DELAWARE RIVER ESTUARY STAGE 2 PCB TMDL
Polychlorinated Biphenyls - EPA Method 1668A
Project Quality Control Requirements

INTRODUCTION:

This document provides a summary of the analysis quality control requirements for the Polychlorinated Biphenyls (PCBs) analysis by EPA Method 1668A for the Delaware River Estuary Stage 2 PCB TMDL. Additional information on sampling and analytical requirements can be found on DRBC's website (http://www.state.nj.us/drbc/PCB_info.htm). This summary of quality control requirements is based on EPA Method 1668A, (Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, EPA-821-R-00-002, December 1999) with project specific modifications to meet the Data Quality Objectives (DQOs) for the Stage 2 PCB TMDL. This QC summary primarily addresses aqueous analysis associated with Point Source Discharge samples. Revision may be necessary in the future to address additional matrices and DQOs. EPA Method 1668A is a Performance Based method. Project specific requirements stated in this QC summary must be met to ensure consistency amongst participants in the project and cannot be modified. Questions or concerns with the QC requirements should be discussed with the Delaware River Basin Commission prior to implementing any changes.

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Sample Collection, Preservation, Storage and Holding Times	Samples must be collected in amber glass (or aluminum foil for tissue samples) following conventional sampling practices. • A two (2) liter (L) aqueous sample size will be collected for this project. Two, 2-L amber glass containers for aqueous sample collection should originate from the analysis laboratory and the container quality be verified for cleanliness. Documentation showing traceability and cleanliness of the containers must be maintained at the laboratory. A 2-L sample and 2-L replicate sample will be collected per location. The replicate is available in the event reextraction and reanalysis due to failing QC is necessary. • The laboratory will supply reagent grade water for use in collection of field blanks. A sufficient quantity of water should be provided to collect a 2-L field blank.	• Samples should be stored at <6°C until delivery to the laboratory. • If stored in the dark at <6°C aqueous samples may be stored for up to one year. (If residual chlorine is present, 80 mg of thiosulfate per liter of water should be added.) • If stored in the dark at <-10°C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year. • If stored in the dark at <-10°C, extracts may be stored for up to one year.	• There are no demonstrated holding times for CBs. • Resample if able or deemed necessary for project DQOs. Otherwise, qualify results based on professional judgment if the potential for a low bias exists due to excessive holding times.

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Aqueous Sample Extraction and Cleanup	Extraction and cleanup of the sample must use one of the techniques described in EPA Method 1668A. • The entire contents of the 2-L sample volume must be extracted (do not separate solids if greater than 1% as described in Section 11.5 of the Method 1668A- extract the sample as is). The exact volume extracted must be documented and used in calculation of the sample concentration. All spike additions must be added to the 2-L bottle containing the sample prior to extraction. • Laboratories may purchase glassware/extraction equipment to accommodate the larger 2-L sample volume (Note: the method typically extracts 1-L of aqueous sample). Alternatively, the laboratory may serially extract the 2-L volume in the same device one-liter at a time or extract two 1-L portions simultaneously in two different apparatus set-ups. Combine the solvent if serial or sequential extractions were performed prior to extract concentration and cleanup. • Sample extracts will be concentrated to a final volume of 20 ul.	• Method blanks, OPR samples, field blanks or other QC samples must be processed identically to the samples including the same extract cleanups.	• Contact the client for guidance if the sample size or matrix does not allow these conditions to be met.
Retention Time Calibration	• This project requires the use of the SPB-octyl column. • Each diluted individual congener solution (Section 7.10.2.1.2 of the method) is injected to establish the beginning and ending retention times for the scan descriptions in Table 7. • The diluted combined 209-congener solution is injected (Section 7.10.2.2 of the method).	• The absolute retention time (RT) of CB 209 must exceed 55 minutes on the SPB-octyl column. • The RT and relative RT (RRT) for all congeners must be within the windows in Table 2 of the method and the column performance specifications in Sections 6.9.1-6.9.1.2 of the method must be met.	• If the absolute RT of CB 209 does not meet criterion, the GC temperature must be adjusted and the test repeated until the minimum RT criterion is met. • Adjust chromatographic conditions and scan descriptors until all criteria are met. NOTE: Laboratories with newer injection technology such as Electronic Pressure Control (EPC) may render the RT requirement for CB 209 obsolete. The RT and RRT for all congeners and coeluting congeners must be documented at the same frequency as stated in this section for systems using EPC.

