to 54 ppb, thus creating an expansion in impaired water bodies that require a Total Maximum Daily Load (TMDL). The TMDL process is initiated with a study designed to identify on-going sources or conveyances of PCBs that are contributing to the impairment. One of several categories targeted in the source investigation study, and the focus of this guidance, includes Virginia Pollutant Discharge Elimination System (VPDES) point source dischargers. VPDES effluent data requested for TMDL development is generated in accordance with the point source monitoring guidance entitled **TMDL Guidance Memo No. 09-2001, Amendment No. 1. Guidance for monitoring of point sources for TMDL development using low-level PCB method 1668 (referred to as TMDL GM No. 09-2001)** which can be found at the following link: http://www.deq.virginia.gov/Programs/Water/WaterQualityInformationTMDLs/TMDL/PCBTMDLs.aspx.

The Environmental Protection Agency's (EPA) Method 1668 is a performance based method that allows analytical laboratories the ability to improve upon the already low Method Detection Levels (MDLs) and Minimum Levels (MLs) through laboratory modifications (versions A, B, or C; EPA 1999a, 2008, 2010) provided the performance based criteria are met. With these modifications, a laboratory can detect and report PCBs at environmentally relevant water concentrations such as Virginia's Water Quality Criterion (WQC = 0.00064 µg/L or 640 pg/L; DEQ 2010, 9VAC25-260) which is expressed as Total PCBs (tPCB).

Pursuant to the projected expansion of TMDL development and continued effluent data submittals associated with existing PCB TMDLs, the Department of Environmental Quality (DEQ) expects an increase in effluent PCB submittals by VPDES point sources generated using EPA method 1668. To efficiently manage the increase in effluent PCB data submittals and considering the complexity of a multi-analyte method, a procedure to consistently review PCB congener data and determine tPCB concentrations is necessary. Furthermore, there is a need to use selected qualified data for calculating tPCB for TMDL development as inclusion of these data is an important component to fully account for PCB loadings. The procedure will provide a means of ensuring that data generated from laboratories using the method are formatted and presented to DEQ uniformly and meet the specifications of **TMDL GM No. 09-2001**.

The purpose of this guidance is to establish standardized procedures for performing a review of PCB data generated with method 1668 as well as calculating tPCB generated under **TMDL Guidance Memo No. 09-2001**. The approach will ensure the Data Quality Objectives (DQOs) necessary for TMDL development are maintained throughout the process. While VPDES dischargers are emphasized under this and the aforementioned guidance, both guidance documents are also relevant to non-VPDES samples (i.e., ambient water, etc.) provided the specified analytical approach is followed.

EPA recommends use of low-level PCB Method 1668 data generated in support of TMDL development. However because it has not yet been promulgated in 40 CFR Part 136, **data generated under this guidance should not be used for compliance purposes**.

II. Definitions

A PCB "congener" is any single, unique, well-defined chemical compound in the PCB category. The name of a congener specifies the total number of chlorine substituents and the position of each chlorine atom. For example: 4,4'-Dichlorobiphenyl is a congener comprising the biphenyl structure with two chlorine substituents, one on each of the #4 carbons of the two rings. In 1980, a numbering system was developed which assigned a sequential number to each of the 209 PCB congeners.

"Blank Correction" is a process where a PCB congener measured in a sample and also measured in a laboratory or field based blank, is subtracted from the sample concentration if it is less than 5 times the greater of the associated blank concentration(s) for that same congener. The process considers all 209 PCB congeners and once corrected the data are considered to be "censored". The full process is explained in Appendix B.

"Estimated Detection Limit" is the lowest concentration at which a PCB congener can be detected assuming a response signal that is 2.5 x background noise signal. The EDL calculation can be found in **TMDL GM No. 09-2001**, Appendix D, Attachment 2.

"Estimated Maximum Possible Concentration" (EMPC), is calculated from PCB congeners that are characterized by a response with signal to noise (S/N) ratio of at least 2.5 to1 for both the quantitation ions, but that do not meet the ion abundance ratio criteria specified in the method. The specific calculation procedure for EMPC can be found in Appendix D. Attachment 3 of **TMDL GM No. 09-2001**.

"Equipment (Rinsate) Blank" is a sample of analyte-free water instantaneously poured over or pumped through decontaminated field sampling equipment. The sample is collected either in the laboratory or in the field prior to the collection of environmental samples to assess the adequacy of the decontamination process. When collected in the field, the blank also includes site exposure.

"Field Blank" is a sample of analyte-free water poured or pumped into a container in the field to assess contamination from field conditions during sampling. For purposes of this guidance, there are occasions where a field blank is collected concurrently with effluent through a dual set-up using two composite samplers over a period of 24 hours. The inclusion of this approach considers field conditions over the duration of the effluent collection period.

"Homolog" is a group of congeners containing the same amount of chlorine atoms but in different positions. PCB congeners contain from 1-10 chlorine atoms.

"J" value is a reported result that is an estimate. The value is less than the minimum calibration

level but greater than the estimated detection limit (EDL).

"Method Blank" is a laboratory generated sample of an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

"Method 1668" (versions A, B or C) is an analytical method developed by the EPA Office of Water's Office of Science and Technology for use in Clean Water Act programs. This method is used to determine chlorinated biphenyl congeners in environmental samples by isotope dilution and internal standard high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Lacking promulgation (as of March 2014), this analytical method has been recommended by EPA for data generation related to TMDL development.

"Minimum level of quantitation" (ML), as described in 1668 revisions A, B and C is the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. Laboratories often refer to this term as the "reporting level". The ML calculation can be found in **TMDL GM No. 09-2001**, Appendix D, Attachment 2.

"µg/L" refers to micrograms per liter (µg/L) and corresponds to parts per billion (ppb) (1.0 E-6).

"ng/L" refers to nanograms per liter (ng/L) and corresponds to parts per trillion (ppt) (1.0 E-9).

"pg/L" refers to picograms per liter (pg/L) and corresponds to parts per quadrillion (ppq) (1.0 E-12) (EPA 1999a, 2008, 2010). Of note, results are typically reported using this unit.

