Validation of Chlorinated Biphenyl Congener Analytical Data (EPA Method 1668)

Effective Date: 4/24/2017

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Hazard Class: ☒ Low ☐ Moderate ☐ High/Complex
Usage Mode: ☒ Reference ☐ UET ☐ Both UET & Reference

The Responsible Manager has determined that the following organizations' review is required for initial procedure release as well as subsequent major revisions. Review documentation is contained in the Document History File.

Technical Leads Quality Assurance

Classification Review: ☒ Unclassified ☐ UCNI ☐ Classified

Name (print)	Z#	Signature	Date
Diana Hollis	111125	/s/ Diana Hollis	4/18/2017

Responsible Manager, Division and Title

Name (print)	Z#	Signature	Date
Nita Patel	153003	/s/ Nita Patel	4/20/2017

REVISION HISTORY

Document No./Revision No.	Issue Date	Action	Description
OIO-TP-5170, Rev. 0.1	4/20/2016	Minor Revision	Periodic Review, changed Document type and Organization. Replacing SOP-5170.
ER-AP-20318, R0	4/24/2017	Major Revision	Revised to reflect the guidance from the National Functional Guidelines for High Resolution Superfund Methods Data Review, April 2016 (EPA-542-B-16-001) holding time requirements and remove NNSA Model Validation

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1. PURPOSE

This procedure represents the minimum standards for evaluating chlorinated biphenyl congener analytical data.

2. SCOPE

This document is intended to assist in the technical review of analytical data generated by environmental laboratories. Qualification of data is the product of data validation, analytical laboratory analysis, and focused validation that describe validation anomalies and their consequences.

3. BACKGROUND

Data qualifiers and reason codes are assigned to analytical results from chlorinated biphenyl analyses according to the specifications in this method-specific procedure. These guidelines are developed using the EPA method-specific data quality criteria and/or National Functional Guidelines for High Resolution Superfund Methods Data Review.

4. PRECAUTIONS AND LIMITATIONS

Nothing in this procedure precludes the data validator from going beyond the minimum requirements specified within this procedure. If additional directions are required, the data validator shall reference EPA method-specific guidelines and/or EPA National Functional Guidelines for High Resolution Superfund Methods Data Review. Implementation of this procedure may be followed by a more focused and data use-specific evaluation of the data by the project chemist, especially if the implementation of this procedure indicates the data may contain technical deficiencies.

5. PREREQUISITE ACTIONS

Data Validators must:

- Possess a minimum of a bachelor's degree in chemistry or one of the physical sciences and either two (2) years of experience in generating analytical data in an environmental analytical laboratory OR two (2) years of data validation experience.
- Complete Attachment 1, Data Validation Cover Sheet, and Attachment 2, Chlorinated Biphenyl Congener Analytical Data Validation Checklist, during data validation.
- Refer to Attachment 3, Theoretical Ion Abundance Ratios and Quality Control Limits for EPA Method 1668; and Attachment 4, Quality Control Acceptance Criteria for Chlorinated Biphenyls in Calibration Verification, Initial Precision and Recovery, Ongoing Precision and Recovery, and Samples for EPA Method 1668, for additional guidance.

6. PERFORMANCE

6.1 Validation Process

EIM applies a subset of qualifiers described in this procedure to analytical data using auto-validation subroutines. EIM auto-validation applies qualification to analytical records using tests listed in Attachment 2 that have a Valid Reason Description containing "(AV)". When the project leader requests a focused validation the assigned data validator completes the following steps to assess all potential analytical data qualification:

[1] **REVIEW** the qualifiers assigned during EIM auto-validation to verify that qualifiers were assigned consistently with this procedure. If auto-validation qualification is found to be inconsistent with this procedure then the validator initiates a change request using ER-AP-20304, Change Control for Data in the Environmental Information Management (EIM) Database.

[2] **PRINT** Attachment 1 and **REVIEW** the data package for potential qualification using Attachment 2.

[3] **NOTE** conditions causing recommendation for qualification and options for qualification.

[4] **FILL** out Attachment 1 and **FORWARD** to the project leader with conditions and options.

The project leader is the responsible party for making the decision of record if validation qualifiers should be assigned and EIM validation records updated. This record of decision is added to comments section of Attachment 1.

Once the decision of record has been made, Attachment 1 is sent to the Sample Management Office (SMO) staff. The SMO staff re-print the data validation record from EIM and add Attachment 1 that includes the record of decision to the final records package.

6.2 Analyte Quantitation

The assignment of the detection status to analytical measurements is the first step of analytical data validation. Most validation qualifiers and validation reason codes are applied based on the measurement's initial detection status. Results that are less than the report method detection limit (RMDL) are qualified as nondetect with the U validation qualifier. Results greater than or equal to the RMDL and less than the report detection limit (RDL) are qualified as detected and estimated with the J validation qualifier. Results greater than or equal to the RDL are qualified as detected with the NQ validation qualifier.