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Mass Spectrometer Resolution	• The instrument is tuned using perfluorokerosene (PFK, or other reference material). • Static resolving power checks must be performed at the beginning and at the end of each shift.	• A minimum resolving power of 10,000 for a significant PFK fragment in the range of m/z 300-350. The deviation between the exact m/z and the theoretical m/z (Table 7 of the method) for each exact m/z monitored must be less than 5 ppm.	• Any problems must be corrected before analyses can proceed. • Any samples in the previous shift that may be affected by poor resolution must be reanalyzed.
Ion abundance ratios and signal-to-noise (S/N) ratios	The low calibration standard concentration for this project must be 0.5 ng/ml. A 1 or 2 µL aliquot of the 0.5ng/ml calibration solution is injected.	• All CBs and labeled compounds in the 0.5 ng/ml standard must be within the QC limits in Table 8 of the method for their respective ion abundance ratio. • The peaks representing the CBs and the labeled compounds in the 0.5 ng/ml calibration standard must have S/N ≥ 10.	The mass spectrometer must be adjusted and this test repeated until the m/z ratios fall within the limits specified If the adjustment alters the resolution of the mass spectrometer, resolution must be verified prior to the repeat of the test.
Initial Calibration	• Established initially and when calibration verification fails criteria. • Calibration by isotope dilution is performed at a minimum of 5 (6 may be used) concentration levels for each of the toxic/level of chlorination (LOC) congeners (refer to Table 3 of the method). • The low calibration standard concentration for this project must be 0.5 ng/ml. • Calibration by internal standard is performed for each native congener for which a labeled congener is not available, the labeled toxics/LOC/window-defining congeners, and the labeled cleanup congeners. For the native congeners, calibration is performed at a single point using the CS-3 standard. For the labeled congeners, calibration is performed using the data from the 5 (or 6) points in the calibration of the toxics/LOC congeners.	%RSD≤20% among relative response (RR) for each native toxic/LOC congener in order to use the average RR (as calculated in Section 10.4.2 of the method). Otherwise, the complete calibration curve for that congener must be used over the calibration range.	• Reanalyze the initial calibration curve and/or evaluate/correct instrument malfunction to obtain initial calibration that meets criteria. • Sample results above highest standard concentration require dilution and reanalysis. In addition, the concentration of the labeled injection internal standard must be adjusted to 100 pg/µL.

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Calibration Verification	• Performed at the beginning of each 12-hour shift during which analyses are performed. • The CS-3 calibration verification (VER) standard and the diluted combined 209 congener solution are analyzed.	• The m/z abundance ratios for all congeners must be within the limits in Table 8. • The GC peak representing each native CB and labeled compound in the VER solution must be present with a S/N ratio of at least 10. • The concentration of each compound must be within the limit in Table 6 of the method.	• Adjust system, if necessary, and recalibrate. Criteria must be met before sample, blank, IPR, and OPR analysis may begin. • If the adjustment alters the resolution of the mass spectrometer, resolution must be verified prior to the repeat of the verification test.
Retention Times	• This project requires the use of the SPB-octyl column. • Retention times are verified using the calibration verification analysis. • Coeluting congeners must be reported according to the scheme defined in the Qualifier Codes for the project (http://www.state.nj.us/drbc/PCB-DataQualFlags.pdf)	• The absolute RTs of the labeled toxics/LOC/window-defining standard congeners in the verification test must be within ±15 seconds of the respective RTs in the calibration. • The RRTs of the native CBs and labeled compounds in the verification test must be within their respective RRT limits in Table 2 of the method.	Adjust system or replace GC column and repeat the verification test or recalibrate. (See previous note concerning GC systems with EPC.)
GC Resolution and minimum analysis time	As part of calibration verification, the diluted combined 209-congener solution is analyzed.	The resolution and minimum analysis time specifications in Sections 6.9.1.1.2 and 6.9.1.1.1 of the method must be met for the SPB-octyl column.	Adjust GC analysis conditions until the specifications are met, or the column must be replaced and the calibration verification tests repeated or the system recalibrated. (See previous note concerning GC systems with EPC.)
Ongoing precision and recovery (OPR)	• Prepared with each batch of samples (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples). • Analyzed prior the analysis of samples from the same batch.	The recoveries of the toxic/LOC CBs must be within the OPR limits given in Table 6 of the method.	If any individual concentration falls outside of the range, the extraction/concentration processes are not being performed properly. The problem must be corrected and the sample batch must be reprepared, extracted, and cleaned up and the OPR test repeated.