"On-going Precision and Recovery" (OPR) samples are used to ensure that laboratory performance is in control during analysis of the associated batch of field samples. OPR can also be referred to as Lab Control Spike (LCS), Laboratory Fortified Blank (LFB), or Quality Control (QC) check sample.

"Total PCB" (tPCB) is defined as the summation of PCB congeners, out of the possible 209, that remain after the blank correction method applied under the framework of this guidance. The final tPCB concentration following blank correction is referred to as "censored". "Uncensored" tPCB is defined as the summation of concentrations from all detected PCB congeners, including those qualified with a "J" or "EMPC", out of the possible 209. Censored PCB results are to be used for TMDL related activity including development and implementation.

III. Procedure

The objective of this guidance is to provide an approach to 1) review PCB results to ensure the data meet analytical requirements of the method and specific decision rules included in **TMDL GM No. 09-2001** and 2) to calculate an appropriate tPCB concentration from applicable data sets. A blank correction procedure is included within this guidance where PCB congener data are

automatically adjusted based on their background availability from the laboratory or field thereby resulting in "censored" tPCB results. "Uncensored" results include the data as received by the laboratory. A list of Virginia Environmental Laboratory Accreditation Program (VELAP) certified laboratories that meet the analytical protocol requirements of the point source monitoring guidance can be found at the following link: http://www.deq.virginia.gov/Portals/0/DEQ/Water/TMDL/PCB/pcblabs.pdf. If a VELAP certified laboratory was used for PCB analysis and is not on the aforementioned list, the data can be accepted provided the performance requirements of **TMDL GM No. 09-2001,** Appendix D were met.

A. Data Receipt and Acceptance

For proper evaluation and storage of the complex PCB data sets, it is vital that information be analyzed and received from permittees as specified in **TMDL GM No. 09-2001, Amendment No. 1.** *(Note: appendices and other references in this section pertain specifically to the point source monitoring guidance).*

- A description identifying the effluent flow condition (i.e., wet or dry condition) during the sampling period should be included in the Chain of Custody Electronic Deliverable Data (EDD).
- PCB data should be analyzed in accordance with Appendix D.
    - Adherence to the method 1668 analytical specifications included in this Appendix should enable the laboratories to control background PCB concentrations such that low EDLs (e.g., < 5 pg/L) and MLs (e.g., ≤ 10 pg/L) can be attained on a congener basis. However, on a sample basis there can be variation in achievable EDLs and MLs among the 209 PCB congeners. For example, some congeners will respond differently to extraction and clean-up techniques, or will have altered measurement responses due to interferences. This is typical of multi-analyte methods where the outcome can include higher reporting levels for some congeners.
- The appropriate EDD format and files are specified in Appendix E and are available on DEQ's TMDL website.
    - Receiving data in an electronic spreadsheet is crucial for managing raw PCB congener results. The results provided in an electronic format allow 1) the easy summation of individual PCB congeners into tPCB, 2) the facilitation of data correction procedures, and 3) the incorporation of results into a database for storage. The data format also provides the flexibility to perform further assessment.
    - The permit holder should be contacted in those instances when information is lacking or data have been submitted but do not meet the formatting requirements. Facility location and sampling (chain of custody) spreadsheets are often inadvertently excluded from the submittal. These spreadsheets are required for data upload.

B. Data Quality

Data quality checks should be performed to ensure the data meet the quality control requirements of method 1668 and **TMDL GM No. 09-2001.** To assist with the goal of producing best estimates of PCB concentrations, DQOs established under this and the aforementioned guidance provide consistent approaches for sample collection and analysis, include specific data acceptance criteria, as well as allow consistent reporting and evaluation. Review of data submittals included

in the Excel spreadsheet (.csv) and the .pdf "hardcopy" formats is necessary to verify sample collection information as well as establish consistency between the reported data contained in the various formats of the electronic EDD.

Considering the large size of PCB data sets, for purposes of reviewing data, performing data quality checks and tPCB calculation, the data are most easily managed when copied and pasted into the Excel "tPCB Auto-Calculation" spreadsheet tool available on DEQ's PCB TMDL website [1]. An explanation of this process can be found in a "How To" supporting document also found on the website. Use of this tool enables quick evaluation of the various sample types described in III.B.1 and 2 below.

1. Method Blank

Method blanks are an important quality control measure and are included with each "batch" of twenty samples. These blanks, which are run early in the analysis sequence of samples, measure the amount of PCB contamination that originates from the laboratory by providing information on the general cleanliness of the laboratory as well as potential contamination from glassware, solvents, instrument carryover, etc.

A method blank correction procedure is included as part of this guidance to reduce the potential impact of laboratory background contamination on tPCB results. However, the requirements specified below must be met prior to acceptance of the blank correction procedure results. The automated blank correction procedure occurs within the Excel "tPCB Auto-Calculation" spreadsheet tool which is described in a "How To" supporting document found on DEQ's PCB TMDL website [1] with examples presented in Appendix B. Equipment/field contamination is also considered but is addressed separately in sections III.B.2. below.

- The acceptance guideline for method blanks is a tPCB concentration $\leq$ 300 pg/L (see Appendix A of this guidance and/or **TMDL GM No. 09-2001**).
    - Approved laboratories routinely meet this guideline. Usual method blank concentrations range from 0 to 150 pg/L tPCB (mean = 108 pg/L) although slight fluctuations can occur within laboratories (DEQ, 2012. PCB Access Database).
    - For rare occurrences where the method blank exceeds 300 pg/L, it should be determined if the background contamination markedly impacted the overall results using a blank evaluation and assessment process.
        - If, for example, the "uncensored" tPCB effluent concentration is greater than the method blank by at least one order of magnitude, the final "censored" effluent result should be minimally biased lower by excessive background contamination (i.e., laboratory contamination is not significant to the end result). These results would be acceptable (see Appendix B, Example 2. A.).