Criteria	Validation Qualifier	Validation Reason Code
Target analyte result is < RMDL; a nondetect	U	U_LAB
Target analyte result is ≥ RMDL and < RDL; a detect	J	J_LAB
Target analyte result is ≥ RDL; a detect	NQ	NQ

Since a result can have only one validation qualifier and one validation reason code the sequencing of validation steps is important. Analyte quantitation occurs first, then analyte identification, because most other validation functions depend on the correct identification and quantitation of the analytical parameter. When two or more qualifiers can be applied to a record, the qualifier representing the more severe consequence to data usability supersedes the qualifier with less severe consequence. The R validation qualifier has the greatest impact on data usability and supersedes other validation qualifiers.

6.2 Analyte Quantitation (continued)

Order Of Severity	Validation Qualifier	Description
1	R	The reported sample result is classified as rejected due to serious noncompliance regarding quality control acceptance criteria. The presence or absence of the analyte cannot be verified.
2	UJ	The analyte is classified as not detected, with an expectation that the reported result is more uncertain than usual.
3	U	The analyte is classified as not detected.
4	J	The analyte is classified as detected but the reported concentration value is expected to be more uncertain than usual.
5	NQ	No validation qualifier flag is associated with this result, and the analyte is classified as detected.

LANL project chemists may identify quality deficiencies in analytical results affecting analyte quantitation. These deficiencies can include analytical results with detection limits elevated above project data-quality objectives, concentrations above the calibration range of the instrument or method, results exhibiting carryover or detector contamination, large relative percent difference between dual-column detects, chromatographic interference from another analyte, and other quality deficiencies. The reason codes of CB15 or CB19 are applied to affected records by the project chemist to identify these quality deficiencies when they are identified.

6.3 Analyte Identification

The identification of an analytical parameter is the second step of analytical data validation. Identification of chlorinated biphenyl compounds depends upon the relative retention time of the compound of interest to the known retention time of the compound in the calibration standard, and the relative intensity of the mass spectrum of the compound of interest in a sample to the known intensity of the compound in a calibration standard. When mass spectral analyte identification criteria are not met the CB8 series of reason codes are applied to affected parameters. When relative retention time criteria are not met the CB0 series of reason codes are applied to affected parameters.

6.4 Holding Times and Sample Preservation

Sample handling requirements are specified to ensure integrity and defensibility of analytical measurements. Samples are to be prepared and analyzed within specified time limits. Samples are also preserved chemically and physically by controlling temperature and light. When sample handling requirements are not met the CB9 series of reason codes are applied to affected samples.

6.5 Initial and Continuing Calibration

Calibration is performed to set the operating range of the instrument and to ensure that the instrument is performing within specifications. The initial calibration and verification is performed prior to the start of analyses. Continuing calibration checks and instrument performance samples are performed periodically during analysis to ensure the instrument is providing accurate results. When initial calibration criteria are not met the CB7 series of reason codes are applied to affected analytes in all samples analyzed after the unacceptable initial calibration to the next acceptable initial calibration for that instrument. When continuing calibration criteria or are not met the CB7 series of reason codes are applied to affected analytes in all samples analyzed after the unacceptable continuing calibration to the next acceptable continuing calibration for that instrument. When instrument performance checks do not meet criteria the CB16 series of qualifiers are applied to affected analytes in all samples analyzed after the unacceptable instrument performance check to the next acceptable instrument performance check for that instrument.

6.6 Surrogates

Surrogates are compounds not normally found in the environment, but which have quantitation limits and retention times similar to the analytes of interest in a sample. Surrogates are added to samples, standards, and QC samples to determine the effectiveness of analyte quantitation. Sample results are not adjusted based on surrogate recoveries. When surrogate recovery criteria are not met the CB3 series of reason codes are applied to affected samples.

6.7 Internal Standards

Internal standards are compounds not normally found in the environment, but which are easily measurable. They are added to samples, standards, and QC samples to compensate for fluctuations in the analytical system. Sample results are quantitated or adjusted by the relative response of associated internal standards. When internal standard criteria are not met the CB1 series of reason codes are applied to the affected sample.

6.8 Blanks

The Method Blank is an analyte-free matrix that is prepared and analyzed in the laboratory with the samples. The method blank determines contamination from the analytical processes. Method blanks are prepared with every preparation batch. If more than one method blank is associated with a given sample, qualification is based upon a comparison with the associated blank having the highest concentration of the parameter. When method blank criteria are not met the CB4 series of reason codes are applied affected samples.

A statistically derived blank subtraction can be performed using EPA 1668 series methods. The process for generating and reviewing method blank corrected results is described in Attachment 5.

6.9 Ongoing Precision and Recovery Standard (OPR)

The ongoing precision and recovery standard (OPR) is created by adding known amounts of parameters of interest to an aliquot of a blank matrix. The OPR is used to evaluate the effect of the analytical process of the recovery of analytes. The OPR must be established for every batch of samples extracted and analyzed and must meet the recovery and %RSD limits listed in Attachment 4 of this procedure. If the OPR criteria are not met and reanalysis was not performed, the laboratory performance and method accuracy are in question. If recoveries for more than half of the compounds in the OPR analysis are below the acceptance range, the laboratory has shown that it cannot meet program-required detection limits. When OPR criteria are not met the CB12 series of reason codes are applied to all associated samples in the extraction and analytical batch.

7. RECORDS

Records generated by this procedure will be submitted to the Environmental Protection Records Management Office for document management in accordance with Institutional Records Management Procedure, P1020-1 and EP-AP-10003, Records Management.

