SOP NO. HW- 46
REVISION 1
September 2008

USEPA REGION II DATA VALIDATION

STANDARD OPERATING PROCEDURE for EPA METHOD 1668, REVISION A, AUGUST 2003 "Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS"

and

STATEMENT OF WORK for ANALYSIS of CHLORINATED BIPHENYL (CB) CONGENERS, CBC01.0, May 2005

PREPARED BY: George Karras DATE: 9/17/08
George Karras, Chemist, Hazardous Waste Support Section

PREPARED BY: Russell Arnone DATE: 10/14/08
Russell Arnone, Chemist, Hazardous Waste Support Section

CONCURRED BY: Linda M. Mauel DATE: 10/16/08
Linda Mauel, Chief, Hazardous Waste Support Section

APPROVED BY: Robert Runyon DATE: 10/16/08
Robert Runyon, Chief, Hazardous Waste Support Branch

ANNUAL REVIEW

APPROVED BY: Russell Arnone DATE: 08/11/09
Name

APPROVED BY: _____ DATE: _____
Name

TABLE OF CONTENTS

Optional Quality Control and Assurance Requirements for Validation

I.0 Scope and Application

1.1 SOW CB01.0 (Reference 2) and Method 1668 Revision A, Reference 1 are for the determination of chlorinated biphenyl congeners (CBs) in water, soil, sediment, tissue and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

1.1.1 Twelve (12) polychlorinated biphenyls (PCBs) in Table 1, Method 1668A designated as toxic by the World Health Organization (WHO) plus the remaining 197 CBs, approximately 125 of which are resolved adequately on a SP octyl gas chromatographic column as individual congeners. The remaining approximately 70 congeners are determined as mixtures of isomers (co-elution).

1.1.2 The 12 CBs and the earliest and latest eluted congener at each level of chlorination (LOC CB) are determined by the isotope dilution quantitation technique; the remaining congeners are determined by the internal standard quantitation technique.

1.1.3 The PCB toxicity equivalent (TEQ) for the toxics in a sample can be calculated using the toxicity equivalency factors (TEFs) (Reference 3).

1.1.4 A second column option (DB-1) should be used to resolve two toxic PCB congeners with IUPAC numbers 156 and 157 that are not resolved on the SPB-octyl column and for the resolution of other congeners. Procedure can be found in Appendix A/Method 1668A.

1.2 The detection and quantitation levels in this method are usually dependent on the level of interferences and laboratory background levels rather than instrument limitations. The estimated minimum levels of quantitation (EMLs) in Table 2/Method 1668A are the levels at which the CBs can be determined with laboratory contamination present.

1.3 This method is "performance-based." The laboratory is permitted to modify the method to overcome interferences or lower the cost of analysis, provided that all performance criteria are met as described in section 9.1.2 of the method 1668A.

2.0 Applicability

The attached Standard Operating Procedure (SOP)/Checklist is applicable to polychlorinated-biphenyl data obtained using SOW/CB01.0 and EPA Method **1668A**, Chlorinated Biphenyl Congeners (CBs) by isotope Dilution using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), **August 20, 2003.** Its scope is to facilitate the data validation process of the data reported by the contracting laboratory and to ensure that the data is being reviewed in a uniform manner. This SOP is based upon the quality control and quality assurance requirements specified in Method **1668A and SOW CB01.0.**

3.0 **Responsibilities/Scope**

3.1 The reviewer must be knowledgeable of the analytical method and its QC Criteria.

3.2 The reviewer must complete the following:

3.2.1 Data Assessment Checklist - The data reviewer must read each item carefully and must check "yes" if there is compliance, "no" if there is non compliance and "N/A" if the question is not applicable to the data.

3.2.2 Data Assessment Narrative - The data reviewer must present professional judgement and must express concerns and comments on the validity of the overall data package. The reviewer must explain the reasons for rejecting and/or qualifying the data. Example of Data Assessment format is provided in Attachment A.

3.2.3 **Communication** Record Log - All **communication must be in writing, and it** must be documented on the **Communication** Record Log Sheet. A photocopy of the **Communication** Record Log is attached to the Data Assessment package.

3.2.4 Paperwork - Upon completion of the review the following are to be maintained with the data package and returned to the authorized person :

a. completed data assessment checklist and narrative (original)
b. Two copies of the data assessment narrative
c. **Communication** record Log (original and copy)

3.3 Rejection of Data - All values determined to be unacceptable on the Analysis Data Sheet (Form I) must be flagged with an "R". The qualifier "R" means that due to significant QA/QC problems the analysis is invalid and it provides no information as to whether the compound is present or not. Once the data are flagged with "R" any further review or consideration is unnecessary. The qualifier "J" is used to indicate that due to QA/QC problems the results are considered to be estimated. The qualifier "NJ" indicates that there is presumptive evidence for the presence of the compound at an estimated value.

The data reviewer must explain in the data assessment narrative why the data was qualified. He or she must also indicate all items of contract non-compliance. All qualifications and corrections on the Analysis Data Sheet must be made in Red pencil.

4.0 Definitions

CALIBRATION STANDARD (CAL): solutions containing known amounts of selected analytes, internal standards and recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CALIBRATION VERIFICATION (VER): a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time window for each homologue.

CHLORINATED BIPHENYL CONGENER (CB) - One of the 209 individual chlorinated biphenyl congeners determined using this method.

ESTIMATED METHOD DETECTION LIMIT (EMDL): the lowest concentration at which CB can be detected with common laboratory interferences present.

ESTIMATED MINIMUM LEVEL (EML): The lowest concentration at which a CB can be measured reliably with common laboratory interferences present.

FIELD BLANK: An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

FIELD CHAIN OF CUSTODY: see Traffic Report

GC: Gas chromatograph or gas chromatography.

GEL PERMEATION CHROMATOGRAPHY (GPC): removes many high molecular weight interferences that cause GC column performance to degrade. It may be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds.

HRGC/HRMS: high resolution gas chromatography/ high resolution mass spectrometry.

INITIAL CALIBRATION STANDARD SOLUTION (CS-0.2 to CS-5): analysis of analytical standards for a series of different specified concentrations. The initial calibration is used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INITIAL PRECISION AND RECOVERY (IPR): four aliquots of a reference mixture spiked with the analytes of interest and labeled compounds and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. **An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.**

INTEGRATED ION CURRENT: electronic output to computer from instrument to provide a hard copy of area and height of a peak that may or may not be an analyte of interest.

INTERNAL STANDARDS (IS): a labeled compound used as a reference for quantitation of other labeled compounds and for quantitation of native CB congeners.