[1] (http://www.deq.virginia.gov/Programs/Water/WaterQualityInformationTMDLs/TMDL/PCBTMDLs.aspx)

        - On occasion a laboratory will submit a result with a method blank concentration that exceeds the acceptance guideline. In these instances to determine if the sample is acceptable, professional judgment may be necessary (see Appendix B, Example 2. B.).
            - With a minimal effluent PCB screening requirement it is important that "censored" results be representative of the effluent and not be exceedingly affected with blank correction resulting from poor laboratory practices. Generally these data should not be accepted as the laboratory practices were not in accordance with **TMDL GM No. 09-2001**.
- Individual congeners in a method blank should be present at concentrations $\leq$ 20 pg/L. If this threshold is exceeded, the congener should be greater than 10X that of the blank for the same congener in the associated effluent (see Appendix A.1.).
    - The following recommendations apply for those instances where individual PCB congeners exceed this threshold.
        - Sample results should not be rejected based on 1-2 individual congeners that exceed this threshold. The impact of these elevated congeners will likely be mitigated through the use of correction procedures. Where more than 2 individual congeners are present at elevated levels, acceptance may be considered on a case by case basis but laboratory procedure would have to be questioned.
            - A possible exception to this guideline and applicable when using professional judgment is addressing the extremely ubiquitous PCB 11. A sample result should not be deemed unacceptable if PCB 11 is detected at elevated levels since this congener has been found in products containing diarylide yellow dye such as found in legal pad paper (Rodenburg, 2009), for example.

2. Equipment (Rinsate)/Field Blanks

In accordance with **TMDL GM No. 09-2001**, blank collection for PCB analysis is at the discretion of the permit holder. However, if intermediary containers or an apparatus other than the actual shipping vessel are used, collection of equipment blanks is recommended. An example includes pumping and collection of PCB-free reagent grade laboratory water through automated compositing equipment prior to actual sample collection. This can be performed in the lab or preferably in the field, which has the advantage of also serving as a field blank. On occasion a blank referred to as a "field blank" is submitted along with effluent samples. For purposes of this guidance, equipment blanks differ from field blanks as they are collected instantaneously in the field through an automated sampler (or other piece of sampling equipment) whereas field blanks are collected in the field through an automated sampler but are collected as time-based aliquots.

A blank correction procedure is included as part of this guidance to reduce the potential impact from laboratory background and/or extraneous equipment/field contamination on tPCB results. The automated blank correction procedure occurs within the Excel "tPCB Auto-Calculation"

spreadsheet tool which is described in a "How To" supporting document found on DEQ's PCB TMDL website (see Section VI. for the link) with an example presented in Appendix B. However, the requirements specified below must be met prior to acceptance of blank data for use in the correction procedure.

- This section is not applicable in cases where results from an equipment blank or field blank have not been submitted with effluent PCB results.
- The equipment/field blank must be representative of the identical sampling event during which the effluent sample(s) were obtained.
- When results are available, decision rules in Appendix A.2. are used and the tPCB threshold of $\leq$ 500 pg/L must be met (threshold based on 90th percentile tPCB concentration of equipment/field blank dataset, DEQ 2012. PCB Access Database, Appendix D). Specific congener rules apply as well.
- Equipment Blanks
    - Although there are exceptions preventing the collection of effluent directly in the sample bottle, use of sampling equipment such as pumps and hoses, dip poles, and the like are considered optional. When used, equipment can provide an opportunity to introduce another possible source of contamination. As such, it is the responsibility of the sampler(s) to be aware of background contamination that may be associated with the equipment and associated blank water. This may require analysis of the blank source water (if obtained from a source other than the laboratory) and pre-verification that the equipment is cleaned properly, both by analysis using method 1668. The ability to conform to the requirements included in Appendix D of **TMDL GM No. 09-2001** should be established prior to actual field monitoring with equipment.
    - Equipment blanks provide an assessment on the cleanliness of the sampling apparatus. Data have shown a split of 30/70 percent respectively from equipment contamination and laboratory background (DEQ, 2012. PCB Access Database). Of note, the majority of these blanks (> 90%) have yielded results < 300 pg/L (DEQ, 2012. PCB Access Database).
- Field Blanks
    - The source of PCB contamination may have originated from the field, during sample transport or may be an artifact of laboratory background (i.e., approximately 80% of the tPCB can be attributed to laboratory background, not field contamination, once the field blank has been corrected for laboratory contamination; DEQ, 2012. PCB Access Database).
    - Field blanks may have been collected and analyzed at a facility.
        - For TMDL screening of selected municipal outfalls, field blanks are often collected concurrent with 24h composite effluent samples using automated samplers. The sampling apparatus (i.e., "equipment") as well as the wastewater are exposed to possible background PCB concentrations derived from the site or "field" over a 24 hour period.
- When equipment/field blank results are provided, and significant contamination is observed (defined as tPCB > 500 pg/L), a blank evaluation and assessment process should be performed.
    - If, for example, the "uncensored" tPCB effluent concentration is greater than the

equipment/field blank by at least one order of magnitude, the final "censored" effluent result should be minimally biased lower by excessive field/equipment contamination (i.e., extraneous contamination should not be relevant to the end result). An example includes a tPCB effluent concentration of 6,513 pg/L and a blank concentration of 787 pg/L. These results would be acceptable.

- If necessary, determine the impact of laboratory background contamination on the equipment/field blank using the correction procedure described in Appendix B (this would include treating the equipment/field blank in the Excel "tPCB Auto-Calculation" spreadsheet tool as an effluent sample to establish the impact of laboratory background). Once the original result is adjusted for laboratory background contamination, the amount of equipment/field blank contamination can be readily established and compared to representative equipment/field contribution (note: the guideline is 30**%** equipment contribution based on the available equipment blank results of which 70% can be attributed to laboratory background [DEQ, 2012. PCB Access Database], and **20%** field contribution based on the available field blank results).
    - For sample acceptance, professional judgment may be necessary in cases where the equipment contribution exceeds the 30% guideline within an equipment blank or 20% guideline within a field blank. Consideration may be given to the magnitude of the exceedence coupled with the determination of the origin of the contamination, if possible. The source of blank water is important to consider. If significant contamination appears to have originated from poor equipment cleaning, sample collection and/or handling (for equipment blanks), or from poor sample collection and/or handling (for field blanks), samples should not be accepted. If a sample is not accepted, the recommended follow-up action would be to resample and analyze using the approach outlined in **TMDL GM No. 09-2001**. An alternative would be to exclude the use of the equipment/field blanks in the correction procedure (see Appendix B, Examples 3. A. & B).