- Completed Data Validation Cover Sheets (Attachment 1)
- Completed Chlorinated Biphenyl Congener Analytical Data Validation Checklists (Attachment 2)

8. REFERENCES

EP-AP-10003, Records Management

ER-AP-20304, Change Control for Data in the Environmental Information Management (EIM) Database

P1020-1, Laboratory Records Management

9. ATTACHMENTS

Attachment 1: Data Validation Cover Sheet
Attachment 2: Dioxin/Furan Analytical Data Validation Checklist
Attachment 3: Theoretical Ion Abundance Ratios and Quality Control Limits for EPA Method 1668
Attachment 4: Quality Control Acceptance Criteria for Chlorinated Biphenyls in Calibration Verification, Initial Precision and Recovery, Ongoing Precision and Recovery, and Samples for EPA Method 1668
Attachment 5: Protocol for Method Blank Correction in PCBs Analyzed by Method 1668

ATTACHMENT 1

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Data Validation Cover Sheet

Section I.

Request Number: _____ Validation Date: _____ Lab Code: _____

Contract Laboratory Name: _____

Validator: _____ Organization: _____

Analytical Suite (Check All That Apply):

☐ **TPH-GRO**	☐ **High Explosives**	☐ **Dioxin Furans**	☐ **LCMSMS Perchlorates**
☐ **TPH-DRO**	☐ **Metals & Cyanide**	☐ **PCB Congeners**	☐ **Organochlorine Pesticides/Polychlorinated Biphenyls**
☐ **General Chemistry**	☐ **Radiochemistry**	☐ **LCMSMS High Explosives**	

☐ **Other (Describe):** _____

_____

Section II. Completeness Check

YES	NO	N/A	(check one)	YES	NO	N/A	(check one)
☐	☐	☐	1. Chain-Of-Custody Form(S)	☐	☐	☐	6. Raw/BSS Data
☐	☐	☐	2. Case Narrative	☐	☐	☐	7. Quality Control Forms
☐	☐	☐	3. Sample Result Forms	☐	☐	☐	8. Quantitation Reports
☐	☐	☐	4. Sample Chromatograms	☐	☐	☐	9. TICS Forms
☐	☐	☐	5. Standard Chromatograms	☐	☐	☐	10. TICS Mass Spectra

Comments/problems noted (include information about requests for further information submitted to the contract laboratory and agreed-upon date of resolution and contract laboratory point of contact):

Validator's Signature: _____ Date: _____

(Attach additional comment sheets as necessary)

ATTACHMENT 2

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Yes	No	N/A	Chlorinated Biphenyl Congener Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Holding Time and Sample Preservation					
☐	☐	☐	1. The preserved sample was extracted > 365-day holding time. (AV)	R, CB9b	J, CB9b
☐	☐	☐	2. The sample extract was analyzed > 365-day holding time. (AV)	R, CB9b	J, CB9b
Calibration – Initial and Continuing					
☐	☐	☐	3. The affected results were not analyzed with a valid 5-point calibration curve and/or a standard at the reporting limit.	UJ or R, CB7	J, CB7
☐	☐	☐	4. The affected analytes were analyzed with an initial calibration curve with multipoint calibration correlation coefficient is <0.995. Isotope dilution shall be used for calibration of the toxics and beginning and ending LOC CBs. A 5- or 6-point calibration is prepared for each native congener.	N/A, CB7a	J, CB7a
☐	☐	☐	5. The %RSD for any target compound is >20% but ≤40%.	UJ, CB7a	J, CB7a
☐	☐	☐	6. The %RSD for any target compound is >40% but ≤60%.	R, CB7a	J, CB7a
☐	☐	☐	7. The %RSD for any target compound is >60%.	R, CB7a	R, CB7a
☐	☐	☐	8. The r2 value for any target compound is <0.99 but ≥0.9.	N/A, CB7a	J, CB7a
☐	☐	☐	9. The r2 value for any target compound is <0.90 but ≥0.8.	UJ, CB7a	J, CB7a
☐	☐	☐	10. The r2 value for any target compound is <0.8.	R, CB7a	J, CB7a

ATTACHMENT 2

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Yes	No	N/A	Chlorinated Biphenyl Congener Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Calibration – Initial and Continuing (continued)					
☐	☐	☐	11. The affected analytes did not meet the ion abundance ratios criteria in the initial calibration and/or continuing calibration verification (CCV). Calibration using internal standards is used for determination of native CBs for which a labeled compound is not available. For these CBs, calibration is performed at a single point. Compounds should be quantitated using the appropriate reference internal standard listed in Table 2 of the method. Ion abundance ratios must meet the criteria in Attachment 3 of this procedure, Theoretical Ion Abundance Ratios and QC Limits for EPA Method 1668, or must be within 15% of the theoretical ratio of the ion monitored.	N/A	R, CB7b
☐	☐	☐	12. The initial calibration verification (ICV) and/or CCV were recovered outside the method limits (see CB7a for initial calibration verification specifications). At the beginning of each 12-hour period during which analysis is performed, calibration is verified for all native CBs and labeled compounds. The ion abundance ratios for all CBs must be within the limits in Attachment 3 of this procedure, and all compounds must meet the calibration verification recovery limits listed in Attachment 4 of this procedure, Quality Control Acceptance Criteria for Chlorinated Biphenyls in Calibration Verification, Initial Precision and Recovery, Ongoing Precision and Recovery, and Samples for EPA Method 1668. RRTs of native CBs and labeled compounds in the calibration verification must be within ±0.5% of the mean RRT determined from the initial calibration or most recent calibration verification standard. The diluted combined 209 congener solution must be analyzed as a final step in the calibration verification and must meet the minimum analysis and resolution specifications of the method.	UJ, CB7c	J, CB7c