INTERNAL STANDARD (LABELED) : all five or any one of the five $^{13}C_{12}$-labeled CBs congeners spiked into the concentrated extract immediately prior to injection of an aliquot of the extract into the HRGC/HRMS. The five labeled internal standards in this method are CBs with IUPAC numbers 9, 52, 101, 138, and 194.

INTERNAL STANDARDS QUANTITATION: a means of determining the concentration of (1) a naturally occurring (native) compound by reference to a compound other than its labeled analog and (2) a labeled compound by reference to another labeled compound.

ION ABUNDANCE RATIO: mathematical comparison of selected pair of ions stipulated by the method for each target analyte. The ratio between each pair of ions must fall within established limits. These ions are needed for the identification and quantitation of target analytes.

ISOMER: chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties.

ISOTOPE DILUTION QUANTITATION: A means of determining a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched. In this method, all 12 carbon atoms in the biphenyl molecule are enriched with carbon-13 to produce $^{13}C_{12}$-labeled analogs of the chlorinated biphenyls. The $^{13}C_{12}$-labeled CBs are spiked into each sample and allow identification and correction of the concentration of the native compounds in the analytical process.

LABELED ANALYTE (or analog): an analyte that has isotopically carbon added to its chemical structure. These compounds are used to established identification (retention time) and used for quantitation of unlabeled analytes.

LOC: Level of Chlorination

MASS/CHARGE: usually expressed as m/z.

METHOD BLANK (MB): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with samples. The MB is used to determine if analytes or interferences are present in laboratory background environment, the reagents, or the apparatus..

MINIMUM LEVEL OF QUANTITATION (ML): The 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 clean up procedures have been employed.

MAXIMUM CONCENTRATION LEVEL (MCL): Highest level of concentration for each analyte depending upon upper concentration of analyte. Usually used to determine upper level of the concentration range.

ONGOING PRECISION AND RECOVERY (OPR): a method blank spiked with known quantities of analytes and analyzed like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

PERCENT MOISTURE: an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at this degree including water. % moisture is determined from decanted samples and from samples that are not decanted.

PERCENT VALLEY: see Resolution.

PERFLUOROKEROSENE (PFK): compound used to calibrate the exact m/z scale of the CB congeners in the HRGC/HRMS.

PERFORMANCE EVALUATION MIXTURE (PEM): See Performance Evaluation (PE) Sample.

PERFORMANCE EVALUATION (PE) SAMPLE: a chemical waste, soil or water sample containing known amount of CB congeners.

QUALITY CONTROL CHECK SAMPLE (QCS): A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

RECOVERY: a determination of the accuracy of the analytical procedure made by comparing measured values from a fortified (spiked) sample against the known spiked values.

RELATIVE RETENTION TIME (RRT): ratio of the retention time of the analyte versus the retention time of the corresponding internal standard. RRT for each analyte must be within range established by the method.

RELATIVE RESPONSE (RR): the ratio of the area response of the mass spectrometer to a known amount of an analyte (unlabeled to labeled) versus a known concentration in standard solution, plotted using linear regression. The RR is used to determine instrument performance and is used in the quantitation calculations.

RELATIVE STANDARD DEVIATION (RSD): The standard deviation times 100 divided by the mean. Also termed "coefficient of variation".

RESPONSE FACTOR (RF): the ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of internal standard as measured in the initial and continuing calibrations. The RF is used to determine instrument performance using correlation coefficient and is used in the quantitation calculations.

RESOLUTION: the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RINSATE/RINSE BLANK: a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SAMPLE DELIVERY GROUP (SDG): a unit within a single case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer samples within a case

SELECTED ION MONITORING (SIM): a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SELECTED ION CURRENT PROFILE (SICP): the line described by the signal at an exact m/z, i.e. a plot of ion abundance versus time for each ion which provides the retention time, peak area and height.

SIGNAL TO NOISE (S/N) RATIO: the height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

TOXICITY EQUIVALENCY FACTOR (TEF): an estimate of the toxicity of a specific CB congener relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin.

TOXICITY EQUIVALENCY (TEQ): the toxicity equivalent concentration in an environmental sample. It is the sum of the concentration of each individual toxic PCB and multiplied by their respective TEFs.

TRAFFIC REPORT (TR): sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and documents sample condition and receipt by the laboratory (may also be called Field Chain of Custody).

VALIDATED TIME OF SAMPLE RECEIPT (VTSR): the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample traffic report.

WINDOW DEFINING MIXTURE (WDM): a mixture containing the first and last eluting isomer for each congener. The retention time for each first and last eluting isomer establishes the retention time window for each congener. All analytes in the standards (calibrations, internal standards, recovery standards, Clean-up standard) and identified analytes in samples must have a reported
retention time within the established window. It is analyzed before any calibration standard, at the beginning of each 12 hour time period or when there is a shift greater than 10 seconds between retention time of recovery standards in standards or any analysis from retention time in recent calibration verification.

PACKAGE COMPLETENESS AND DELIVERABLES

CASE/SDGNUMBER:_____ SITE:_____
LAB:_____

CHECKLIST

I.0 Data Completeness and Deliverables

1.1 Does the Traffic Report or Field Chain of Custody list all samples? [ ] ___ ___

1.2 Is the Case Narrative, extraction logs, % solid worksheet, analysis logs present? [ ] ___ ___

1.3 Are the Case Number and SDG numbers contained in the case narrative? [ ] ___ ___

1.4 Do the Traffic Reports or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical problems, or other comments affecting the quality of the data? ___ [ ] ___

ACTION: Use professional judgement to evaluate the effect of the noted problems on the quality of the data.

ACTION: **As per Field Chain of Custody/Region II requirements, if any sample analyzed as a soil, contains 50% to 90% water, all data shall be flagged as estimated "J". If a soil sample contains more than 90% water, then qualify positive hits "J", and non detects "R".**

NOTE: Samplers are required to maintain all types of environmental samples in the dark at < 4 ° C from the time of collection until receipt at the laboratory.

2.0 Reporting Requirements and Deliverables

2.1 All deliverables must be clearly labeled with the Case number and the associated sample/traffic number. Missing or illegible or incorrectly labeled items must be identified. The Project Officer must immediately be contacted and requested to ask laboratory to submit the missing or incorrect items.