3. Miscellaneous QC Checks

The sections below include quality control items that should be checked to ensure the acceptance criteria of method 1668 have been met. For additional information and detail regarding acceptance criteria and corrective action when the analytical system is out of compliance with method 1668, please refer to Appendix D. of **TMDL GM No. 09-2001**.

Note: DEQ reserves the right to request additional data in those instances where PCB results have been submitted, reviewed and determined to be of questionable stature (e.g., OPR out of range, etc.).

a. Calibration Verification (VER)

Calibration verification is a routine requirement that the laboratory must perform at the beginning of each 12-hour shift.

- Continuing Calibration Verification (identified as "CCV") information should be spot checked within the "hardcopy" .pdf and the Excel .csv spreadsheet to determine

compliance with CCV requirements. Refer to Appendix D of **TMDL GM No. 09-2001** for acceptance criteria.

- PCB data should be appropriately qualified if the analytical process is determined to be out of compliance.

b. On-Going Precision and Recovery (OPR)

Serving as an analytical system check, OPR samples consist of reagent grade water that is spiked with known quantities of "native" PCB congeners and C^{13} labeled analogs and are analyzed exactly like field samples. The purpose is to ensure that laboratory performance is in control during the analysis of the associated batch of samples. It should be noted this quality control requirement can also be referred to as Lab Control Spike, Laboratory Fortified Blank (LFB), or QC check sample.

- OPR samples are run prior to the field samples so it is necessary these results be in the specified ranges.
  - See Appendix D of **TMDL GM No. 09-2001**; the method also allows laboratories to develop their own QC charts that provides a statement of accuracy for each congener.
- These QC data are found in the Excel .csv spreadsheet with the "OPR" identifier found in column G.
- It is the responsibility of the lab to ensure their system is in compliance. If one or more congeners do not meet the method specifications or fall outside the range in the individual lab's QC chart, the lab is required to take corrective action.
  - If any individual concentration falls outside the range, there was a problem with the extraction/analytical process. The problem should have been corrected and the OPR test repeated. If not, the data should be appropriately qualified.
- OPR Duplicate Analysis - Although not required by the method (and not required by DEQ), OPR duplicate analyses may be performed as a check on laboratory precision. Adhering to the EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (EPA, 2008), the results should yield a relative percent difference (RPD) of $\leq$ 20%.

c. PCB (Labeled Toxics/LOC/Window Defining Standard Spikes) Recoveries

Compounds enriched with carbon-13 to produce C^{13} labeled analogs are used as extraction, clean-up and injection standards. Extraction standards include twenty-seven compounds that bracket the first and last PCB within each homolog group. These labeled PCB compounds are injected into each field sample prior to extraction and provide a measure of the entire analytical process. Labeled clean-up standards (28L, 111L, and 178L) are spiked into each extract prior to clean-up to measure the efficiency of that process. Finally, labeled injection internal standards (9L, 52L, 101L, 138L, and 194L) are added to the extract prior to injection into the instrument for purposes of calibration.

- For sample integrity, the labeled analogs must fall within a specified range (See Table 6 in EPA Method 1668 Versions A, B, or C).
  - For each sample, these QC data are found in the Excel .csv file below PCB congeners 1-209 in columns AG to AH and the .pdf "hardcopy" document.
  - Method performance is questionable for that compound in the sample if it falls

outside the specified range. It is therefore the responsibility of the laboratory to follow the procedures outlined in the method (i.e., additional clean-up procedures, sample dilution, etc.) to ensure labeled analog recoveries are acceptable.

C. Total PCB (Calculation)

"Total PCB" (tPCB) is defined as the sum of remaining PCB congeners out of the possible 209 resulting from the blank correction method applied under the framework of this guidance. The "censored" data derived from this guidance for a given effluent will include "J" flagged congeners as well as those identified with "EMPC", when they have not been eliminated through the blank correction process (i.e., an effluent congener result that is qualified may be eliminated if there is a corresponding blank result). The rationale for inclusion of these qualified data is for a more conservative approach that is applicable to TMDL development. PCB congeners flagged with a "U" (or "ND") are not included in the total PCB value.

- For a given effluent result, blank correction and addition of PCB congeners is most easily performed in the Excel "tPCB Auto-Calculation" spreadsheet tool (see link identified in Section VI. for the "How To" supporting document and/or Appendix B).
- Of the data qualifiers presented in Appendix C, PCB congener data are most often reported with the following flags e.g., C, B, J, U or ND, EMPC.
    - The relevance of the "B" flag, as reported by the laboratory, is eliminated since the blank correction procedure is used to correct effluent results when compared to available blanks. However, PCB congeners that are eliminated due to censoring will be flagged with a "B" in DEQ's "uncensored" database
- Miscellaneous flags:
    - When data flags "D", "NR", or" X" are used, ensure an adequate explanation by the laboratory has been provided in the .pdf hardcopy regarding the qualification.
    - The guideline presented in III.B.3.c. above is applicable when data qualifier "V" is used.
    - Data qualified with an "E" are not acceptable.
- The final "censored" tPCB concentrations obtained from effluents or regulated stormwater samples will be used for calculation of PCB loadings for direct comparison with Waste Load Allocations (WLA). Multiple "censored" results will be used to derive the final tPCB concentration from which a mean concentration is derived.
    - "Censored" tPCB results obtained from effluents that were collected as split (duplicate) samples should be averaged for a final concentration of the sample event that they represent.

IV. References

Environmental Protection Agency (EPA). 1999a. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, EPA-821-R-00-002, December 1999. *(with corrections and changes through August 20, 2003)*

Environmental Protection Agency (EPA). 2007. Solutions to Analytical Chemistry Problems with Clean Water Act Methods. EPA 821-R-07-002. March, 2007.