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Yes	No	N/A	Chlorinated Biphenyl Congener Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Calibration – Initial and Continuing (continued)					
☐	☐	☐	13. If the verification limits are not met for any calibration verification compound and the recovery is above the verification limits, qualify all associated detects as J+.	UJ, CB7c	J+, CB7c
☐	☐	☐	14. The ion abundance ratio for any calibration verification compound is outside of the method limits.	UJ, CB7c	J, CB7c
☐	☐	☐	15. The verification limits are not met for any calibration verification compound and the recovery is below the verification limits, and ≥10%.	UJ, CB7c	J-, CB7c
☐	☐	☐	16. The verification recovery is <10%.	R, CB7c	R, CB7c
☐	☐	☐	17. The ICV and/or CCV were not analyzed at the appropriate method frequency. At the beginning of each 12-hour period during which analysis is performed, calibration is verified for all native CBs and labeled compounds.	UJ, CB7d	J, CB7d
☐	☐	☐	18. Required calibration information is missing or samples were analyzed on an expired calibration. Contact the SMO or external laboratory for information.	R, CB7f	R, CB7f
☐	☐	☐	19. The instrument performance sample did not meet either the resolution or the retention window criteria. Gas chromatograph/mass spectrometer (GC/MS) instrument performance checks are performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific. Conformance is determined using standard materials; therefore, these criteria should be met in all circumstances.	R, CB16	R, CB16
☐	☐	☐	20. The required instrument performance sample information is missing. Contact the SMO or external laboratory for information.	R, CB16c	R, CB16c

ATTACHMENT 2

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Yes	No	N/A	Chlorinated Biphenyl Congener Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Blanks					
☐	☐	☐	21. The sample result is ≤5 times the concentration of the related analyte in the method blank. (AV)	N/A	U,CB4
☐	☐	☐	22. The affected analytes are considered estimated and biased high because this analyte was identified in the method blank, but was >5 times the concentration in the method blank. (AV)	N/A	J, CB4a
☐	☐	☐	23. The sample result is ≤5 times the concentration of the related analyte in the trip blank, rinsate blank, or equipment blank. (AV)	N/A	U, CB4d
☐	☐	☐	24. Required method blank information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, CB4e	R, CB4e
☐	☐	☐	25. The absence of sample carry-over must be determined and verified. If any target analyte found in the sample requiring dilution exceeded the high calibration standard and was also found in the following sample at a concentration < 5x the reporting limit, qualify the result for that analyte in the second sample.	N/A	R, CB4f
Surrogates					
☐	☐	☐	26. The labeled compound recovery is <10 percent recovery (%R).	R, CB3	J-, CB3
☐	☐	☐	27. The labeled compound is less than the lower acceptance limit (LAL) but ≥10%R. The recovery of each labeled compound must be within the limits in Table 6 of the method.	UJ, CB3a	J-, CB3a
☐	☐	☐	28. The labeled compound recovery is greater than the upper acceptance limit (UAL). The recovery of each labeled compound must be within the limits listed in Table 6 of the method.	N/A	J+, CB3b
☐	☐	☐	29. Required labeled compound information is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, CB3d	R, CB3d

ATTACHMENT 2

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Yes	No	N/A	Chlorinated Biphenyl Congener Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Analyte Identification					
☐	☐	☐	30. The retention time criteria were not met. The absolute retention time (RT) of chlorinated biphenyl (CB) 209 must be ≥55 minutes if the SPB-octyl column is used. If a GC column or column system is used instead of the SPB-octyl column, the absolute RT of CB 209 must be greater than or equal to the laboratory-established minimum RT for CB 209. If the laboratory has not established a minimum RT value for CB 209, the RT for CB 209 must be ≥55 minutes. If a GC column or column system was used instead of the SPB-octyl column and the absolute RT is less than the laboratory-established minimum RT for CB 209, or <55 minutes if the laboratory has not established a minimum RT. The absolute RTs of the labeled defining standard congeners in the verification test must be within ±15 seconds of the respective RTs in the calibration or, if an alternate column or column system is employed, within ±15 seconds of the respective RTs in the calibration for the alternate column or column system. The relative retention times (RRTs) of native CBs and labeled compounds in the verification test must be within their respective RRT limits or, if an alternate column or column system is employed, within their respective RRT limits for the alternate column or column system. The RRT of each CB must be within ±0.5% of the mean RRT determined from the initial calibration or ±0.5% of the RRT from the most recent calibration verification standard.	R, CB0	R, CB0
☐	☐	☐	31. Required retention time documentation is missing. Data may not be acceptable for use. Contact the Sample Management Office (SMO) or external laboratory for information.	R, CB0b	R, CB0b
☐	☐	☐	32. For identification of any CB or labeled compound, the ion abundance ratios must be within the limits specified in Attachment 4 of this procedure, or within ±15% of the calibration verification standard.	N/A	R, CB8
☐	☐	☐	33. The ion ratio documentation is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	N/A	R, CB8a