2.2 The following forms were taken from the CLP SOW, CBC01.0 and should be specified in the Project Plan. A comparison of CLP forms must be made against the Laboratory's version. Some information may not be found on the exact form as the CLP version but may be located on another form. As long as the information is present and accessible, it is not a problem. Are these forms (CLP or lab's version) present?

a. Toxic CB Congener Sample Data Summary (Form I CB-1) [ ] ___ ___

b. Toxic CB Congener Toxicity Equivalency (Form I CB-2) [ ] ___ ___

c. CB Congener Sample Data Summary (Form I CB-3) [ ] ___ ___

Note: Form I is used for tabulating and reporting sample analysis, including dilutions, reanalysis, blank, LCS/Ongoing Precision and Recovery (OPR) and requested matrix spike and matrix spike duplicated for target compounds.

d. CB Congener Total Homologue Concentration Summary (Form II CB) [ ] ___ ___

Note: Form II is used to report the concentration of the mono- through nano-chloro

biphenyl homologue for each sample.

e. CB Congener Method Blank Summary (Form IV CB-1) [___] ___ ___

Note: Form IV summarizes the samples associated with each method blank analysis.

f. CB Congener Descriptor Switching Resolution Summary (Form V CB-1) [___] ___ ___

Note: Form V CB-1 is used to report the descriptor switching windows for each level of chlorination for each 12-hour time period and to summarize the date and time of analysis, including dilutions, reanalysis, standards, blanks, and requested MS/MSD associated with each analysis of the instrument performance check solution.

g. CB Congener Ion Abundance Ratio Summary (Form V CB-2) [___] ___ ___
h. CB Congener (Labeled) Ion Abundance Ion Ratio Summary (Form V CB-3) [___] ___ ___

Note: Form V CB-2 & CB-3 are used to report the ion abundance ratios and signal-to-noise (S/N) ratios for the congeners contained in the LOC/WDM for each 12-hour time period.

i. Toxic CB Congener Initial Calibration Response Factor Summary (Form VI CB-1, CB-2)[___] ___ ___

j. Individual Congener Initial Calibration Response Factor Summary (Form VI CB-3) [___] ___ ___

Note: Form VI is used to report the relative response factors (RRF), average RRF, % RSD and RRT for the five or six-point initial calibration at the specific concentration levels.

k. Toxic CB Congener Continuing Calibration Summary (Form VII CB-1) [___] ___ ___

l. Toxic CB Congener (Labeled) Continuing Calibration Summary (Form VII CB-2) [___] ___ ___

m. Individual Congener Continuing Calibration Summary (Form VII CB-3) [___] ___ ___

n. Toxic CB Congener Continuing Calibration Time Summary (Form VII CB-4) [___] ___ ___

o. Toxic CB Congener (Labeled) Continuing Calibration Summary (Form VII CB-5) [___] ___ ___

p. Individual Congener Continuing Calibration Summary (Form VII CB-6) [___] ___ ___

Note: Form VII is used to report the calibration verification of the HRGC/HRMS system by the analysis of specific calibration verification standard(s). The form is required for each 12-hour time period.

k. CB Congener Analytical Sequence (Form VIII CB) [___] ___ ___
Note: Form VIII is used to report the analytical sequence for CB congener analyses.

ACTION: If forms are missing, contact the Project Officer to confirm which forms if any were specified in the Project Plan. If the forms are required, inform the Project Officer or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

Note: The above forms might be different or the laboratory might combine several forms into a single one. For example, the Target Analyte, Concentration and Q (qualifier) columns in the "CB Congener Sample Data Summary" form might include columns for IUPAC NO., Co-elution, Reporting Limits, Ion Abundance Ratio and Relative Retention Time (RRT).

2.3 GC/MS Displays
Are the following GC/MS displays present?

a. Standard and sample SICP/SIM chromatograms must list date and time of analysis; the file name; sample number; and instrument I.D. number [ ] ___ ___

b. Percent peak resolution valley [ ] ___ ___

c. Window Defining Mixture raw data [ ] ___ ___

d. SICP/SIM mass chromatograms must display ions used for quantitation, ion abundance ratio, absolute retention time/scan number, signal noise ratio [ ] ___ ___

e. Integrated area of the two ions must be listed for all peaks with signal noise ratio of 2.5 or greater (>10 for calibration and internal standards). [ ] ___ ___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/ resubmittal or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.4 Are the following Chain of Custody Records and in-house Laboratory Control Documents present?

a. Chain of Custody Records/Traffic Report [ ] ___ ___

b. Sample Shipment Records [ ] ___ ___

c. Sample log-in sheets [ ] ___ ___

d. GC/MS Standard and Sample Run Log in chronological order [ ] ___ ___

e. Sample Extraction Log [ ] ___ ___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.5 Was the sample data package paginated and one sided? [ ] ___ ___

ACTION: If no, document difficulties of reviewing data caused by lack of pagination in Data Assessment Report.

3.0 Holding Times

3.1 There are no demonstrated maximum holding times associated with CBs in aqueous, solid, semi-solid, tissues and other matrices. Aqueous samples must be preserved (pH 2-3) and stored up to one year in the dark at 0-4° C. Solid, semi-solids, multi-phase, and tissue samples must be stored in the dark at <-10° C.

4.0 Instrument Performance

4.1 Mass Spectrometer (MS) Resolution

Perfluorokerosene (PFK) tuning must be performed prior to analyzing calibration solutions, blanks, samples, and QC samples. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. A minimum required resolving power of 10000

should be obtained for PFK ion at mass 330.9792 or any significant PFK fragment in the range of 300-350.

A manual estimate of the resolving power can be done using the resolution check printout/calibration reports that contain the peak profiles of masses 300 to 350. At mass 330.9792, the first horizontal guideline above the baseline is the 5% line (some MS data system might not show this line). The ppm measurement of the window is usually given at 200 ppm, thus every vertical guideline represents 50 ppm. If the PFK peak is within 100 ppm at 5% height, resolution is equal or greater than 10,000.

NOTE: Because of the extensive mass range covered in each function (native, group and labeled congeners) it may not be possible to maintain 10,000 resolution throughout the mass range during the function. Therefore, resolution must be ≥ 8,000 throughout the mass range and must be ≥ 10,000 in the center of the mass range for each function.

4.1.1 Estimating resolving power (RP) from the resolution check printout containing the peak profiles of masses 300-350

A. Search the data package for the mass 330.9792 PFK peak ion (usually present before the calibration raw data).
A. Locate the 5% line which is the first horizontal gridline above the baseline.
C. At the top left hand corner of the profile, the ppm measurement of the window can be found (usually 200 ppm). Each vertical gridline represents 50 ppm.
D. If the PFK peak is within 100 ppm at 5% height, the resolution is greater than 10,000.