Environmental Protection Agency (EPA). 2008. Method 1668B, Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. EPA-821-R-08-020, November 2008.

Environmental Protection Agency (EPA). 2008. U.S. EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review. EPA-540-R-06-01. June 2008.

Environmental Protection Agency (EPA). 2010. Method 1668C, Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. EPA-820-R-10-005, April 2010.

Rodenberg, L. A., J. Guo, S. Du, G. J. Cavallo. 2010. Evidence for Unique and Ubiquitous Environmental Sources of 3,3'-Dichlorobiphenyl (PCB 11). Environ. Sci. Technol. 2010. 44, 2816-2821.

Virginia Department of Environmental Quality (DEQ). 2009. TMDL Guidance Memo No. 09-2001. Guidance for monitoring of point sources for TMDL development using low-level PCB method 1668. http://www.deq.virginia.gov/Programs/Water/WaterQualityInformationTMDLs/TMDL/PCBTMDLs.aspx.

Virginia Department of Environmental Quality (DEQ). 2010. 9 VAC 25-260 – Virginia Water Quality Standards. February 2010. http://www.deq.virginia.gov/Programs/Water/WaterQualityInformationTMDLs/WaterQualityStandards.aspx.

Virginia Department of Environmental Quality (DEQ). 2012. Polychlorinated Biphenyl (PCB) Access Database.

V. Appendices

A.1. Method Blank Contamination Rules
A.2. Field/Equipment Blank Contamination Rules
B. Method Blank Correction Procedure
C. Data Qualifiers for PCB Analytical Results
D. Supporting data used to establish percentiles for rinsate and field blank decision rules.

VI. "How To" (Supporting) Documents*

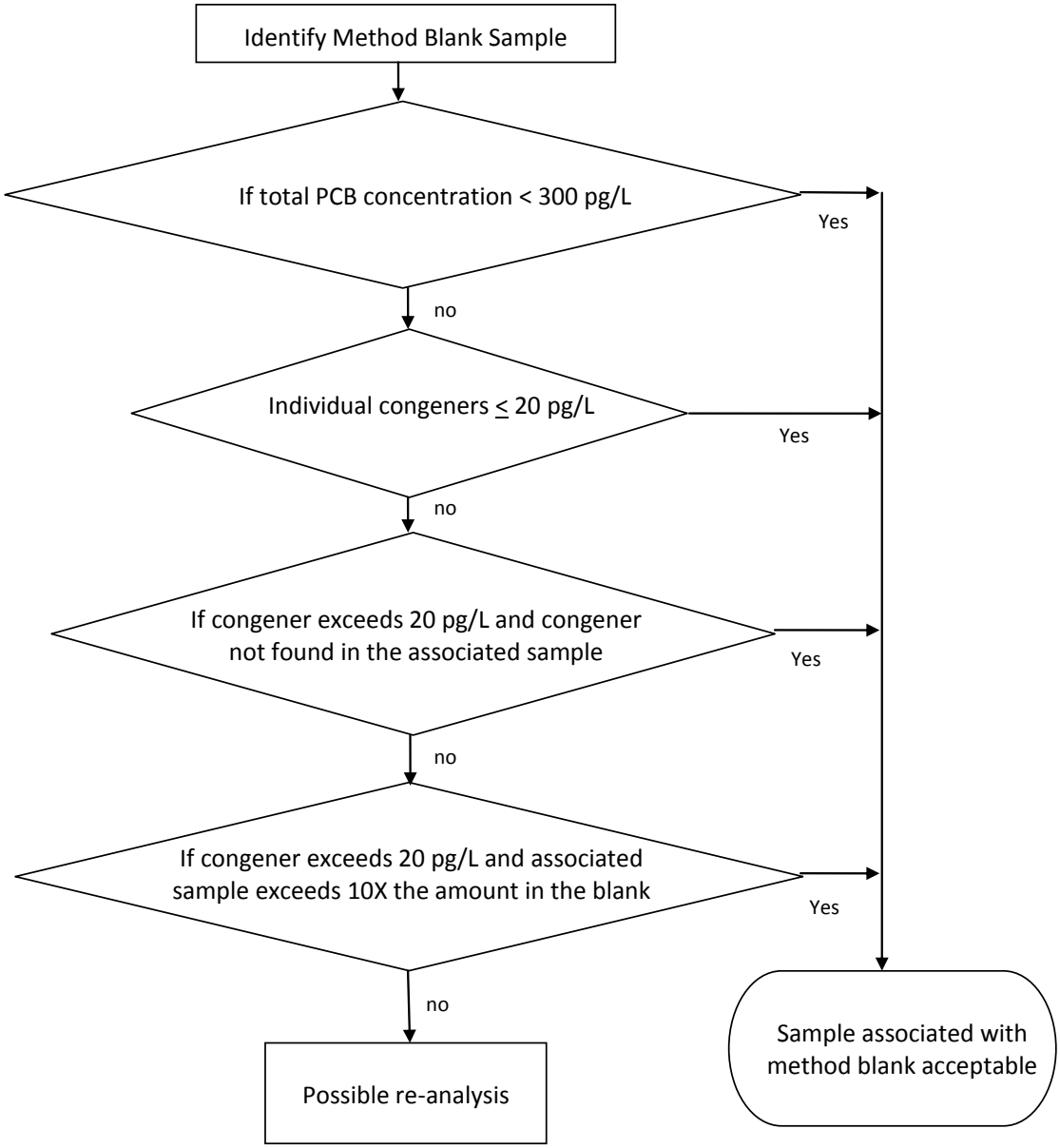
1. "How To" Review, Blank Correct and Calculate Total PCB
2. Excel "tPCB Auto-Calculation" spreadsheet tool (An interactive Excel tool for adjusting tPCB concentrations)

* http://www.deq.state.va.us/Programs/Water/WaterQualityInformationTMDLs/TMDL/PCBTMDLs.aspx