ATTACHMENT 2

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Yes	No	N/A	Chlorinated Biphenyl Congener Analytical Data Validation Checklist	Assign Qualifier Listed Below If Criterion = Yes	
(Check One)				Non-detected Analyte	Detected Analyte
Ongoing Precision and Recovery					
☐	☐	☐	34. The ongoing precision and recovery (OPR) sample percent recovery was <10%.	R, CB12	J-, CB12
☐	☐	☐	35. The OPR sample percent recovery was less than the LAL but >10%.	UJ, CB12a	J-, CB12a
☐	☐	☐	36. The OPR sample percent recovery was greater than the UAL.	N/A	J+, CB12b
☐	☐	☐	37. The OPR sample documentation is missing. Data may not be acceptable for use. Contact the SMO or external laboratory for information.	R, CB12c	R, CB12c
☐	☐	☐	38. More than half of the compounds in the OPR analysis exceed the acceptance range.	UJ, CB12d	J, CB12d
☐	☐	☐	39. More than half of the compounds in the OPR analysis are below 10%.	R, CB12d	J-, CB12d
Analyte Quantitation					
☐	☐	☐	40. The non-detected analytes have elevated detection limits and may not meet project data-quality objectives because the sample was diluted without any target analytes identified as a result of matrix interference. Reject non-detected results if the analytical laboratory cannot provide proof for matrix interference.	UJ, R, CB15	NA
☐	☐	☐	41. The Los Alamos National Laboratory (LANL) project chemist identified quality deficiencies in the reported data that require further qualification. This code can be used only under advisement by the LANL project chemist.	UJ, R, CB19	J, R, CB19
☐	☐	☐	42. Qualification of data via data validation did occur, however no data quality control requirements in this procedure were applicable. Adhere to the external laboratory qualifiers found within the Form 1 analytical data summary sheets generated by the external laboratory. (AV)	U, U_LAB	J, J_LAB NQ, NQ (No qualification)

ATTACHMENT 3

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Theoretical Ion Abundance Ratios and QC Quality Control Limits for EPA Method 1668

Chlorine Atoms	m/zs Forming Ratio	Theoretical Ratio	Lower QC Limit	Upper QC Limit
1	m/m+2	3.13	2.66	3.60
2	m/(m+2)	1.56	1.33	1.79
3	m/(m+2)	1.04	0.88	1.20
4	m/(m+2)	0.77	0.65	0.89
5	(m+2)/(m+4)	1.55	1.32	1.78
6	(m+2)/(m+4)	1.24	1.05	1.43
7	(m+2)/(m+4)	1.05	0.89	1.21
8	(m+2)/(m+4)	0.89	0.76	1.02
9	(m+2)/(m+4)	0.77	0.65	0.89
10	(m+2)/(m+4)	0.69	0.59	0.79

ATTACHMENT 4

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Quality Control Acceptance Criteria for Chlorinated Biphenyls in Calibration Verification, Initial Precision and Recovery, Ongoing Precision and Recovery, and Samples[a] for EPA Method 1668

Cogener	IUPAC Number[b]	Test Conc (ng/mL)	Calibration Recovery[c] (%)	Initial Precision and Recovery		OPR (T)	Labeled Compound Recovery in Samples (%)
				RSD (%)	X (%)		
2-MoCB	1	50	70-130	40	60-140	50-150	
4-MoCB	3	50	70-130	40	60-140	50-150	
2,2'-DiCB	4	50	70-130	40	60-140	50-150	
4,4'-DiCB	15	50	70-130	40	60-140	50-150	
2,2',6-TrCB	19	50	70-130	40	60-140	50-150	
3,4,4'-TrCB	37	50	70-130	40	60-140	50-150	
2,2',6,6'-TeCB	54	50	70-130	40	60-140	50-150	
3,3',4,4'-TeCB	77	50	70-130	40	60-140	50-150	
3,4,4',5-TeCB	81	50	70-130	40	60-140	50-150	
2,2',4,6,6'-PeCB	104	50	70-130	40	60-140	50-150	
2,3,3',4,4'-PeCB	105	50	70-130	40	60-140	50-150	
2,3,4,4',5-PeCB	114	50	70-130	40	60-140	50-150	
2,3',4,4',5-PeCB	118	50	70-130	40	60-140	50-150	
2',3,4,4',5-PeCB	123	50	70-130	40	60-140	50-150	
3,3',4,4',5-PeCB	126	50	70-130	40	60-140	50-150	
2,2',4,4',6,6'-HxCB	155	50	70-130	40	60-140	50-150	
2,3,3',4,4',5-HxCB[d]	156	50	70-130	40	60-140	50-150	
2,3,3',4,4',5'-HxCB[d]	157	50	70-130	40	60-140	50-150	
2,3',4,4',5,5'-HxCB	167	50	70-130	40	60-140	50-150	
3,3',4,4',5,5'-HxCB	169	50	70-130	40	60-140	50-150	
2,2',3,4',5,6,6'-HpCB	188	50	70-130	40	60-140	50-150	
2,3,3',4,4',5,5'-HpCB	189	50	70-130	40	60-140	50-150	
2,2',3,3',5,5',6,6'-OcCB	202	50	70-130	40	60-140	50-150	
2,3,3',4,4',5,5',6-OcCB	205	50	70-130	40	60-140	50-150	
2,2',3,3',4,4',5,5',6-NoCB	206	50	70-130	40	60-140	50-150	
2,2',3,3',4,5,5',6,6'-NoCB	208	50	70-130	40	60-140	50-150	