4.2 Gas Chromatographic (GC) Column Resolution

For the SPB-octyl column, the retention times (RT) for decachlororbiphenyl (PCB 209) in the Labeled/LOC/Window Defining Standard must be greater than 55 minutes and uniquely resolve congeners 34 from 23 and 187 from 182. Congeners 156 and 157 must co-elute within 2 seconds at the peak maximum.

4.2.1 The uniquely resolved congeners must resolve with a valley height less than 40% of the shortest of the two peaks.

Was this criterion met? [__] ___ ___

Note: The criteria for chromatographic resolution must be met for all standards. The data validator should use professional judgment to determine severity of the problem and its effect on the final results.

ACTION: If the percent valley criteria are not met for the uniquely resolved congeners, qualify positive reported values "J" (estimate) or reject "R" all data collected during the 12-hour time window. Document in Data Assessment Report under contract non-compliance.

4.2.2 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)? [__] ___ ___

4.2.3 Is the absolute retention time of CB congener 209 greater than 55.0 minutes with the SPB-octyl capillary GC column? [__] ___ ___

ACTION: If no, use professional judgment to assess the effect on the validity of the data. Make a note in the Data Assessment Report under contract non-compliance..

4.2.4 The relative retention times (RRT) of the native CBs and labeled congeners in the calibration verification standard (VER CS-3) must be within their respective RRT limits listed in Table 2/Method 1668A/CB01.0.

Was this criterion met? [__] ___ ___

ACTION: If no, use professional judgment to assess the effect on the validity of the data. Make a note in the Data Assessment Report under contract non-compliance.

4.3 Window Defining Mixture

4.3.1 The Window Defining Mixture (WDM) standard contains 27 labeled congeners (Table 3/Method 1668A) and is analyzed to establish the beginning retention time (RT) and ending RTs of each level of chlorination (LOC, homologue group).

Note: The WDM are also used to set the descriptor switching time such that congeners that elute from the HRGC during a given RT window will also be those congeners for which the ions are monitored.

Did the laboratory label the WDM congeners in each sample Quant report? [___] ___ ___

ACTION: If no, contract project officer or the laboratory for missing data.

4.3.2 Frequency of Window Defining Mixture - must be analyzed as follows:

1. After HRMS PFK tune and before any initial calibration.

2. Once at the beginning of each 12-hour period during which standards or samples are analyzed.

3. Whenever adjustments or instrument maintenance activities are performed.

Note: The standard CS1 can be used before any initial calibration and CS3 can be used before any continuing calibration.

ACTION: Were the above criteria met? [___] ___ ___

4.3.3 The CB congeners must be within QC limits for their respective ion abundance ratio and must have signal-to-noise (S/N) ratios $\geq$ 10.

Was this criteria met? [___] ___ ___

If no, did the lab perform reanalysis? Use professional judgment to assess the effect on the validity of the data. Make a note in the Data Assessment Report under contract non-compliance.

5.0 Initial Calibration

The Isotope dilution technique is used in the calibration of Toxics/LOC CB Congeners using labeled reference compounds. An Internal Standard calibration is applied to the determination of the native CB Congeners for which a labeled is not available, to the determination of the labeled Toxics/LOC/Window Defining Congeners and Labeled Internal Standards except CB 178.

Was the above calibration performed at the frequency specified above? [___] ___ ___

5.1 The method allows the Laboratory to perform quantitative analysis by isotope dilution and internal standard.

1. Isotope Dilution: performed for the twenty seven (27) CB Congeners. The relative response (RR) (labeled to native) vs concentration is calculated and the response of each Toxics/LOC CB relative to its labeled analog is determined using the area response of both primary and secondary exact m/z ratios. For labeled compounds, a calibration is performed using the data from five (or six) points in the calibration for the native Toxics/LOC CB Congeners.

2. Calibration by Internal Standard: for the native congeners (other than the native Toxics/LOC

CB Congeners), calibration is performed at a single point using the diluted combined 209-Congener Standard solution.

5.1.1 The following MS/DS conditions must be used:

5.1.1.1 Mass calibration as per Section 4.1? [___] ___ ___

5.1.1.2 Were SIM data acquired for each of the ions listed in Table 7/Method 1668A including interfering ions? [___] ___ ___

5.2 Were the following criteria met?

5.2.1 The SPB-Octyl column must resolve CB-34 from CB-23, CB-187 from CB-182, and CB-156 and CB-157 must coelute within 2 seconds at the peak maximum. Resolution must have a valley height less than 40 percent of the shorter of the two peaks. [___] ___ ___

5.2.2 For analysis on a DB-1 (or equivalent) column the chromatographic resolution is evaluated by the analysis of the CS3 continuing calibration standard during both the initial and continuing calibrations. Resolution must have a valley less than 25% for CB-156 and CB-157. [___] ___ ___

5.2.3 The relative ion abundance criteria listed in Table 8 (see analytical method) must be met for all PCB congeners peaks, including the labeled internal standards, clean-up standards, and recovery standards in all solutions. The lower and upper limits of the ion abundance ratios represent a ±15 percent window around the theoretical abundance ratio for each pair of selected ions. [___] ___ ___

5.2.4 Are the two SIM ions for each homolog within 2 seconds of the corresponding labeled analyte ions? [___] ___ ___

5.2.5 The relative ion abundance criteria listed in **Table 8** (see analytical method) must be met for each PCB congener peak. [___] ___ ___

5.2.6 For all calibration solutions the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be ≥ 10. [___] ___ ___

5.2.7 The percent relative standard deviations (% RSD) for the mean relative response factors (RRF) must be ≤ 20%. [___] ___ ___

5.2.8 The relative response factor (RRF) for each congener standard must be greater than 0.05. [___] ___ ___

5.2.9 For all calibration solutions, the retention times (RT) of the congeners must fall with the appropriate RT window established by the window defining mix analysis. In addition, the absolute RT of the of the recovery standards, internal standards and clean-up standards will not change by more than ± 15 seconds between the initial CS3 and the analysis of any other standard. [___] ___ ___

ACTION:

1. If mass calibration criteria as specified in Section 4.1 were not met, make a note in Data Assessment.

2. If the selected monitoring ions specified in **Table 7/Method 1668A** were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.

3. If the 40% percent valley resolution for CBs listed in section 5.2.1 above were not met, quality

positive data "J". Do not qualify non-detects.

4. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

5. If the ion abundance ratio for an internal or labeled standard falls outside the QC limits flag the associated positive hits with "J". No effect on the non-detects.

6. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.

7. If the %RSD for each analyte exceeds 20%, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

8. If the DB-1 column was used, did the resolution have a valley of less than 25% for CB-156 and CB-157? If not met, qualify the analytes as estimate ("J"). Do not qualify non-detects.

9. If the RRF < 0.05, flag associate sample positive results for that specific congener as estimate "J".

10. Non compliance of any other criteria specified above should be evaluated using professional judgement.

5.2.10 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CBs and labeled standards were used. In addition, verify that the appropriate labeled standard was used for each analyte.

ACTION: If calculations were not performed correctly, notify the Project Officer to initiate resubmittals from the laboratory.

6.0 System and Laboratory Performance (Calibration Verification)

At the beginning of a 12-hour shift during which analyses are performed, the HR/MS system performance tune is verified prior to analyzing the calibration verification standard CS3. If required, the diluted combined 209-congener standard solutions must also be analyzed at the beginning of the 12-hour period, but after the CS3. The CS3 standard must analyzed at the end of the 12-hour. This closing CS3 standard may also be used as the beginning of the next 12-hour period.

Only if the laboratory meets all performance criteria may samples, blanks, and recovery standards be analyzed.

6.1 Calibration Verification

6.1.1 Were the relative ion abundance ratio for each congener in the CS3 standard within their respective criteria? [___] ___ ___

6.1.2 Were the peaks representing each unlabeled and labeled compound in the verification standard present with signal to noise ratio (S/N) greater or equal to 10? [___] ___ ___

6.1.3 For each congener, were the per cent recovery within the limit (Table 6/method 1668A)? (Native Toxics/LOC: 70-130%; Labeled Toxics/LOC/Window-Defining: 50-150% and 60-130% for the cleanup standards) [___] ___ ___

6.1.4 Were the relative retention time (RRT) of the congeners within the limits defined in Table 2/Method 1668A? Note: RRT should be listed in each sample quant report. [___] ___ ___

ACTION: If no to section 6.1.1 - 6.1.4, qualify affected congener with "J" qualifier.

6.2 Instrument Sensitivity Test

6.2.1 Project technical specifications may require the laboratory to perform a GC/MS sensitivity test using the CS-0.2 standard. The following guidance is offered:

6.2.2 The test must be demonstrated every 12 hours by analysis of a CS-0.2 standard which must pass the following criteria

6.2.2.1 The absolute RT for the ending recovery standards $^{13}C_{12}$-CL_4-CB-52, $^{13}C_{12}$-CL_5-CB-101, $^{13}C_{12}$-Cl-CB-138, and $^{13}C_{12}$-CL_7-CB-178 must be within 10 seconds of the initial CS3.

6.2.2.2 The signal/noise ratio for the CS-0.2 standard must be at least 10:1 (or 3:1 for di- and nona-PCBs for unlabeled compounds and labeled internal and recovery standards.

6.2.2.3 Ion abundance ratio must be met.

ACTION:

1. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

2. If the signal noise ratio (S/N) is below control limits, use professional judgement to determine the quality of the data.

3. The RT of the recovery standards from CS3 to the CS-0.2 will indicate the stability of the column during the 12 hours. If these criteria were not met, the estimate all reported values (J) and (UJ) non-detects associated with RT shifts greater than ± 10 seconds.

6.3 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CBs and labeled standards were used. In addition, verify the appropriate labeled standard was used for each analyte.

7.0 Sample Analysis and Identification

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration column.

7.1 A CB congener or labeled compound is identified in environment samples, blanks, or QC samples when all of the following qualitative criteria are met.

7.1.1 The signals for the two exact m/z ratios in **Table 7/Method 1668A** must be present and must maximize within the same two scans (area count for the m/z should be present in the Quant report) [ ] ___ ___

7.1.2 The signal-to-noise (S/N) ratio for each ion peak at each exact m/z must be ≥2.5 for each congener detected in a sample extract and ≥10 for all congener in the calibration standards (Note: The SN ratio should be available in each sample Quant report) [ ] ___ ___

7.1.3 The relative ion abundance criteria for all CB Congener detected as well as labeled compounds, cleanup and internal standards must be within the limits of Table 8 or within ±15% of the ratio in the midpoint calibration (CS-3) standard or calibration verification (VER), whichever is most recent. [ ] ___ ___

7.1.4 The relative retention time (RRT) for each detected peak must be within the RRT QC limits specified in Table 2 of the method (Note: The RRT values should be present in each sample Quant report). [ ] ___ ___

Note: For native congeners determined by Internal Standard Quantitation, a given congener may fall within more than one RT and mis-identified unless the RRT window are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. The RT and RRT values should be available in each sample Quant report.

ACTION: If the identification criteria (section 7.1.1 - 7.1.4) were not met, check sample Quant report to verify the congener is listed as "non-detect".

7.2 Quantitative Determination

7.2.1 Isotope Dilution Quantitation

7.2.1.1 Were the Labeled Toxics/Level of Chlorination (LOC)/Window-Defining Congeners (WDC) and Cleanup standards added to every sample? [___] ___ ___

ACTION: If no, contact project officer to contact the laboratory. Note problem in data assessment.

Note: Corrections for recovery of CB can be made because the native compound and its Labeled analog exhibit similar effects upon extraction, concentration and Gas Chromatography. Relative response (RR) are used in conjunction with the calibration data to determine the concentrations in the final extract providing the labeled compounds spiking levels are constant.

7.2.1.2 The percent recovery for the Labeled Toxics/LOC/Window Defining Congeners for each sample is 25-150%, except 15-150% for $^{13}C_{12}$ -2- MoCB and $^{13}C_{12}$ -4- MoCB. 30 -135% for Cleanup Standards. Was this criteria met? [___] ___ ___

ACTION: If no, qualify affected native congener with "J". Make a note in the data assessment.

7.2.1.3 The integrated ion current for the labeled compounds, internal standards, and cleanup standards have a signal noise ratio at least 10 times background noise. [___] ___ ____
ACTION: If not, verify that the sample in question was reanalyzed. If s/n ratio is less than 10, qualify affected native congener with "J".