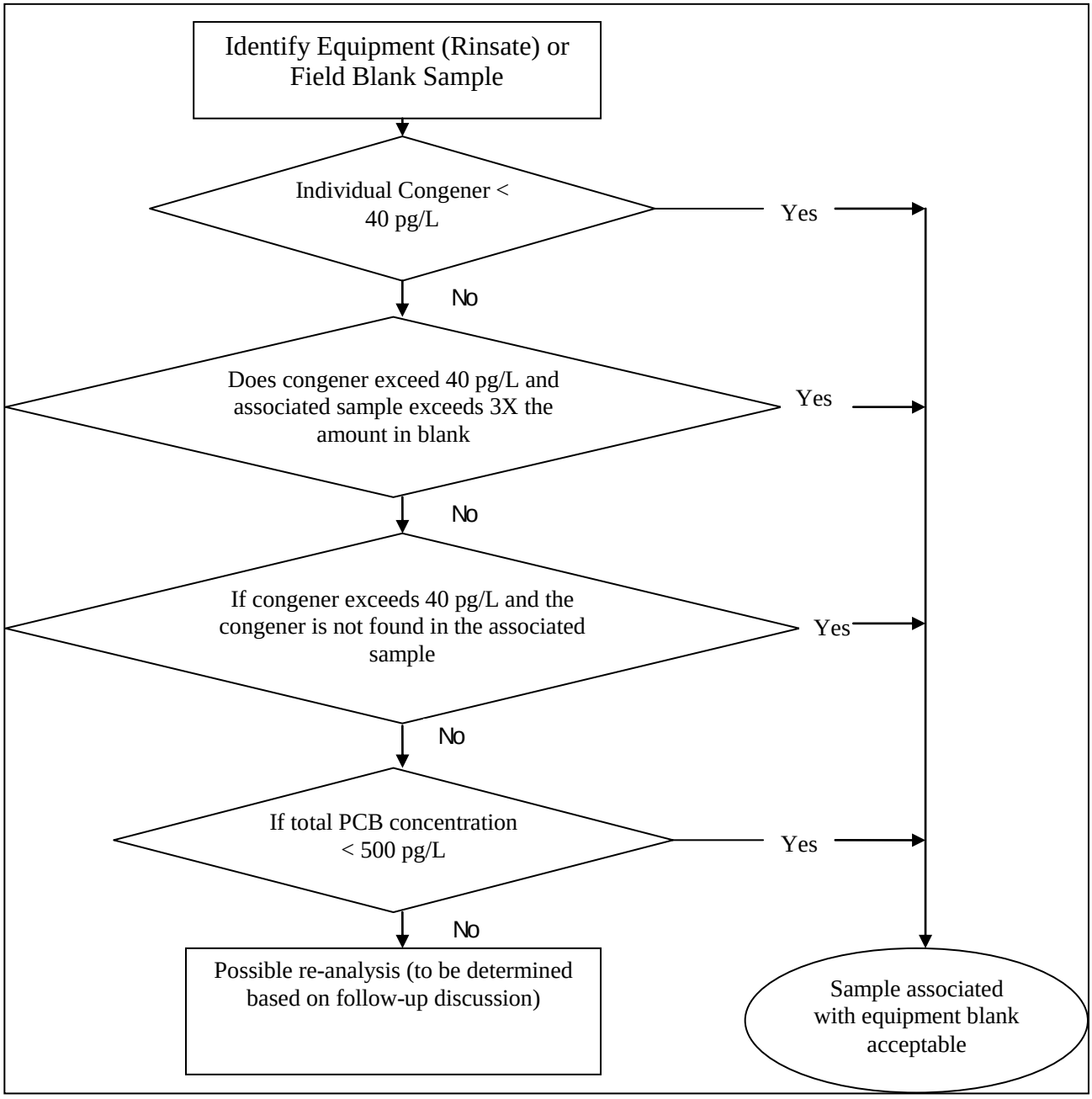
Appendix A

A.1.

Method Blank Contamination Rules



Equipment/Field Blank Contamination Decision Rules
A.2.



Appendix B (Method Blank Correction Procedure)

DEQ acknowledges that simple exposure during sample collection in the field or from laboratory background carryover during analysis are prospective PCBs sources that can impact results generated using ultra low level EPA Method 1668. This is magnified by the fact that the method allows an analytical chemist to evaluate a water matrix at the low pg/L level on a PCB congener basis. In order to minimize or eliminate the contribution of extraneous laboratory background or field exposure contamination in a final tPCB sample concentration, DEQ recommends samples be adjusted using a correction factor by integrating both method blanks and field (or rinsate) blanks into the process. Given that the method targets and produces results from multiple analytes, the PCB correction procedure is implemented on a congener basis as opposed to subtracting a total blank concentration from the final tPCB effluent concentration.

The recommended approach will only apply where affected PCB congeners are detected in the method blank, a field or rinsate blank, and corresponding congeners are detected in associated samples from a given batch or group of samples collected during the same sampling event (i.e., effluent sample(s) and associated equipment/field blanks) . The foundation of this approach stems from *EPA's Region III Interim Guidelines for the Validation of Data Generated Using Method 1668 PCB Congener Data* (EPA 2004) with supporting rationale contained in EPA guidance *Solutions to Analytical Chemistry Problems with Clean Water Act Methods* (EPA, 2007). There is recognition that when a contaminant is found in a sample at a concentration that is at least 5X that of the blank, the contaminant is most likely present in the sample and the result is considered at the upper limit of the true concentration. In this instance, no correction is made. The rationale for correcting results when the sample concentration is < 5X that of the blank concentration is due to the inability to judge whether the contamination in the sample originated from the laboratory or field. DEQ believes the more conservative 5X approach offers greater protection to the fish consumption use. Of note, additional support was provided by an EPA chemist (personal communication with Stevie Wilding, 1668 Chemist, US EPA Fort Meade, 2011) in the use of the recommended approach. The stepwise correction method is applied as follows:

- In the Excel "tPCB Auto-Calculation" spreadsheet tool (see DEQ's PCB TMDL website for the interactive tool and "How To" supporting document: http://www.deq.virginia.gov/Programs/Water/WaterQualityInformationTMDLs/TMDL/PCBTMDLs.aspx), the method blank and the rinsate or field blank (if available) results are aligned congener by congener with the associated sample result(s).
- The method blank and the rinsate or field blank congener concentrations are multiplied by 5 and the product is compared with the corresponding effluent sample congener result. The spreadsheet automatically establishes the following:
    - If a PCB congener is in a blank, but not present in the sample there is no adjustment.
    - If a PCB congener is in a blank (method and rinsate or field) and in the associated sample at a concentration < 5X that of the highest applicable blank, the congener concentration from the sample is set to "0".
        - Setting the congener concentration to "0" is recommended for two reasons: 1) it would be inappropriate to generate a negative concentration, and 2) the detected congeners are at very low concentrations.
    - If a PCB congener is in a sample at a concentration $\geq$ 5X that of the highest blank concentration (method and field or rinsate), the sample congener concentration is retained as reported by the laboratory and included in the tPCB calculation.

- Prior to storing the raw, "uncensored" results in a database, PCB congeners in samples identified as adjusted will be qualified with a "B".

- The correction procedures included in this Appendix are mainly used when the tPCB concentration for the applicable blanks (method and rinsate or field) are below the maximum allowed for that blank type (i.e., 300 pg/L for method and 500 pg/L for rinsate or field). Refer to Appendix A or Sections III.B.1. and 2.of this guidance, particularly for special circumstances.
- By following the steps described in the "How To" supporting document for the Excel "tPCB Auto-Calculation" spreadsheet tool, the blank correction procedure is automatically performed once the raw data have been imported to the "tPCB Auto-Calculation" spreadsheet. The spreadsheet also produces final tPCB calculation of "uncensored" and "censored" (adjusted) concentrations.

Example 1. Overview with an Example of the PCB Method Blank Correction Approach
The information presented below provides a simplistic illustration as to how PCB data generated using EPA Method 1668 can be corrected using field and laboratory background blank data. Automatic calculations are included in the "tPCB Auto-Calculation" spreadsheet tool presented on DEQ's PCB TMDL website (see link above).

Step 1: Data in columns B & D multiplied by 5 = Result in Columns C & E, respectively. Note each congener is treated individually.

- The highest adjusted result in column F is carried forward to column B in table 2.b. below.

Table 1.a. Example of how PCB blank concentrations are adjusted (5X) and selected for blank correction as performed in the "tPCB Auto-Calculation".

A	B	C	D	E	F
IUPAC_PCB_#	Original Method Blank Conc_Found (pg/L)	Method Blank Adj conc (X5) pg/L	Original Associated Field or Rinsate Blank (pg/L)	Associated Field or Rinsate Blank (X5) pg/L	Highest Conc. of MB or Field/Rinsate Blank Selected (pg/L)
1	0	0	2.96	14.8	14.8
2	0	0	0	0	0
3	0	0	0	0	0
4	4.16	20.8	4.28	21.4	21.4
5	0	0	0	0	0
6	1.5	7.5	2.12	10.6	10.6
7	0	0	0.766	3.83	3.83
8	6.92	34.6	7.31	36.55	36.55
9	1.01	5.05	0.86	4.3	5.05
10	0	0	0	0	0
11	10.6	53	51.4	257	257
12	1.05	5.25	0	0	5.25
13	0	0	0	0	0
14	0	0	0	0	0
15	2.26	11.3	2.48	12.4	12.4
16	3.1	15.5	0	0	15.5
17	2.94	14.7	0	0	14.7
18	5.33	26.65	6.11	30.55	30.55
19	0	0	0	0	0
20	5.58	27.9	24.5	122.5	122.5

Note: For simplicity, only the first 20 PCB congeners are presented (altogether there are 209).

Table 1.b. Definitions for information contained in Table 1.a. above.

Column A	IUPAC PCB Congener number
Column B	Original PCB congener concentration in method blank
Column C	PCB Method Blank Conc. x 5
Column D	Original PCB congener concentration in field or rinsate blank
Column E	PCB Field or Rinsate Blank Conc. x 5
Column F	Higher concentration of the 2 blank types that will be used to compare with the actual sample concentration

Step 2: Each PCB result in column C is compared individually with the corresponding method blank or field/rinsate datum in column B (recall the original blank data were multiplied by 5 –see table 1.a. above). To correct the data using the 5X approach, the following rules are applied:

- If column C result < column B result, the data point is set to "0" – refer to column D (e.g., PCB 1).
- If column C result > column B result , the data point is retained – refer to column D (e.g., PCB 4).
- If column B contains a "0", the result in column C is maintained at the original level – refer to column D (e.g., PCB 10 or 19).

Table 2.a. The example includes the final outcome once the correction procedure has been completed. Ultimately the complete suite of 209 congeners in column D would be summed for a final tPCB concentration.

A	B	C	D
IUPAC_PCB_#	Highest Conc. of MB or Field/Rinsate Blank Selected (pg/L)	**Unadjusted** Sample 1 Original Conc. Found (pg/L)	**Adjusted** Sample 1 Adjusted Concentration
1	14.8	2.69	0
2	0	0	0
3	0	0	0
4	21.4	42.36	42.36
5	0	0	0
6	10.6	1.89	0
7	3.83	0.671	0
8	36.55	9.22	0
9	5.05	0.963	0
10	0	0.493	0.493
11	257	26	0
12	5.25	1.85	0
13	0	0	0
14	0	0	0
15	12.4	6.08	0
16	15.5	5.83	0
17	14.7	5.49	0
18	30.55	11.8	0
19	0	2.07	2.07
20	122.5	18.8	0

Note: For simplicity, only the first 20 PCB congeners are presented (altogether there are 209).

Table 2.b. Definitions for information contained in Table 2.a. above.

Column A	IUPAC PCB Congener number
Column B	Higher concentration of the 2 blank types that will be used to compare with the actual sample concentration – taken from col. F in table 1.a. above
Column C	Unadjusted (uncensored) effluent concentration
Column D	Adjusted or "censored" effluent concentration

Example 2. Exceedence of a Method Blank Decision Rule

A.