ATTACHMENT 4

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Cogener	IUPAC Number[b]	Test Conc (ng/mL)	Calibration Recovery[c] (%)	Initial Precision and Recovery		OPR (T)	Labeled Compound Recovery in Samples (%)
				RSD (%)	X (%)		
DeCB	209	50	70-130	40	60-140	50-150	
$^{13}C_{12}$-2-MoCB	1L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-4-MoCB	3L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2'-DiCB	4L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-4,4'-DiCB	15L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',6-TrCB	19L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	50-150	50	35-135	30-140	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	50-150	50	35-135	30-140	25-150

ATTACHMENT 4

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Cleanup Standard							
$^{13}C_{12}$-2,4,4'-TrCB	28L	100	60-130	45	45-120	40-125	30-135
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	45	45-120	40-125	30-135
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	45	45-120	40-125	30-135

[a] Quality control acceptance criteria for initial precision and recovery, ongoing precision and recovery, and samples based on a 20-µL extract final volume.

[b] Suffix "L" indicates labeled compound.

[c] Refer to Section 15.3 of the method.

[d] Polychlorinated biphenyls 156 and 157 are tested as the sum of two concentrations.

ATTACHMENT 5
Protocol for Method Blank Correction in PCBs Analyzed by Method 1668

EPA Method 1668 Blank Correction

Introduction

This protocol describes the process for blank correcting analytical data generated using Method 1668 by Los Alamos National Laboratory (LANL). This blank correction protocol will be used to perform method blank subtraction for liquid (aqueous) samples analyzed by the EPA Method 1668. Method blank subtraction is performed by the analytical laboratory. The analytical laboratory will provide method blank corrected results in the electronic data deliverable (EDD).

Method Blank Correction

The presence of background PCBs is a significant issue when using Method 1668. "Industrial processes, urban incineration, leaking electrical transformers, hazardous waste accidents, and improper waste disposal practices have released appreciable quantities of PCBs into the environment. This contamination has resulted in the global distribution of these compounds via the atmosphere and their ubiquitous presence in ambient air." (Ferrario, Byrne et al. 1997)

Because of their ubiquitous presence in the environment at concentrations that are detectable using EPA Method 1668, detectable baseline concentrations of PCBs are introduced into samples and quality control samples in the analytical laboratory. When determining baseline concentrations of PCBs a statistically based method blank subtraction process is recommended.

To accomplish method blank subtraction the average plus two standard deviations for the chosen method blank population is subtracted from the analytical result for each congener. The average plus two standard deviations calculated from ten or more method blanks is called the method blank correction value (MBCV). The MBCV is subtracted from each congener result to obtain the method blank corrected result (MBCR).

The basis for using the average plus two standard deviations to calculate the MBCV is in section 17.6.1.4.4 in Method 1668. These method revisions reference a paper on managing background contamination (Ferrario, Byrne et al. 1997).

In this document, when reference is made to "congeners" it is to be understood that the statement applies to individual congeners as well as coeluting congeners.