7.2.1.4 Did the laboratory provide a "sample calculation" for one of the reported value? [___] ___ ___

ACTION: Check one value and if not in agreement with the reported value, have Project Officer contact laboratory for a sample calculation.

$$C_{ex}\ (ng/ml) = \frac{(A1_n + A2_n)CI}{(A1_l + A2_l)RR} \qquad RR = \frac{(A1_n + A2_n)C_l}{(A1_l + A2_l)C_n}$$

C_{ex} = Concentration of congener in the extract.
$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the congener.
C_l = Concentration of the labeled compound in the calibration standard.
C_n =Concentration of the native compound in the calibration standard.
RR = Relative Response

7.2.2 Internal Standard Quantitation and Labeled Compound Recovery

7.2.2.1 The concentration in the extract of the native compounds other than those in the Native Toxics/Labeled /LOC standard, in the Labeled cleanup standard and in the Labeled injection internal standard (except the Labeled CB 178) using the response factors determined from the calibration data and the following equations:

$$C_{ex}\ (ng/ml) = \frac{(A1_s + A2_s)C_{is}}{(A1_{is} + A2_{is})RF} \qquad RF = \frac{(A1_s + A2_s)C_{is}}{(A1_{is} + A2_{is})C_s}$$

C_{ex} = Concentration of labeled compound in the extract.
$A1_s$ and $A2_s$ = Areas of the primary and secondary m/z's for the congener.
$A1_{is}$ and $A2_{is}$ = Areas of the primary and secondary m/z's for the internal standard
C_{is} = Concentration of the internal standard.
C_s = Concentration of the compound in the calibration standard.
RF = Response Factor

Note: The internal standard and associated CB congeners can be found in Table 2 of the method.

7.2.2.2 The percent recovery of the Labeled Toxics/LOC/Window-defining CBs and the Labeled cleanup standard CBs are computed using the concentration in the extract determined above and the following equation:

$$Recovery\ (\%) = \frac{Concentration\ found\ (ng/ml)}{Concentration\ spiked\ (ng/ml)} \times 100$$

7.2.2.3 The concentration of the native CB in the solid phase is computed using the following equation:

$$Concentration\ in\ the\ solid\ (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

C_{ex} = Concentration of the compound in the extract.
V_{ex} = The extract volume in ml.
W_s = The sample dry weight in kg.

7.2.2.4 The concentration of the native CB in the aqueous phase is computed using the following equation:

$$Concentration\ in\ the\ aqueous\ phase\ (pg/L) = 1000 \times \frac{(C_{ex} \times V_{ex})}{V_s}$$

C_{ex} = Concentration of the compound in the extract.
V_{ex} = The extract volume in ml.
V_s = The sample volume in liters.

7.2.2.5 The analyte concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range. Was this criterion met? [___] ___ ___

NOTE: When the sample extract is diluted by the factor necessary to bring the concentration within the calibration range, the analyst should adjust the concentration of the Labeled injection internal standard to 100 pg/uL in the extract and analyze an aliquot of the diluted extract.

7.3 Clean-up procedures

Clean-up may not be necessary for relatively clean samples (drinking waters, ground waters etc). If the matrix required clean-up, the laboratory has 6 different procedures to choose from (Section 7.5/Method 1668A). Before using any clean-up procedure, the laboratory must demonstrate that the Initial Precision and Recovery (IPR) requirements of the

method can be met using the clean-up procedure.

Labeled clean-up standards $^{13}C_{12}$-2,4,4-TriCB (CB-28), $^{13}C_{12}$-2,3 3,5,5'-PeCB (CB-111), $^{13}C_{12}$-2,2',3,3'5,5',6-HPCB (CB-178) are added to the sample just before the back extraction with base and acid procedure. This occurs before any recommended clean-up procedures are initiated.

7.3.1 Was the percent recovery of the clean-up standards within the recommended range 30-135%? [ ] ___ ___

ACTION: If no, and the recovery is less than 30%, qualify all data as estimated "J". If recovery is 0 %, qualify all positive data as estimated "J" and reject "R" all non-detects for that sample.
If recovery is > 135, qualify positive results as estimated, "J".

7.3.2 Check the chromatograms that clean-up procedure was needed for each sample. Were any clean-up procedures needed for either water or soil samples? ___ [ ] ___

ACTION: If yes, check extraction log to verify which clean-up procedures if any were performed. The laboratory is not limited to only one procedure.

1. If no clean-up was performed and the chromatograms indicated that some should have been performed. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of required clean-up for complex samples in Data Assessment.

2. If one type of clean-up was performed, but the chromatograms indicate that additional clean-up should have been utilized. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of additional clean-up for complex samples in the Data Assessment.

7.3.3 If clean-up procedures were used, did the Laboratory perform clean-up procedures on the Initial Precision and Recovery samples as required by the method? [ ] ___ ___

ACTION: If no, use professional judgement to assess the effect of the interference on the validity of the data. Document lack of IPR documentation for clean-up procedures in the Data Assessment.

8.0 Estimated Detection Limits (EMDL)

8.1 Was an EDL calculated using the formula in section 8.2 for CB congeners reported as non-detect? [ ] ___ ___

ACTION: 1. If EDL of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

8.2 Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

$$EDL\ (pg/g) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{(W) \times (His^1 + His^2) \times RR}$$

WATER

$$EDL\ (pg/L) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{(V) \times (His^1 + His^2) \times RR}$$

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the non-detect isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor

Qis = quantity (ng) of the appropriate internal standard added to the sample prior to extraction.

RR = Relative response factor from the initial calibration.

V = Volume of sample extracted in liters.

W = Sample dry weight.

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the Project Officer to request recalculations from the laboratory.

ACTION: If the spot check calculations yielded EDLs ≤ 15% difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

9.0 Method Blanks

9.1 Has a method blank per matrix been extracted and analyzed with each batch of 20 samples? [ ] ___ ___

9.2 If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event? [ ] ___ ___

9.3 Were the method blanks treated as a sample, i.e. spiked with Labeled Toxics/LOC/Window Defining Mixture, Labeled Internal and Labeled Cleanup standards? [ ] ___ ___

Note: 1 Liter of reagent water is used for aqueous samples, 10 gram sand for soil/sediment samples and 1.0 gram of corn oil for tissue samples.

9.4 Were any CB present in the method blank at a concentration less than the estimate minimum level (EML) of Table 2/Method 1668A or one-third the regulatory compliance limits? [ ] ___ ___

Note: The EML in Table 2 of the method are based on common contamination levels. A laboratory may establish an minimum level (ML) for a CB lower than the EMLs in Table 2. MLs may be established as low as the lowest calibration point. Check project plan regarding compliance limits.

ACTION: 1. If the proper number of method blanks were not analyzed, document in Data Assessment. If the validator feels that the validity of the data is seriously compromised and validation of data without the method blanks would be flawed, then notify the Project Officer. If decision is made to proceed with the validation process, consider the following actions: no action taken on non-detected analytes. If an analyte has a reported concentration that is > 5 times the EML, qualify "J" and all concentrations ≤ 5 times the EML are qualified "R" due to possibility of contamination.