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Method Blank	• Prepared with each batch of samples (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples). • Analyzed prior the analysis of samples from the same batch immediately following the analysis of the OPR. • The reference matrix must simulate, as closely as possible, the sample matrix under test. • When a reference matrix that simulates the sample matrix under test is not available, reagent water can be used to simulate water samples; playground sand or white quartz sand can be used to simulate soils; filter paper can be used to simulate papers and similar materials; and corn oil can be used to simulate tissues.	• Method blanks must meet the decision rules specified on DRBC's web site: http://www.state.nj.us/drbc/PCB-MethodBlankRules.pdf	If the method blank acceptance criteria is exceeded, analysis of samples must be halted until the sample batch is re-extracted (using the replicate sample) and the extracts re-analyzed, and the blank associated with the sample batch shows no evidence of contamination above the acceptance criteria. All samples must be associated with an acceptable method blank before the results for those samples may be reported or the specific conditions preventing the ability to achieve the method blank acceptance criteria discussed with the client.
Labeled Toxics/LOC/window-defining standard spike	All samples must be spiked with labeled compounds to monitor method performance. The spiking of the extraction standards must occur prior to extracting the sample. The addition of the cleanup standards must occur before the fractionation, while the addition of the injection standards is conducted prior the GC/MS analysis.	The recovery of each labeled compound must be within the limits in Table 6.	If any labeled compound falls outside of limits, the method performance is unacceptable for that compound in that sample. Additional cleanup procedures must be employed to attempt to bring the recovery within the normal range. If the recovery cannot be brought within the normal range after all cleanup procedures have been employed, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are analyzed.

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Qualitative/Quantitative Issues	Identification of a CB or labeled compound in a standard, blank or sample occurs when must meet all criteria are meet. • Report results for all 209 PCB congeners. The Qualifier Codes provides a mechanism to report coeluting congeners (http://www.state.nj.us/drbc/PCB-DataQualFlags.pdf). • Report results according to the hardcopy data package deliverable and Electronic Data Deliverable (EDD) specifications posted on DRBC's web site (http://www.state.nj.us/drbc/PCB_info.htm).	• The signals for the two exact m/z's in Table 7 must be present and must maximize within the same two scans. • The S/N for the GC peak at each exact m/z must be ≥ 2.5 for each CB detected in a sample extract, and ≥ 10 for all CBs in the calibration and verification standards. • The ratio of the integrated areas of the two exact m/z's specified in Table 7 must be within the limit in Table 8, or within ±15% of the ratio in the midpoint (CS3) calibration or calibration verification, whichever is most recent. • The RRT of the peak for a CB must be within the RRT QC limits specified in Table 2, or if an alternate column or column type is employed, within its respective RRT QC limits for the alternate column or column system. • Because of congener overlap and the potential for interfering substances, it is possible that all of the identification criteria above may not be met. It is also possible that loss of one or more chlorines from a highly chlorinated congener may inflate or produce a less-chlorinated congener that elutes at the same retention time. If identification is ambiguous, an experienced spectrometrist must determine the presence or absence of the congener.	• Congeners that are not detected are to be reported to the sample specific Estimated Detection Limit (EDL). EDLs must be calculated as described on DRBC's web site (http://www.state.nj.us/drbc/PCB-EDL.pdf) • If a peak does not meet the qualitative identification criteria (most commonly the ion abundance ratio criteria), the quantitative result for that congener must be reported as an Estimated Maximum Possible Concentration (EMPC).