Calculating the MBCV

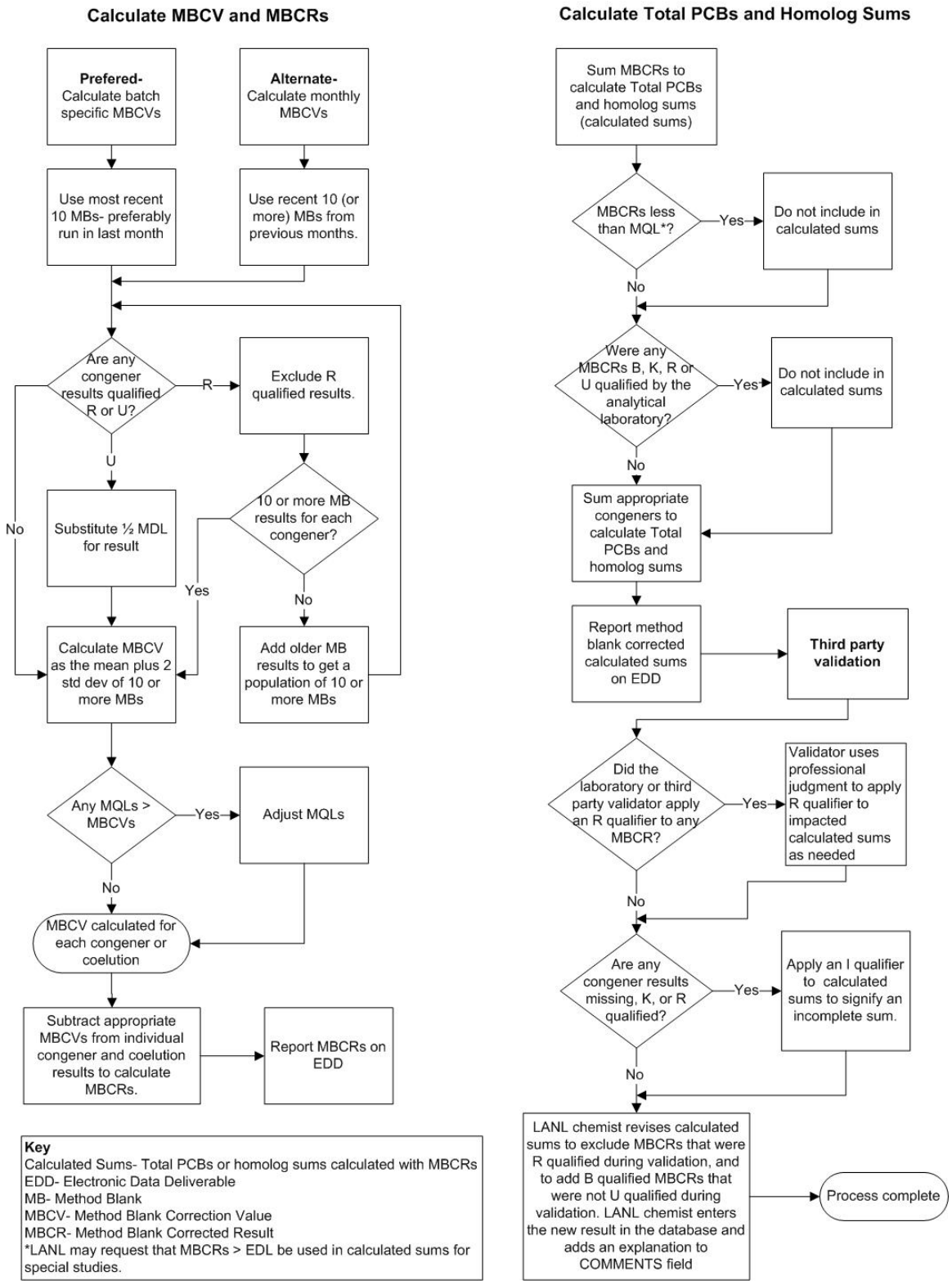
A MBCV will be calculated for each congener. The MBCV is calculated as the average plus two standard deviations for ten or more method blanks.

The procedure for calculating the MBCV is shown in the flow chart in Figure 1. The analytical laboratory will provide only method blank corrected results in the EDD and only method blank corrected results will be transferred to the pubic in the IntellusNM database. The method blanks used to generate the MBCV must be analyzed during the same period that samples are analyzed, ideally over a one month period. If 10 method blanks are not run in a one month period the previous 10 method blanks run by the analytical laboratory, without regard for the time frame over which they were run, will be used. Method blanks used in this calculation will be reported down to the MDL or EDL as stipulated by the analytical method.

The data package provided by the analytical laboratory will include the raw, uncorrected results. The data package will provide sufficient information to recreate the calculation of the method blank corrected results. The data package will identify the method blank results used in the calculation and will provide the MBCV for each congener.

Both the raw results and the MBCRs will be provided in the data package. The raw, uncorrected results will not be provided in the EDD.

Figure 1. Flow Diagram of LANL Process for Method Blank Subtraction



Laboratory Qualification

The B qualifier is applied to sample results that are considered not detected due to method blank contamination. The B qualifier is only applied to sample results within the batch containing the method blank with elevated results. A method blank is not used to B qualify itself. The MBCV is calculated using method blanks that were run with previous batches.

EPA guidelines for data validation for Method 1668 consider the impacts of blank contamination on the batch. EPA Region III guidance states, “Any measurement of PCB congeners in a sample that is also measured in any associated blank (lab or field), and the sample concentration is less than 5 times the blank concentration, the result in the sample is qualified B due to blank contamination.” (EPA 2004, Section 7.3) This is referred to as the “5X rule.”

The 5X rule addresses unusually elevated batch specific contamination that is above the statistically generated ambient background using the method blank correction process. The MBCR for the method blank will be used when applying the 5X rule. The method blank MBCR is compared to the sample MBCR when applying the 5X rule. Only individual congener results will be validated according to the 5X rule. The 5X rule is not applied to Total PCBs or homolog sums.

The Q qualifier is used when the laboratory reports congener results that are analyzed on a GC column that does not meet the method requirements for GC resolution AND the laboratory does not confirm those results on a secondary column capable of meeting the method requirements. The Q qualifier indicates that the analysis did not meet method requirements for GC resolution. However, the reported concentration does represent a coelution of PCBs rather than interferences. As such, it is included in the calculated sums. PCBs from different homolog groups do not coelute and will not lead to errors in the homolog sums.

The K qualifier is used by the analytical laboratory to identify congener results with a peak detected, but do not meet quantification criteria. The result reported represents the estimated maximum possible concentration.

The J qualifier is used by the analytical laboratory to identify congener results that are greater than the MDL or EDL and less than the reporting limit (RL)

Calculating the MBCV with Qualified Results

Table 1 shows how qualified results are used in the method blank correction process. Method blank results qualified as J, K, and Q are used as reported when calculating the MBCV. These results are considered the best estimate of the true congener value. One half the MDL, or EDL, is substituted for non-detect (U qualified) congener results. R qualified results are not used in calculating the MBCV and do not count towards the ten method blanks required to calculate the MBCV.

Table 1. Data Qualifiers

Qualifier	Description	Use to calculate MBCV[a]	Include in homologue and total PCBs
B	Analyte was measured in a lab or field blank at less than 5 times the blank concentration.	NA[b]	No
J	Qualified as estimated. Result is between the RL and the MDL.	Yes	Yes
K (EMPC)	Peak detected, but did not meet quantification criteria; result reported represents the estimated maximum possible concentration.	Yes	No
Q	Single column result, not confirmed by second column when using non-standard column.	Yes	Yes
R	The data are unusable (compound may or may not be present.)	No	No
U	Non-detect	Substitute ½ MDL	No

[a]MBCV – method blank correction value

[b]NA- Not Applicable

Qualified Results Used to Calculate Sums

Total PCBs, homolog sums, and Toxicity Equivalents (TEQs) are calculated from the summation of individual congeners in this discussion. Table 1 shows how qualified results are to be used when summing congener results. Only unqualified results, and J and Q qualified results are used when calculating sums. B, K, R, or U qualified results are excluded from the calculated sums.

Method Blank Corrected Results

Method blank correction does not affect the laboratory's detection limits or reporting limits. (Note that if EDLs are reported by the analytical laboratory they will be captured in the MDL field.)

Qualified Results Used to Calculate Total PCBs or Homolog Sums

If a congener's result is qualified as B based on the 5X rule applied based on raw results then that congener's MBCR is not included in the Total PCBs or homolog MBCR sums. Similarly, sample results qualified as K, R, or U are not included in Total PCBs or homolog sums. Occasionally, congener results are missing. When congener results are missing or are qualified as K or R the calculated sums that would have included those results will be identified as incomplete estimates of the calculated sum during third party

validation. Congener results that are B or U qualified represent non-detects and do not lead to the calculated sum being identified as incomplete.

The LANL procedure is shown in Figure 1. LANL will censor MBCRs at the MDL or the RL depending on the intended use of the data. The analytical laboratory must be notified of the censoring criteria required.

Generally, results to be used for compliance purposes, such as samples collected for the NPDES Individual Permit (IP) for stormwater releases, LANL will report results less than the RL as <RL and will not include these results in the calculated sums per guidance in the IP.

For results to be used for investigational purposes, for example results to be used in the background study (LANL 2009), LANL may choose to report results greater than the MDL or EDL. In this case congener results less than the MDL or EDL will be reported as <MDL or <EDL respectively. The calculated sums will include all results greater than the MDL or EDL.

MQLs will be updated by the analytical laboratory every six months or less (EPA 2009). If an MBCV is found to be greater than the RL for a given congener the RL will be adjusted when the discrepancy is observed. This is consistent with guidance provided in Method 1668 (EPA 2003) and in the IP (EPA 2009). The relevant sections of Method 1668 and the IP and are provided in Appendix A.

The analytical laboratory EDD will include Total PCBs and homolog sums calculated with the MBCRs excluding results less than the RL (or less than the MDL or EDL) and excluding results qualified with B, K, R, or U.

Obtaining Raw, Uncorrected LANL Data

If EPA, New Mexico Environment Department, other regulator, agency, community group, or individual wishes to review the method blank correction process or the raw, uncorrected data they will request such information from the LANL Point of Contact (POC) for the sample set(s) in question. The POC will request that LANL Sample Management Office assemble the appropriate data set(s), data packages, and summaries of the method blank correction process as appropriate.

Field, Equipment, or Trip Blank Correction

Field, equipment, and trip blanks will be method blank corrected. Field, equipment, and trip blanks are used to evaluate data quality.

Validation

Only “I" or R validation qualifiers will be applied to calculated homologue and total PCB sums during third party validation. (Note that in this document only “I” qualifiers are identified with quotation marks to make this document easier to read.)

If a sample includes missing congener results or congener results qualified with K or R the calculated sums will have an “I” qualifier applied to signify that the result is an incomplete sum. “I” qualifiers are applied to the VALID_FLAG_CODE field by the third party validators.

If the validator agrees that the B qualifier was correctly applied by the analytical laboratory the B qualified data is U qualified during validation. This U qualified MBCR is treated as a non-detect and is not included in a calculated sum. This does not cause an “I” qualifier to be applied to the calculated sum as the B qualified MBCR is a non-detect. It is not missing.

It may be appropriate to R qualify a calculated sum when the analytical laboratory or a third party validator applies an R qualifier to one or more congener results. Minor retention time shifts or other issues may cause the validator to apply an R qualifier. Such minor issues may not justify rejecting the calculated sum. In this case the validators will use professional judgment in applying R qualifiers to calculated sums.

In rare cases the third party validation may not confirm that a B qualifier was appropriately applied by the analytical laboratory. In this case no U qualifier is applied by the validator. When this occurs the LANL chemist will modify the calculated sum to include the B qualified data that was not included in the calculated sum by the analytical laboratory.

Conclusion

Method 1668 is the only EPA method that allows method blank subtraction. The ubiquitous nature of PCBs makes method blank subtraction an essential part of low level PCB analyses and is applied independently of the 5x rule for qualification of analytical results for batch specific PCB congener qualification. This document is to be used as a reference to guide analytical laboratories and data management organizations management of data generated using this method.

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