Unadjusted Result	Adjusted Result	Method Blank
1,758 pg/L	**1,371 pg/L**	**350.3 pg/L**
Explanation – While the method blank exceeded the decision rule, the impact to the censored result was minimal. Also of note, the method blank did contain PCB 44 at an excessive level (76.5 pg/L or 22% of tota concentration); however, the concentration of PCB 44 in the sample was slightly less than that of the MB and was eliminated by the blank correction process. By weighting the available information, the sample is acceptable.		

B.

Unadjusted Result	Adjusted Result	Method Blank
847 pg/L	**138 pg/L**	**332 pg/L**
Explanation –The method blank exceeded the decision rule and the impact to the censored result appears excessive. In this instance it is unknown if the unadjusted concentration is due to actual contamination in the effluent or has been contaminated by poor laboratory practices. This is an example where the sample should not be accepted.		

Example 3. Exceedence of Equipment/Field Blank Decision Rule

A.

Unadjusted Result	Adjusted Result	Equipment/Field Blank	Method Blank
2,080 pg/L	**1,208 pg/L**	**679 pg/L**	**8 pg/L**
Explanation – The excessive equipment/field blank result does bring into question the sampling approach at this site. The cleanliness of the equipment and source of the blank water can also be brought into question. With the low MB, extraneous contamination has come from a source other than the laboratory. All available results should be compared with this result prior to making a final decision for acceptance.			

B.

Unadjusted Result	Adjusted Result	Equipment/Field Blank	Method Blank
1,301 pg/L	**11.6 pg/L**	**752 pg/L**	**76 pg/L**
Explanation – The equipment/field blank exceeds the decision rule of 500 pg/L. Three PCB congeners also do not meet the decision rules. As such, the quality of the blank is highly questionable. In this case, the sample should be recollected and analyzed or should not be used in the blank correction procedure.			

References

Environmental Protection Agency (EPA). 2004. EPA's Region III Interim Guidelines for the Validation of Data Generated Using Method 1668 PCB Congener Data. April 2004.

Environmental Protection Agency (EPA). 2007. Solutions to Analytical Chemistry Problems with Clean Water Act Methods. EPA 821-R-07-002. March, 2007.

Environmental Protection Agency (EPA). 2011. Personal communication with Stevie Wilding. EPA Region III, Fort Meade, Method 1668 Chemist.

Appendix C

Data Qualifiers for PCB Analytical Results

Qualifier Flag		Description
J	-----	The reported result is an estimate. The value is less than the minimum calibration level but greater than the estimated detection limit (EDL).
U/ND	------	The analyte was not detected in the sample at the estimated detection limit (EDL).
E	------	Exceeds calibration range.
D	------	Dilution data. Result was obtained from the analysis of a dilution.
B	------	Analyte found in sample and associated blank.
C	------	Co-eluting congener. The PCB concentration is reported with the first of two or more co-eluting congeners and subsequent congeners are referred back to the first and qualified with "Cxx".
Cxx	------	Co-elutes with the indicated congener and data are reported under the lowest IUPAC congener. 'xx' denotes the IUPAC number with the lowest numerical designated congener.
NR	------	Analyte not reported because of problems in sample preparation or analysis.
V	------	Surrogate recovery is not within method control limits.
X	------	Results from reinjection/repeat/recolumn data.
EMPC	------	Estimated maximum possible concentration. Indicates that a peak is detected but did not meet all the method required criteria (confirmation ions present but are not within 25% of the ion ratio criteria).

Appendix D

(Supporting data used to establish percentiles for rinsate and field blank decision rules)

Percentiles Derived from Rinsate Blank tPCB data (pg/L)					
5th	10th	25th	50th	90th	95th
12.9	32.0	63.5	168.4	426.5	683.2

Table 1. Supporting Rinsate Blank Data

Sample No.	Rinsate Blank Total PCB (pg/L)
1	729.30
2	135.50
3	1,247.55
4	266.00
5	178.98
6	179.05
7	545.08
8	260.00
9	150.73
10	32.94
11	31.02
12	1.18
13	287.93
14	163.42
15	55.63
16	72.16
17	307.92
18	210.11
19	173.48
20	275.80
21	192.56
22	78.30
23	6.91
24	59.48
25	61.41
26	69.59

Data Source: DEQ's PCB Access Database (as of June 2012)

Percentiles Derived from Field Blank tPCB Data (pg/L)

5th	10th	25th	50th	90th	95th
64.2	149.6	178.3	230.2	495.7	708.8

Table 2. Supporting Field Blank Data

Sample No.	Field Blank tPCB (pg/L)	Sample No.	Field Blank tPCB (pg/L)
1	1,037.0	41	229.0
2	823.0	42	228.5
3	751.8	43	227.9
4	742.0	44	223.4
5	707.0	45	219.2
6	686.8	46	219.0
7	554.0	47	218.4
8	510.0	48	214.6
9	494.1	49	210.0
10	458.0	50	197.0
11	434.0	51	193.0
12	390.0	52	191.5
13	369.9	53	191.4
14	353.0	54	190.5
15	330.9	55	186.3
16	329.8	56	184.0
17	327.8	57	182.2
18	325.1	58	182.2
19	308.7	59	181.2
20	305.0	60	179.6
21	303.9	61	174.5
22	303.0	62	174.0
23	296.0	63	172.6
24	283.5	64	170.8
25	274.6	65	169.8
26	267.8	66	168.6
27	260.6	67	167.9
28	256.4	68	165.6
29	254.2	69	162.6
30	252.5	70	161.7
31	250.0	71	152.5
32	244.1	72	151.9
33	242.0	73	128.8
34	238.8	74	105.4
35	236.6	75	80.7
36	236.5	76	64.7
37	235.7	77	55.3
38	235.2	78	44.6
39	232.0	79	42.0
40	231.4	80	22.7

Data Source: DEQ's PCB Access Database (as of June 2012)