2. A. If the congener concentration in the sample is less than five times the concentration in the blank, flag the congener reported value with a "U" qualifier.

B. If the concentration of the congener in the sample is greater than five times the concentration in the blank, no action is needed.

10.0 Labeled Internal and Cleanup Compound Recoveries

10.1 Were the samples spiked with all the labeled compounds as specified in the method? [___] ___ ___

10.2 Are all labeled compound recoveries within the required limits ? [___] ___ ___

Note: The percent recovery for the Labeled Toxics/LOC/Window Defining Congeners is 25-150%, except 15-150% for $^{13}C_{12}$ -2- MoCB and $^{13}C_{12}$ -4- MoCB. 30-135% for Cleanup Standards.

10.3 If not, were samples reanalyzed? [___] ___ ___

ACTION: 1. If the labeled compound recovery was below the lower limit, qualify as estimate with "J" the positive data for the associated compound.

2. No action on non-detects if the labeled compound recovery is above the upper limit.

3. If the labeled compound recovery is 0%, notify project officer. At a minimum, qualify positive value as estimate "J" and reject non-detects with "R" qualifier.

Note 1: If a labeled compound recovery is low, and the cleanup standards are not, the recovery problem may be associated with the extraction procedure or related to a particular difficult matrix. In this case, reanalysis may only serve to confirm a "matrix effect".

Note 2: Low recoveries of the labeled compounds **and** Cleanup standards suggest that losses may be due to the performance of the clean up steps. Re-extraction and reanalysis of the sample may yield better results.

Recalculate the percent recovery for each labeled standard in the sample extract, Rec_l, using the formula:

$$\% Rec_l = \frac{(A_{l1} + A_{l2}) \times Q_{is} \times 100}{(A_{is1} + A_{is2}) \times RF \times Q_l}$$

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled compound.

$A_{is1} + A_{is2}$= integrated areas of the two quantitation ions of the appropriate internal standard.

Q_l = quantity of the appropriate labeled compound

Q_{is} = quantity of the appropriate internal standard injected

RF = Response factor of the labeled compounds as determined by the five-point calibration.

11.0 Determination of CBs on a DB-1 Column

11.1 The DB-1 column is optional and is capable of uniquely resolving the congener 156 and 157 that are not resolved on the SPB-octyl column and for resolution of other CB congeners. Was the laboratory required to analyze sample extracts on the DB-1 column? [___] ___ ___

Note: The two-column system is capable of resolving a total of approximately 180 CB congeners.

ACTION: If yes, were the WDM, and Cleanup standards added to all samples, standards, blanks, etc? If no, check PO or project plan regarding modifications. [___] ___ ___

Note: Window-defining congeners - the beginning and ending congeners at each level of

chlorination are the same as for the SPB-octyl column.

12.0 Sample Reanalysis

12.1 The Project Officer will evaluate the need for reanalyzing the samples with qualified data based on site-specific Data Quality Objectives.

12.2 Due to a variety of situations (see below) that may occur during sample analysis, the laboratory is required to reanalyze or re-extract and reanalyze certain samples. If a reanalysis was required but was not performed, contact the Project Officer to initiate reanalysis. List in data assessment all re-extractions and reanalyses and identify the sample data summaries which must be used by the data user (when more than one analysis is submitted for a sample).

Lab must re-extract and/or re-analyzed samples when the following criteria are not met:

1. WDM must be met before any standard, samples, QC samples and required blank are analyzed.

2. Initial calibration criteria as outline in section 5.2.1, 5.2.3 - 5.2.9 above must be met.

3. Calibration verification standard criteria as outline in section 6.1.1 - 6.1.4 above must be met.

4. A method blank was not extracted and analyzed with each batch of samples/instrument.

ACTION: For criteria 1, 2, 3, or 4 notify the Project Officer to discuss possible re-analysis of sample by the laboratory.

13.0 Precision and Recovery (PAR)/Laboratory Control Sample (LCS)

The laboratory is required to show initial demonstration of capability, to evaluate and document data quality. Laboratory performance is compared to established performance criteria to determine if results of analyses meet the performance characteristics of the method.

The laboratory must perform and submit data to establish the ability to generate acceptable precision and accuracy.

13.1 Did the laboratory analyzed an Initial Precision and Recovery (IPR) standard containing the Native Toxics/LOC congeners, Labeled Toxics/LOC/WDM and Labeled cleanup standards? [ ] ___ ___

ACTION: If no, contact the Project Officer to request resubmittals from the laboratory.

If data is not available, check the project plan or discuss the issue with the Project Officer. If a decision is made to proceed with validation, use professional judgement. All data at a minimum should be qualified as estimated "J". Technically according to the method, data and system performance is unacceptable for all compounds. Analyses should not have continued as per the method. Document under contract non-compliance in Data Assessment.

13.2 Did the IPR standard deviation (s) and average concentration (x) passed criteria as outlined below? [ ] ___ ___

1. %RSD < 40% and 60-140% recovery for Native Toxics/LOC congeners
2. %RSD < 50% and 35-135% recovery for Labeled Toxics/LOC/WDM (20-135% for $^{13}C_{12}$ -2- MoCB and $^{13}C_{12}$ -4- MoCB)
3. %RSD < 45% and 45-120% recovery for Labeled cleanup standards

ACTION: If no, qualify effected congeners as estimate "J"

The laboratory must analyzed an Ongoing Precision and Recovery standard (OPR) periodically, at the beginning of 12 hour shift after the analysis of the CS3 calibration verification (CV), and before the analysis of any sample in each set .

13.3 Was the Ongoing Precision and Recovery (OPR) standard analyzed at the required frequency? [ ] ___ ___

13.4 Did the OPR standard passed the concentration criteria limits in outline below? [ ] ___ ___

1. 50-150% recovery for Native Toxics/LOC congeners
2. 30-140% recovery for Labeled Toxics/LOC/WDM (15-140% for $^{13}C_{12}$ -2- MoCB and $^{13}C_{12}$ -4- MoCB)
3. 40-125% recovery for Labeled cleanup standards

ACTION: If no, qualify affected congeners as estimate "J". All samples that do not have a passing OPR standard are potentially affected for that analyte.

Note: The laboratory might use laboratory control sample (LCS) for IPR and laboratory control sample duplicate (LCSD) for OPR.

The following sections may be incorporated in the validation process on a case by case basis depending upon the requirements of the Project Plan. Sometimes a laboratory will provide data for some of the following sections on a routine basis. If not a requirement of the Project Plan, then professional judgement is needed to qualify data based on additional information.

14.0 Toxicity Equivalency Factor (TEF)

NOTE: Certain CB congeners have been shown to cause toxic responses similar to those cause by 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), the most potent congener. The concept of toxic equivalency factor (TEF; Reference 3) has been developed to facilitate risk assessment and regulatory control of exposure.

The TEF value concentrations are listed in the following Table 1 (Reference 3)

Target Analyte	TEF Value
CB-77	0.0001
CB-81	0.0001
CB-105	0.0001
CB-114	0.0005
CB-118	0.0001
CB-123	0.0001
CB-126	0.1
CB-156/147	0.0005
CB-167	0.00001
CB-169	0.01
CB-189	0.0001

When calculating the 2,3,7,8-TCDD Toxicity Equivalency of a sample for the above CB congeners, only the positive reported values must be included in the calculations. The Toxicity Equivalency (TEQ) concentration is the sum of each concentration of each individual toxic congener value and multiplied by their respective TEF value.

14.1 Did the lab include EDL values in the TEF adjusted concentration calculations? [ ] ___ ___

ACTION: 1. If yes, the toxicity equivalency calculations were not calculated properly, notify the Project Officer to arrange for laboratory resubmittals.

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congener concentration.

15.0 Rinsate Blank/Rinse Blank *(Region 2 QA guidelines recommend rinse blanks for all projects)*

15.1 One rinsate blank should be collected for each batch of 20 soil samples or one per day Whichever is more frequent. Were rinsate blanks collected at the above frequency? [ ] ___ ___

15.2 Do any rinsate blanks show the presence of any CB congener at amount above the detection limits (i.e. reported as positive value)? [ ] ___ ___

ACTION: If any qualification is needed due to rinsate blank contamination, follow the guidelines outlined under Method Blanks, section 9, Actions 1 and 2.

16.0 Performance Evaluation Sample (PES)

NOTE: This type of sample may not be available at this time. In many cases, laboratories will substitute matrix spike/matrix spike duplicate (MS/MSD). If PEM(s) were not analyzed but MS/MSD data were submitted, skip this section and go to section 17.

16.1 One or more PES is supplied to the Laboratory. The frequency of this QC sample is one per group of 20 environmental samples or one per samples collected over one week period, whichever occurs first (check project plan).

16.2 Was a PES analyzed at the frequency described above? [ ] ___ ___

16.3 Were the percent recovery of CB congeners within the 50 to 150 percent control limits? [ ] ___ ___

ACTION: 1. If any CB congener fall outside the 50-150 percent control limit, flag positive and non-detect data as estimate "J". However, if the recovery is below 20%, qualify all associated non-detects "R" and positive hits as "J". Notify the Project Officer. Reanalysis may be initiated.

17.0 Matrix Spike (MS) Field Sample

Note: Matrix spike is not required by this method although Labs may routinely perform this analysis as part of internal QA/QC and submit this data as part of the package. Verify requirements with Project Officer.

17.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix? [ ] ___ ___

17.2 Were the percent recovery of the spiking congeners within 60 to 140 percent? [ ] ___ ___

ACTION: If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 60-140% limits of the matrix spike data may be used to flag data of the spiked sample only. *The* matrix spike *data of the PE blank* sample are more important and must be used primarily in data validation.

17.3 Was a matrix spike duplicate analyzed? [ ] ___ ___

ACTION: No action required. A matrix spike duplicate is not required. Use professional judgement if there is a large difference in concentrations reported between MS and MSD. Qualifications if any, can only be performed on the sample that was used for this criteria.

18.0 Environmental Duplicate Samples *(recommended in Region 2 for all Projects)*

NOTE: Do not confuse an environmental duplicate with a matrix spike duplicate. An environmental duplicate is a sample that has been divided into 2 parts (extracted and analyzed as two different samples) or as 2 separate samples from the same location sent by the sampling crew. This sample is not spike with any additional compounds other than those compounds required by the method for analysis of all routine samples.

18.1 For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency? [ ] ___ ___

18.2 Did results of the duplicate samples agree within 25% relative difference for water samples and 50% for other type of samples? [ ] ___ ___

ACTION: The duplicate results can be used in conjunction of other QC data. Use professional judgement.

19.0 REFERENCES

They are important references for technical information and are submitted here as part of this method's documentation.

1. Method 1668, Revision A, "Chlorinated Biphenyl Congeners in Water, Soil, sediment, Biosolids and Tissue by HRGC/HRMS, August 20, 2003.

2. EPA Statement of Work for Chlorinated Biphenyl (CB) Congeners, Multi-Media, Multi-Concentration, CBC01.0, May 2005.

3. Van den Berg, Linda Birnbaum, Albetus T.C., "Environmental Health Perspectives 106:12, 775-792, 1998.

ATTACHMENT A

PCBs DATA ASSESSMENT

SDG No.
LABORATORY:
SITE:

DATA ASSESSMENT

The current Functional Guidelines for evaluating PCBs organic data have been applied.

All data are valid and acceptable except those analytes which have been qualified with a "J" (estimated), "N" (presumptive evidence for the presence of the material), "U"(non-detects), "R" (unusable), or "JN"(presumptive evidence for the presence of the material at an estimated value). All action is detailed on the attached sheets.

Two facts should be noted by all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. "R" values should not appear on data tables because they can not be relied upon, even as a last resort. The second fact to keep in mind is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data but any value potentially contains error.

Reviewer
Signature:_____ Date:__/__/200_

Verified By:_____ Date:__/__/200_

ATTACHMENT A:

DATA ASSESSMENT

GENERAL COMMENTS:

HOLDING TIME:

BLANK CONTAMINATION:

WINDOW DEFINING MIXTURE:

ION ABUNDANCE:

CALIBRATIONS:

RESOLUTION:

LABELED STANDARDS PERFORMANCE:

INTERNAL STANDARDS:

PEAK IDENTIFICATION:

MATRIX SPIKE/ ENVIRONMENTAL DUPLICATE:

CONFIRMATIONS:

OTHER QC OUT OF SPECIFICATION:

SYSTEM PERFORMANCE AND OVERALL ASSESSMENT:

CONTRACT PROBLEMS NON-COMPLIANCE:

RE-EXTRACTION, REANALYSIS OR DILUTIONS:

DO NOT USE USE

FIELD DOCUMENTS: