CP2-ES-5103/FR1

Polychlorinated Dibenzodioxins/Polychlorinated Dibenzofurans Analyses Data Verification and Validation Paducah Gaseous Diffusion Plant, Paducah, Kentucky

FOUR RIVERS NUCLEAR PARTNERSHIP, LLC

This document is approved for public release per review by:

N/A	N/A
FRNP Classification Support	Date

Polychlorinated Dibenzodioxins/Polychlorinated Dibenzofurans Analyses Data Verification and Validation Paducah Gaseous Diffusion Plant, Paducah, Kentucky

Date Issued—December 2017

U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

Prepared by
FOUR RIVERS NUCLEAR PARTNERSHIP, LLC,
managing the
Deactivation and Remediation Project at the
Paducah Gaseous Diffusion Plant
under Contract DE-EM0004895

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APPROVALS

Polychlorinated Dibenzodioxins/Polychlorinated Dibenzofurans Analyses Data Verification and Validation
Paducah Gaseous Diffusion Plant
Paducah, Kentucky

CP2-ES-5103/FR1

Lisa Crabtree
Environmental Monitoring Manager

Date 12/12/17

Curt Walker
Environmental Services Project Director

Date 12/13/17

DOE Approval Letter: N/A

Date: N/A

Nuclear Safety Documentation: N/A

Non-intent changes per CDL – USQ not required

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REVISION LOG

REVISION NUMBER	DATE	DESCRIPTION OF CHANGES	PAGES AFFECTED
FR0	11/14/17	Bluesheet	ALL
FR1	12/13/17	Non-intent Changes for Bluesheet Incorporation	ALL

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ACRONYMS

CLP	Contract Laboratory Program
COC	chain of custody
CRQL	Contract Required Quantitation Limit
DQO	data quality objective
EDD	electronic data deliverable
EMPC	estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
IDL	instrument detection limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MB	method blank
MS	matrix spike
MSD	matrix spike duplicate
NIST	National Institute of Standards and Technology
PCDD	polychlorinated dibenzodioxins
PCDF	polychlorinated dibenzofurans
PCDPE	polychlorinated diphenyl ether
PFK	perfluorokerosene
PQL	practical quantitation limit
QAPP	quality assurance project plan
QC	quality control
RDL	required detection limit
RF	response factor
RRF	relative response factor
RL	reporting limit
RPD	relative percent difference
RR	relative response
RRT	relative retention time
RT	retention time
SDG	sample delivery group
SMO	Sample Management Office
SOW	statement of work
TCDD	tetrachloradibenzodioxin
TEF	toxicity equivalency factor
WCRM	well characterized reference material
WDM	window defining mixture
%RSD	percent relative standard deviation

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DEFINITIONS

NOTE 1: Qualifier definitions are listed in Appendix A.

NOTE 2: In this procedure, the words "shall" and "must" are used to denote a requirement; the word "should" is used to denote a recommendation; and the word "may" is used to denote permission (neither a requirement nor a recommendation). In conformance to this procedure, all steps shall be performed in accordance with its requirements, but not necessarily with its recommendations; however, justification must be documented for deviations from recommendations.

AFFECTED SAMPLE RESULT—A sample result is considered to be affected when it is significantly influenced by a quality deficiency and is qualified accordingly through analytical data validation.

ANALYTICAL DATA VALIDATION—Analytical data validation is a systematic process, performed independently from the data generator, which applies a defined set of performance-based criteria to a body of data that may result in physical qualification of the data. Data validation occurs prior to drawing a conclusion from the body of data.

ANALYTICAL DATA VERIFICATION—Analytical data verification is a systematic process of evaluating the completeness, correctness, consistency, and compliance of a set of facts against a standard or contract that is performed either by the data generator or by an entity independent to the data generator.

BATCH—A batch is a group of samples prepared at the same time in the same location using the same method, not to exceed 20 samples of similar matrix.

CASE—A finite, usually predetermined number of samples, that have been collected over a given time period from a particular site. A case consists of one or more sample delivery groups.

CHAIN OF CUSTODY (COC)—The history of the transfer of samples from the time of sample acquisition through archival and disposal of samples. COC documentation is required as evidence of sample integrity.

CONTINUING CALIBRATION VERIFICATION (CCV)—A standard solution analyzed at a specified frequency during an analytical run to assure continued validity of the calibration curve.

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL)—The CRQL is the minimum level of detection acceptable under the current Contract Laboratory Program contract.

CORRECTABLE PROBLEM—Correctable problems are deficiencies within data packages that may be rectified through consultation with the laboratory. Correctable problems may be revealed during both data verification and data validation. Correctable problems revealed during verification are those deficiencies that can be addressed by obtaining additional information from the laboratory. Correctable problems revealed during validation are those deficiencies with analyses that can be solved either by a second preparation and/or by analysis of a sample.

DATA QUALITY OBJECTIVES—DQOs are qualitative and quantitative statements derived from the outputs of each step of the DQO process that specify the study objectives, domain, limitations, most appropriate type of data to collect, and specify the levels of decision error that will be acceptable for the decision.

DATA QUALITY OBJECTIVES PROCESS—The DQO process is a quality management tool based on the scientific method and developed by the U.S. Environmental Protection Agency to facilitate the planning of environmental data collection activities. The DQO process enables planners to focus their planning efforts by specifying the use of the data (the decision), the decision criteria (action level), and the decision maker's acceptable decision error rates.

HOLDING TIME—Holding time, as described in this procedure, is defined as the period of time between sample collection and sample activity determination.

INITIAL CALIBRATION—Initial calibration, as described in this procedure, is defined as the standardization of a gas chromatography/mass spectrometry instrument against a traceable standard of known identity and quantity. This standardization prevails until such time as analytical conditions are deemed out of acceptable control limits.

LABORATORY CONTROL SAMPLE—The LCS is a control sample of known composition. Aqueous and solid LCSs are analyzed using the same preparation, reagents, and method employed for field samples.

LABORATORY DUPLICATE—The laboratory duplicate is a randomly chosen split of an analytical sample into two aliquots prior to sample preparation. The purpose of a laboratory duplicate is to monitor the precision of the analytical method.

MATRIX SPIKE (MS)—The MS is a split of a field-originating analytical sample in which one half of the split is spiked with a known amount of radionuclide of interest prior to sample preparation. The purpose of a matrix spike is to measure the effect of interferences from the sample matrix that will preclude accurate quantitation by the instrumentation.

METHOD BLANK—The method blank is a laboratory-generated sample of the same matrix as the analytical samples, but in absence of the analyte of interest. The purpose of a method blank is to monitor the presence of contamination of the analyte of interest in the sample preparation and analysis processes.

NONCORRECTABLE PROBLEM—Noncorrectable problems are deficiencies within data package that preclude the evaluation of data quality by predefined criteria. Noncorrectable problems may be revealed during both data verification and data validation.

QUALITY-INDICATOR SAMPLE—Quality-indicator samples are those samples made ready in the laboratory which provide direct or indirect evaluation of the status of the analytical system and resulting data quality. Collectively, quality indicator samples are the laboratory control sample, laboratory duplicate, matrix spike, and method blank.

PREPARATION BATCH—A preparation batch is a group of sample aliquots prepared together at the same time using the same method and related to the same quality control samples.

RELATIVE PERCENT DIFFERENCE (RPD)—RPD is the measure of precision between two values, defined as the absolute value of the difference between two values divided by the mean of the two values.

RELATIVE RESPONSE FACTOR (RRF)—RRF represents the response of a compound to an analytical instrument relative to the response of an associated standard.

RELATIVE STANDARD DEVIATION (RSD)—RSD is the measure of precision between multiple values, defined as the standard deviation of multiple values divided by the mean of the values.

REQUIRED DETECTION LIMIT (RDL)—The RDL is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

SAMPLE DELIVERY GROUP (SDG)—An SDG is defined by one of the following, whichever occurs first: (1) case of field samples; (2) each 20 field samples within a case; (3) each 14-day calendar period during which field samples in a case are received, beginning with receipt of the first sample in the SDG.

SAMPLE QUANTITATION LIMIT (SQL)—SQLs are detection limits based on the RDL that have been modified due to deviations from analytical method specifications such as sample weight and extract volume or due to dilution or percent moisture.

SAMPLE RESULT—A sample result, as described in this procedure, is a numeric denotation of the concentration, amount, or activity of a specific analytical parameter uniquely associated with an aliquot of environmental media.

STANDARD REFERENCE MATERIAL (SRM)—An SRM is a material or substance of which one or more properties are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. The SRM is characterized by the U.S. National Institute of Standards and Technology (NIST) or other certified testing authority, and issued with a certificate providing the results of the characterization.

STATEMENT OF WORK (SOW)—The validation SOW is a document prepared to function as the mechanism by which validation requirements are communicated from the project to the validation organization.

TRACEABLE REFERENCE MATERIAL (TRM)—A TRM is a NIST prepared standard reference material or a sample of known activity or concentration prepared from a NIST standard reference material (derived standard material).

TURN-AROUND TIME—Turn-around time is contractually specified as the amount of time that elapses between laboratory receipt of the raw samples and subsequent data receipt by the client.

VALIDATION QUALIFIER—A qualifier is an alphabetic character physically or electronically associated with a discrete sample result during validation due to a data quality deficiency, which provides guidance in data usability.

VALIDATION STATEMENT OF WORK—The validation SOW is a document prepared to function as the mechanism by which validation implementation requirements are communicated from the project to the validation organization.

WELL CHARACTERIZED REFERENCE MATERIAL (WCRM)—The WCRM may be derived from a field sample which has been well characterized through multiple analyses, providing a high level of confidence of the concentration in the sample. The WCRM may be submitted to NIST for characterization and classification as a traceable reference material.

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1. INTRODUCTION

1.1 PURPOSE, SCOPE, AND APPLICATION

1.1.1 Purpose

This plan defines the minimum requirements, responsibilities, and methodology for the volatile polychlorinated dibenzodioxin (PCDD)/polychlorinated dibenzofuran (PCDF) analyses data verification and validation.

This plan provides requirements for developing and implementing a validation methodology for PCDD/PCDF SW-846 8290A and U.S. Environmental Protection Agency (EPA) 1613B analytical methods primarily for analytes in aqueous and soil/sediment matrices. It is flexible enough to allow evaluation of data usability for project-specific data quality objectives (DQOs). Data produced by analytical methods for this procedure provides limited guidance (i.e., Appendix A of 40 *CFR* Part 136, *Protection of Environment*, Appendix A, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," method 613, or SW-846 ,method 8280) may necessitate development of modified criteria from this plan; however, the general data validation strategy outlined in this document should be applicable.

Specifications in this plan should be incorporated into project documentation such as the quality assurance project plan (QAPP), into contractual statements of work (SOWs) between the project and the analytical laboratories, and into contractual validation SOWs between the project and the organization chosen to validate the data. If data validation is performed by individuals within the project, the SOW is not required, but a mechanism to specify data validation requirements is recommended. This plan shall be used as a baseline to create project-specific reports needed to perform PCDD/PCDF data verification and validation.

1.1.2 Scope and Application

This plan applies to PCDD/PCDF data verification and validation activities performed by the Sample Management Office (SMO) or its subcontractors.

2. RESOURCES

- Analytical Method
- Laboratory SOW
- Data Validation SOW
- Project-Specific QAPP

3. PREPERFORMANCE ACTIVITIES

Project manager shall ensure that individuals who perform PCDD/PCDF data verification and validation are knowledgeable of the latest version of this plan before beginning any activities.

4. GENERAL INFORMATION

4.1 REQUIRED ELEMENTS OF REVIEW AND VALIDATION

To the extent possible, all laboratory data packages will be produced by the laboratory performing the analysis as Level IV (i.e., EPA Stage 4) laboratory data deliverables. One hundred percent of the data deliverables will undergo a data quality review and validation comparable to a Level I validation (depending on analyte and method). As required by project-specific requirements, the data review and validation effort may be increased to cover a Level II, Level III, or a full Level IV validation of the data package. The activities included in the review and validation effort for each level are provided in Table 1.

Table 1. Required Elements of Review and Data Validation

Report Elements to be Reviewed*	**Level I**	**Level II**	**Level III**	**Level IV**
Cover/Signature Page	x	x	x	x
Table of Contents			x	x
Report Narrative	x	x	x	x
Executive Summary (if included)			x	x
Method Summary/Analyst Summary			x	x
Sample Summary/Sample Data Sheets	x	x	x	x
Shipping and Receiving Documents	x	x	x	x
Client Chain of Custody (COC)	x	x	x	x
Sample Receipt Checklist	x	x	x	x
Interlab COC (where applicable)		x	x	x
Internal COC (if required)			x	x
Glossary of Abbreviations	x	x	x	x
Quality Control (QC) RESULTS				
QC Association Summary		x	x	x
Laboratory Chronicle			x	x
Surrogate and/or Tracer and Carrier Recovery Report		x	x	x
Blank Reports		x	x	x
LCS Reports		x	x	x
MS/MSD and Duplicate Reports		x	x	x
Hold Times and Preservation Requirements	x	x	x	x
(Extended Data Deliverables/Forms)				
CLP-Like Organics				
SUMMARY FORMS			x	x
Summary Forms (Org I–X)			x	x
QC SUMMARY			x	x
QC Forms (Org I–IV, VIII)			x	x
SAMPLE DATA			x	x
Quant Rpt + Chro + Spectra				x
STANDARDS DATA			x	x
Calibration Forms (VI–VII; for GC, VIII–X)			x	x
(Quant + Chro follows each form set)				x
QC DATA			x	x
Tune			x	x
Blank Form I			x	x
Blank Quant Rpt + Chro + Spectra				x
LCS/LCSD Form I			x	x
LCS/LCSD Quant Rpt + Chro + Spectra				x

Table 1. Required Elements of Review and Data Validation (Continued)

Report Elements to be Reviewed*	Level I	Level II	Level III	Level IV
MS/MSD Form I			x	x
MS/MSD Quant Rpt + Chro +Spectra				x
GEL Permeation Data				x
Florisil Data				x
Logs—Instrument, Prep, Standard			x	x
CLP-Like Inorganics				
Cover Page			x	x
Sample Forms (I) (CLP-like)			x	x
Calibration + QC Forms (exp.: II–XIV)			x	x
Instrument Data				x
Preparation Data				x
SHIPPING/RECEIVING DOCUMENTS				
Internal COC (if required)			x	x
Interlab COC (where applicable)			x	x
Client COC	x	x	x	x
Sample Receipt Checklist	x	x	x	x

*Report elements listed represent common elements. The laboratory may provide more or less information as required by the method being analyzed. For example, those wet chemistry methods with no true calibration information will not have calibration forms included in the data package.

The requirements of the Level I and Level II review and validation effort will be referred to as "Data Verification" and will be performed by a member of the SMO. The requirements of the Level III and Level IV review and validation effort will be referred to as "Data Validation," and is typically performed by an entity external to the project. This can be an internal staff member that is not associated with the project, or it may be an independent third party external to Paducah. The following sections summarize the requirements of each type of review and validation efforts.

4.2 DATA VERIFICATION REQUIREMENTS

Data verification is defined as a systematic process, performed either by the data generator (on-site or fixed-base laboratory) or by an entity external to the data generator, which results in evaluation of the completeness, correctness, consistency, and compliance of a data set against a standard or contract.

If data verification is performed by the data generator, a project-level surveillance must be established by which the performance of the verification process is evaluated.

Data verification, at the project level, is conducted by an SMO representative to expedite the review process. If data verification is conducted independently of the data validator, it includes two activities. The first activity entails inventory of the data package to ensure compliance with the contract and SOW, in terms of the required deliverables. The second activity entails various checks of the data quality to determine the need for qualification. This process is commonly referred to as the "contractual screen" and is the beginning of the data validation process in that it encompasses the review of the Level I and Level II validation elements identified in Table 1 above. The data verifier will qualify data based on the review and validation elements in accordance with Section 5.0 of this plan. If the data set is being reviewed and validated at the Level III or IV requirements, then the data verifier will provide a copy of the data verification checklist to the data validator to expedite the validation process, or the data validator will perform both the data verification and the data validation processes.

Data verification should provide a mechanism for problem resolution with the laboratory; it should not be exclusively an after-the-fact identification of noncorrectable deficiencies.

A data verification checklist is completed by the data verifier and takes, as input, the steps in this plan that are listed as "Data Verification." The data verifier shall complete Form CP3-ES-5003-F03, "Data Verification Checklist," in accordance with CP3-ES-5003, *Quality Assured Data*, for all Level II, III, and IV validations.

4.3 ANALYTICAL DATA VALIDATION REQUIREMENTS

Analytical data validation, including laboratory data review, is defined as a systematic process, performed externally from the data generator, which applies a defined set of performance-based criteria to a body of data to determine the quality of reported results. Data validation is not performed by the analytical laboratory, and is independent from sampling, project management, or other decision making personnel for the project. Data validation provides a level of assurance based on a technical evaluation, that an analyte is present or absent and, if present, the level of uncertainty associated with the measurement. Analytical data validation for PCDD/PCDF methods includes a technical review of the laboratory data package specified in the laboratory SOW. Data validation incorporates an evaluation of sample custody, sample handling and preparation, holding times, instrument calibration, instrument performance, batch quality control (QC) samples [e.g., laboratory control sample (LCS)], the identification and quantitation of target analytes, performance standards (e.g., surrogates, internal standards) and the effect QC performance and/or deficiencies have on the quality of analytical sample data.

A data validation report that includes the results of data validation activities must be completed by the data validator for Level III and Level IV data packages and takes, as input, the data verification checklist (or equivalent) and the steps in this procedure that are listed as "Data Validation." Data validation requires that personnel performing it have the appropriate level of training and experience to ensure data review and qualification is completed in a reasonable manner and in accordance with industry practices. Professional judgment may be required when performing data validation. Where professional judgment is used, resulting in either qualification of data or data left unqualified, the rationale for the selection of this path will be fully documented in the data validation report. Documentation will include the following: citations from this plan, other industry standards, and/or the literature demonstrating the reasonableness of the evaluation.

The actions described in this plan must serve as the baseline for incorporation into project data verification/validation activities. Project-specific procedures applying to analytical methods not covered in this document must be reviewed and approved prior to use.

Implementation of this plan is expedited through the agreement of work to be performed by an analytical laboratory in the form of a project-specific laboratory SOW. Deliverable requirements specified in the analytical SOW must be consistent with the requirements of this plan and with the Basic Ordering Agreement contract with the laboratory.

The validation SOW must be written consistent with the requirements and specifications of this plan. The validation SOW is prepared by an SMO representative and communicated to the validation organization (for Level III and Level IV validation only).

The validation SOW will include as attachments full copies of the analytical laboratory data package, as well as an electronic data deliverable (EDD) in the form of a Microsoft Excel file. Placement of the data validation qualifier may be assigned by hand writing on the laboratory report form, initialed and dated, or electronically on provided EDDs in the Validation Code field. If data are not qualified during data validation, an equals sign ("=") shall be entered on the sample result or placed in the Validation Code field of the provided EDD.

Form CP3-ES-5003-F03, "Data Verification Checklist," (in accordance with CP3-ES-5003, *Quality Assured Data*) must be completed for every sample delivery group (SDG) that undergoes Level II, III, or IV data validation. In addition to the data verification checklist, a data validation report must be completed for every SDG that undergoes Level III or IV data validation.

5. PROCEDURE

NOTE: Refer to Appendix A for qualifier descriptions. Refer to Appendix B for qualification guidance due to multiple quality deficiencies. Refer to Appendix C for a listing of relevant equations to use with this plan.

The following is a step-by-step approach to implement analytical data verification and data validation activities. This approach is based on current industry accepted standards. Because changes to methodology and the referenced guidance documents are not within the verifier's or the validator's control, the data verifier and the data validator should always follow the most current methodology and associated guidance documents referenced throughout this text to perform the review and validation of associated data.

5.1 DATA VALIDATION STRATEGY AND SOW DEVELOPMENT

The project team, with input as needed from a quality specialist and/or a representative of the SMO, shall develop a data validation strategy based on inputs identified through the DQO process. The project-specific sampling and analysis plan will define the DQOs and the framework for performing data validation. An SMO representative shall prepare a validation SOW to communicate data verification and validation requirements to the organization performing the work (for Level III and Level IV validation only).

5.2 CUSTODY OF SAMPLES AND SAMPLE DOCUMENTATION

The chain of custody (COC) form provides the basis for the traceability of project samples by documenting the sample from its origin through all steps of the sampling, sample handling, and analysis process. The COC serves as documentation of sample possession from collection through disposal to ensure that sample representativeness is maintained prior to analysis. By documenting personal accountability for samples, the COC is used to ensure that proper custody has been maintained from the time a sample is generated through its final disposition (cradle to grave). Any break in custody, as demonstrated by the series of signatures denoting sample holders, could jeopardize the legal and/or technical defensibility of associated sample data.

While data verification/validation cannot replicate the custody history of a sample (i.e., fully assure the sample truly has been in custody from the field to the final result), an evaluation of field notes, laboratory records, and the COCs provide the best available indicator of sample traceability. A sample is defined as being under proper custody if any of the following conditions are met:

- The sample is within the possession of an authorized person (e.g., field personnel, laboratory personnel, etc.);
- The sample is within view of an authorized person;

- The sample was in an authorized person's possession and then was secured to prevent tampering; or
- The sample is placed in a designated secure area.

NOTE: Data verification of sample documentation includes result report header checks for accuracy from the COC. If sample identity is in question, every attempt should be made to verify the true identity of each sample. When custody problems cannot be resolved, they will affect the defensibility of the sample.

5.2.1 Data Verification

The data verifier shall trace custody of all samples in the reporting batch from field sampling through receipt at the laboratory by reviewing the COCs. If the information is missing, the data verifier will seek to obtain field documentation from the sampler or contract laboratory to determine if the omission affects sample integrity. If there is a break in the signature chain on the COC, or other omissions in the custody record (e.g., date of sample collection, date of transfer to the laboratory, etc.), indicate the problem on the data verification checklist and provide this information to the data validator.

5.2.2 Data Validation

If sample data are not traceable through signature records on COCs or other sample record information demonstrating custody (e.g., laboratory logbooks and/or sample data forms) such that a complete custody history cannot be established, the data validator shall qualify associated results rejected "R."

Custody of Samples	Yes	No	NA
1. Does the data verification checklist or associated attachments in the data report indicate that samples are traceable?			

5.3 HOLDING TIME, TEMPERATURE, AND SAMPLE PRESERVATION

Holding times have been established by EPA to define the maximum period of time during which a sample remains representative of its sampling location. Holding times begin when a sample is collected in the field and are measured by determining the elapsed time from collection through extraction (when applicable) and/or analysis. If the reported data is the result of a dilution, reinjection, or reextraction and analysis, the result must have been generated within the prescribed holding time in order for the result to be considered definitive.

5.3.1 Deliverables

- Field sampling notes
- Field COCs
- Laboratory COCs
- Laboratory reports and/or raw data containing the following: dates of collection; preparation; and analysis for all samples, dilutions, and reextractions.

5.3.2 Criteria

Table 2 provides current industry-accepted standards for sample containers, sample preservation, and holding times for PCDD/PCDF parameters. The data verifier or data validator shall always follow the most current methodology guidance for sample hold time, temperature, and preservation requirements.

Table 2. Holding Time and Sample Preservation Criteria

Sample Type	Sample Matrix	Container	Preservative*	Holding Time
Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans	Aqueous samples with no residual chlorine present	4 × 1 L amber glass container with polytetrafluoroethylene (PTFE)-lined lid, or other size, as appropriate to allow use of entire sample for analysis	0–6°C	None
	Aqueous samples with residual chlorine present	4 × 1 L amber glass container with PTFE-lined lid, or other size, as appropriate to allow use of entire sample for analysis	0–6°C Add 3 mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use.	None
	Solid samples (e.g., soils, sediments, sludges, ash)	250 mL wide-mouth glass container with PTFE-lined lid	0–6°C	None

NOTE: The information presented in this table does not represent EPA requirements but rather is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times should be based on the stated project-specific data quality objectives.
*The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated data quality objectives for a project-specific application are still attainable.

5.3.3 Data Verification

The data verifier shall verify the presence of the pertinent COC forms in laboratory deliverables. If information is missing, the data verifier will seek to obtain field documentation from the sampler and/or the contract laboratory to determine if the omission affects sample integrity. Upon receipt, this information will be placed in the data package for delivery to the data validator. If missing information cannot be obtained or reconstructed from field notes, COCs, etc., the data verifier will note omitted information in the data verification checklist as noncorrectable.

5.3.4 Data Validation

Review the data verification checklist for holding times to confirm all holding times have been met. The data validator shall review field and/or laboratory COC forms, field notes, laboratory report forms, and laboratory raw data, as necessary, to determine the elapsed time from sample collection to sample analysis.

If the elapsed time falls within the prescribed holding time, no actions will be taken and no qualification assigned. Place "=" in the Validation Code field of the EDD.

Table 3 provides general guidance for the qualification of samples based on holding times and sample preservation. The following specific guidance is provided for evaluating data quality.

Table 3. Holding Time and Sample Preservation Validation for PCDD/PCDF Analyses

				Action	
Sample Type	**Matrix**	**Preserved**	**Holding Time**	**Detected Associated Compounds**	**Nondetected Associated Compounds**
Polychlorinated Dibenzodioxins/ Polychlorinated Dibenzofurans	Aqueous samples with no residual chlorine present	Yes	None	No Qualification	
		No	None	J	UJ
	Aqueous samples with residual chlorine present	Yes	None	No Qualification	
		No	None	J	Use Professional Judgment
	Solid samples (e.g., soils, sediments, sludges, ash)	Yes	None	No Qualification	
		No	None	J	UJ

For samples analyzed outside of holding times, the following guidance shall be used:

- If the holding time is exceeded by a factor of < 2, qualify detected results as "J" and nondetected results as "UJ."

- If the holding time is grossly exceeded by a factor > 2, qualify detected results as estimated "J" and nondetected results as rejected "R."

Review laboratory receiving records to determine if samples were received at the appropriate temperature and that proper preservative addition has resulted in the appropriate pH adjustment(s). If records demonstrate samples were received by the laboratory at the proper temperature and with the appropriate pH adjustment, no action is warranted.

If samples have exceeded temperature requirements, the data validator must evaluate the effect on reported results. Depending on the magnitude of the temperature increase, results may or may not be adversely impacted. If prescribed sample receipt temperatures are exceeded, qualify detected analytes "J" and nondetects "UJ."

If samples are received without the proper pH adjustment, qualify detected results as estimated "J" and nondetected results "UJ" or rejected "R." Professional judgment will need to be used to determine the effect of the improper pH and whether the nondetect result should be qualified "UJ" or "R."

- If samples are received at elevated temperature (6°C < sample temperature > 10°C) but have received the proper pH adjustment, qualify detected results "J" and nondetected results "UJ," indicating the

results are estimated. If sample temperatures upon receipt are > 10°C, the data validator must evaluate the integrity of the reported concentrations and the data may require qualification of "R."

- If samples are received at elevated temperature and improper preservation has not been followed (pH adjustment), qualify all affected samples results "R" rejected.

Holding Times and Sample Preservation				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Does the data verification checklist indicate that all samples were analyzed within the appropriate holding time?				J	UJ/R*
2. Were all samples preserved properly?				J	UJ/R**

*Qualify "R" only if holding time has been grossly exceeded either on the first analysis or upon reanalysis.
**Use professional judgment

5.4 INSTRUMENT PERFORMANCE CHECK (REQUIRED FOR CLP METHOD)

Instrument performance is assessed by the analysis of a gas chromatograph (GC) column performance check standard [precision and recovery (PAR) standard in method 1613B] and perfluorokerosene (PFK) molecular leak tuning solution.

5.4.1 Deliverables

- Contract Laboratory Program (CLP) Form 5A or equivalent for PFK instrument performance check; GC column performance check standard (PAR standard for method 1613B) results

- Raw data (required for confirmation)

5.4.2 Frequency

The PFK tune must be performed prior to sample analysis. The GC column performance check standard (PAR standard for method 1613B) must be analyzed at the beginning of each 12-hour shift during which samples will be analyzed.

5.4.3 Criteria

PFK Tune: During each 12-hour analytical cycle, the instrument should be tuned to meet the minimum required resolving power of 10,000 (10% valley) at m/z 380.9760 obtained during peak matching with another high mass ion (m/z 304.9824).

GC Column Performance Check (PAR Standard): Chromatographic separation between 2378-tetrachloradibenzodioxin (TCDD) and other unlabeled TCDD isomers must be resolved by at least 25%.

The mass spectrometer is continuously monitored with PFK. The mass channel that was used to monitor PFK must be inspected for fluctuations.

The deviation between the exact mass measured m/z and the target m/z must be ± 0.0019.

Instrument sensitivity criteria: The peaks representing both native and labeled analytes in the CS3 standard must have signal-to-noise (S/N) ratios ≥ 10:1.

5.4.4 Data Verification

The data verifier shall verify the presence of required reporting forms. If they are not provided, the data verifier shall contact the contract laboratory and request the missing information be provided. If the missing information cannot be provided, the data verifier shall note the omitted information on the data verification checklist as noncorrectable.

5.4.5 Data Validation

Mass spectrometer resolution is critical to the success of this method of PCDD/PCDF analysis. In the event that mass spectrometer resolution is < 10,000, the risk of false positive results may exist. If a demonstration of the required mass resolution is not provided, the reviewer must carefully evaluate other factors to determine whether or not there is sufficient evidence of adequate resolution to preclude interference from other ions with similar mass-to-charge ratios (m/z). This may include, but should not be limited to, other tunes in the data package for the same instrument; the quality and similarity of peak shapes between the calibrations and the samples, baseline noise in calibrations, blanks, and in the lock mass trace; and calibration performance. The appropriate course of action, based on these factors and the professional judgment of the reviewer, may range from no qualification to rejection of all positive results.

Table 4. System Performance Checks Validation

Criteria	Action	
	Detected Compounds	**Nondetected Compounds**
Mass spectrometer resolution of 10,000 is not demonstrated	Professional Judgment	No Qualification
Window defining mixture fails, or window defining mixture adjustments are not made, or window defining mixture is not reported, and calibration standard performance is acceptable	J—Homologue Totals Only	UJ—Homologue Totals Only
Window defining mixture fails, or window defining mixture adjustments are not made, and calibration standards indicate a problem in detecting 2,3,7,8-substituted congeners because of gross errors in the scan descriptor times	R	R
Isomer specificity check fails [GC Resolution (% Valley) of > 25%], or isomer specificity check adjustments are not made	J—all tetra, hexa-congeners	No Qualification
Isomer specificity check fails, or isomer specificity check adjustments are not made, and calibration standards or samples indicate a problem in resolving 2,3,7,8-substituted congeners	R	R
Retention time charges > 15 seconds or RRT changes not within the range	Professional Judgment	
Relative ion abundance criteria is not within 12-hour window in standard	J	UJ
S/N ratio < 10:1 in standard	J	R
%D > criteria in standard	J	UJ

Instrument Performance				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Mass spectrometer resolution of 10,000 is not demonstrated.				*	*
2. Has PFK tuning criteria been met?				J/R	J/R
3. Have fluctuations occurred in the PFK channel?				J/R	N/A
4. Isomer specificity check fails [GC resolution (% Valley) of > 25%], or isomer specificity check adjustments not made.				J	N/A
5. Do positive results exhibit simultaneous peak response for both the quantitation and confirmation ion masses?				J	N/A
6. S/N ratio < 10:1 in standard.				J	N/A
7. Have retention times been established for the PCDD/PCDF isomers in the performance check solution, and retention time criteria met?				R	UJ/R

*Qualify only if the deviation indicates an adverse effect on data quality.

5.5 INITIAL CALIBRATION

Compliance requirements for satisfactory instrument calibration ensure that the instrument is capable of producing acceptable qualitative and quantitative data for all target compounds. The objective of the initial calibration is to establish a linear range, mean relative responses (RRs) of the unlabeled native analytes and the mean relative response factors (RRFs) for the labeled internal standards and cleanup standard. The initial calibration is to be used for routine quantitation of samples using the RRs and RRFs established from the calibration.

5.5.1 Deliverables

- CLP Form 6A or equivalent (dioxin/furan initial calibration data)
- Raw data (required for confirmation)

5.5.2 Frequency

Initial calibration must be performed before any samples are analyzed for PCDDs and PCDFs. Initial calibration also is required if any continuing (routine) calibration does not meet the required criteria.

5.5.3 Criteria

The following subsections present the most common requirements for calibration information related to PCDD/PCDF analysis based on the methods identified in this plan; however, the data validator will need to review the requirements of a specific method and/or the laboratory method that is being reviewed and follow the requirements for that method when validating data. This may mean that the laboratory method will need to be obtained and reviewed prior to data validation. In all cases, specific method requirements for calibration should always be used as the primary guidance when evaluating PCDD/PCDF data.

Each calibration standard must contain $^{13}C_{12}$ labeled internal standards for each congener group (i.e., tetra, octa). At least five different concentrations of each standard shall be used to generate RRFs.

The lower and upper limits of the ion abundance ratios represent a ± 15% window around the theoretical abundance ratio for each pair of selected ions, except for $^{37}Cl_4$-2,3,7,8-TCDD.

For all calibration solutions, the retention time (RT)s of the isomers must fall within the appropriate RT windows established by the window defining mixture (WDM) analysis. In addition, the absolute RT of the internal standard $^{13}C_{12}$-1,2,3,4-TCDD must exceed 25 minutes on the DB-5 (or equivalent) column and 15 minutes on the DB-225 (or equivalent) column to ensure adequate resolution between targets and to separate known interfering substances.

The RRFs and percent relative standard deviation (%RSD) of the five RRFs (CS1–CS5) for each compound applicable to RRF (internal standard) treatment is calculated. The %RSD of the five RRFs (CS1–CS5) must not exceed 35% for these compounds. Likewise, the RR and %RSD of the five RRs (CS1–CS5) for each compound applicable to RR (isotope dilution) treatment is calculated. The %RSD of the five RRs (CS1–CS5) must not exceed 20% for these compounds.

5.5.4 Data Verification

The data verifier shall verify the presence of required reporting forms. If they are not provided, the data verifier will contact the laboratory and request the information be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.5.5 Data Validation

The data validator shall place the following reason codes if the following conditions are met (qualify only if the deviation indicates an adverse effect on data quality):

- Initial calibration sequence was not followed, "C03";
- Appropriate number of standards were not used, "C24"; or
- Inappropriate concentrations, "C18."

The data validator shall inspect the calibration summary and verify agreement with the raw data (quantitation sheets and chromatograms). Check and recalculate at least one of the %RSD values of the mean and standard deviation of the response factors for the labeled and unlabeled standards. Verify that the %RSD for each compound is within the specified range, or that the complete calibration curve was used for quantitation. If the criteria for the initial calibration were not met, qualify detected results as "J" and nondetects as "UJ." For further qualifications, see Table 5.

Table 5. Initial Calibration Validation

Criteria	Action	
	Detected Compounds	Nondetected Compounds
Initial calibrations not performed	R	R
Initial calibration not performed at proper frequency	Professional Judgment	Professional Judgment
Ion abundance ratio is not within ± 15% of theoretical values	Professional Judgment	Professional Judgment
GC Resolution (% Valley) is > 25%	J	UJ
Linearity: RRF %RSDs is not within ± 35%; RR %RSDs is not within ± 20%	J	UJ
Sensitivity < 10:1 S/N ratio for all selected ion current profiles	J	Professional Judgment
Not within appropriate windows and absolute RT of internal standard	Professional Judgment	Professional Judgment

Initial Calibration				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the instrument calibrated at the appropriate frequency?				**	**
2. Is ion abundance ratio within ± 15% of theoretical value?				**	**
3. Is GC Resolution (% Valley) > 25%?				J*	UJ*
4. Were criteria for %RSD of the response factors (8290A) or relative response factors (1613B) met?				J	UJ
5. Is sensitivity < 10:1 S/N ratio for all selected ion current profiles ?				J	*
6. Not within appropriate windows and absolute RT of internal standard.				*	*

*Qualify only if the deviation indicates an adverse effect on data quality.
**Qualify as appropriate.

5.6 CONTINUING CALIBRATION

Continuing calibration ensures that the instrument(s) is capable of consistently producing acceptable qualitative and quantitative data. The instrument(s) is checked over specific time periods during the sample analysis.

5.6.1 Deliverables

- CLP Form 7A or equivalent (dioxin/furan calibration check)
- Raw data (required for confirmation)

5.6.2 Frequency

A continuing calibration check must be performed during every 12-hour time period in which samples were analyzed.

5.6.3 Criteria

Method 8290A: Verify from the raw data that the measured RRs and RRFs of each analyte, labeled and otherwise, in the CS3 solution are within ± 25% (RRs) and ± 35% (RRFs) of the mean values established during initial calibration.

Method 1613B: The concentration of each of the unlabeled and labeled standards must be within the limits given in the method.

5.6.4 Data Verification

The data verifier shall verify the presence of required reporting forms. If they are not provided the data verifier will contact the laboratory and request the information be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.6.5 Data Validation

The data validator shall inspect the continuing calibration summary data and verify agreement with the raw data (quantitation sheets and chromatograms). Verify that the percent difference (%D) (method 8290A) or the concentration (method 1613B) for each compound is within the specified range, or that the complete calibration curve was used for quantitation. If criteria for the continuing calibration were not met, qualify detected results "J" and nondetected results "UJ." For further qualifications see Table 6.

Table 6. Continuing Calibration Validation

Criteria	Action	
	Detected Compounds	**Nondetected Compounds**
Ion abundance ratio is not within ± 15% of theoretical values.	J	Professional Judgment
Absolute RT of internal standard $^{13}C_{12}$-1,2,3,4-TCDD > 25 minutes on DB-5 (or equivalent) column, or > 15 minutes on DB-225 (or equivalent) column	Professional Judgment	Professional Judgment
%D for RRs not within ± 25%; %D for RRFs not within ± 35%	J	UJ
Internal standards in the calibration verification not within 15 seconds of the RT in the initial calibration.	Professional Judgment	Professional Judgment
RRTs in the calibration verification not within the established limits.	Professional Judgment	Professional Judgment
Sensitivity: S/N < 10 for all compounds	J	R

5.7 BLANKS

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. Initial and continuing calibration blanks are used to ensure a stable instrument baseline before analysis of analytical samples. The preparation blank or method blank (MB) is used to assess the level of contamination introduced to the analytical samples throughout the sample preparation process. If contamination is found in any blank, all associated data must be evaluated carefully to determine whether or not there is a systematic problem affecting greater than one sample or if the contamination is an isolated occurrence.

Additionally, the project team may elect to collect and analyzed field and equipment rinseate blanks to evaluate the existence and magnitude of contamination that may arise as a result of field level activities. The field blank provides an indication of ambient conditions during the sampling activities, as well as an indication that the source of decontamination water is free of targeted analytes. The equipment rinseate rinseate blank provides an indication as to whether or not nondedicated sampling equipment has been properly decontaminated, and what, if any, carry over may arise between sampled locations. It has been EPA Region 4 data validation policy to evaluate the field and equipment rinseate rinseate blanks as part of the validation process, but not to qualify the data based on these field samples.

5.7.1 Deliverables

- CLP Form 4A or equivalent (dioxin/furan method blank summary)
- Summary forms of results for all associated blanks
- Raw data (required for confirmation)

5.7.2 Frequency

Method blanks must be extracted for each 20 samples of similar matrix in each SDG or whenever a sample extraction procedure is performed.

Continuing Calibration				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was continuing calibration performed at the appropriate frequency?				*	*
2. Is Ion Abundance Ratio within ± 15% of theoretical value?				J	*
3. Is the %D (method 8290A) or the concentration (method 1613B) for each compound within the method specified range for the continuing calibration analysis?				J	UJ
4. Internal standards in the calibration verification not within 15 seconds of the RT in the initial calibration.				*	*
5. RRTs in the calibration verification not within the established limits.				*	*
6. Sensitivity: S/N <10 for all compounds.				J	R

*Qualify only if the deviation indicates an adverse effect on data quality.
**Qualify "R" as appropriate considering other QC in the data package.

5.7.3 Criteria

No contaminants should be found in any blanks. Reported results must not be corrected by subtracting blank values.

5.7.4 Data Verification

The data verifier shall verify the presence of required reporting forms. If they are not provided, the data verifier will contact the laboratory and request the information be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.7.5 Data Validation

All blanks associated with the case must be evaluated against the sample results in the case; however, qualification should only be applied to those samples directly related to the affected blank (if more than one MB is used per case).

Any compound that is reported in both blank and sample must be evaluated; however, if the same compound is reported in sample(s) and more than one blank, the sample should be evaluated against the blank with the highest concentration of the compound. Differences in weights, volumes, and/or dilution factors between blanks and associated samples must be taken into consideration.

If a compound is found in a blank but not an associated sample, no action is taken.

If any target compounds are detected in an associated blank, the 5 × rule applies:

- If the sample concentration is > the reporting limit (RL) but < 5 × blank concentration, qualify the reported result "U."

- If the sample concentration is < RL and < 5 × blank concentration, qualify the reported result "U."
- If the sample concentration is > 5 × blank concentration, the result is considered positive and no qualifier is applied.

If gross contamination (saturated peaks in blank) is present, qualify all affected results as "R."

If an instrument blank is not analyzed immediately after a sample showing compound(s) at high concentration(s), the data validator must evaluate the analyses following the saturated sample analysis for carryover. Qualify reported compounds significantly affected by instrument carryover as "J" or "R." A summary of these qualifications are included in Table 7.

Table 7. Blank Validation

Method Blank Result	Sample Result	Action
< Contract Required Quantitation Limit (CRQL)	Not detected	No Qualification
	≥ CRQL and > Blank Result	Professional Judgment
≥ CRQL	Not detected	No Qualification
	≥ CRQL and < Blank Result	U*
	> CRQL and ≥ Blank Result	Professional Judgment
Gross Contamination	Positive	R

*The calculated sample result should be reported with a "U" flag in these cases.

Method Blanks				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Were method blanks analyzed at the appropriate frequency?				*	*
2. Are sample results > RL and > 5 × blank result?					
Is sample result > RL and < 5 × blank result?				U	N/A
Is sample result < RL and < 5 × blank result?				U	N/A
Gross contamination?				R	**
3. Have instrument blanks been analyzed after samples showing high concentrations?				**	N/A
4. Confirm from raw data that compounds reported in the MB are detected above the RL.					

*Qualify only if the deviation indicates an adverse effect on data quality.
**Use professional judgment in qualifying data.

5.8 INTERNAL STANDARD (LABELED COMPOUND) SPIKES

The recovery of this spike analysis provides for establishing the performance of the laboratory extraction and analysis. This solution is added to all samples, blanks, and laboratory QC samples prior to extraction. Internal standard performance results are critical to the overall accuracy and precision of the analysis since target compound results for each dioxin and furan isomer are quantitated based on the response of the corresponding labeled isomer.

For method 8290A, this spike is called the Sample Fortification Solution and contains the nine internal standards at the nominal concentrations listed in Table 2 of the method. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances.

For method 1613B, this spike is called the Labeled-Compound Spiking Solution and contains the labeled compounds at the concentrations shown in Table 3 of the method.

5.8.1 Deliverables

- Recoveries for internal standard (labeled-compound) spikes
- Raw data (required for confirmation)

5.8.2 Frequency

All samples, blanks, and QC samples are fortified with internal standard (labeled-compound) spikes.

5.8.3 Criteria

For method 8290: The laboratory performing the analysis will have established acceptance ranges for each internal standard. In the absence of laboratory limits, internal standards should be within the range of 40–135% recovery.

For method 1613B: All concentrations of the labeled compounds should be within the ranges given in Table 7 of the method. When results of these spikes indicate atypical method performance for samples, the samples should have been diluted to bring method performance within acceptable limits.

5.8.4 Data Verification

Verify the presence of required reporting forms. If they are not provided, contact the contract laboratory and request that they be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.8.5 Data Validation

Verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. If any criteria have not been met or if information is omitted from the laboratory report, request the missing information from the laboratory. If the omission is the result of a technical issue or due to an omitted analytical requirement, a member of the SMO will direct the laboratory to complete the analysis in accordance with the SOW.

The data validator shall check the raw data to verify reported recoveries. Compare the reported %Rs to the limits appropriate to the method performed.

- If a labeled compound has a recovery > the upper control limit, qualify detected results for the unlabeled analog in that sample as "J."

- If a labeled compound has a recovery < the lower control limit, qualify any result for the unlabeled analog in that sample as "J" or "UJ," as appropriate.

- If a labeled compound has a recovery < 10%, qualify detected results as "J" and any associated nondetects as "R."

Internal Standard (Labeled Compound) Spikes				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have the proper internal standard spikes been used?				*	*
2. Have the proper internal standard spike concentrations been used?				*	*
3. The following checks are applicable to % recovery:					
Internal standard spike recoveries have been evaluated.					
%R is > upper control limit				J	N/A
%R is < lower control limit				J	UJ
%R is < 10%				R	R

*Qualify only if the deviation indicates an adverse effect on data quality.

5.9 RECOVERY (INTERNAL) STANDARDS

Recovery standards are added to samples after extraction and prior to analysis. Recovery standard peak areas are used in the calculation of quantitative sample results. The commonly used standards are $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD.

NOTE: In method 8290A, this is referred to as the recovery standard. In method 1613B, this is called the internal standard solution.

5.9.1 Deliverables

- Percent recovery for recovery (internal) standard
- Raw data (required for confirmation)

5.9.2 Frequency

All samples, blanks, and QC samples are fortified with recovery (internal) standard spikes.

5.9.3 Criteria

For method 8290A: The laboratory will have established limits that should be followed. In the absence of laboratory defined limits, recovery standard %Rs must be within the range of 40-135%.

For method 1613B: Internal standard recoveries must be within the limits specified in Table 7 of the method.

5.9.4 Data Verification

Verify the presence of required reporting forms. If they are not provided, the data verifier will contact the laboratory and request the information be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.9.5 Data Validation

Verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. If any criteria have not been met or if information is omitted from the analytical laboratory report, request

the missing information be provided. If the omission is the result of a technical issue or due to an omitted analytical requirement, a member of the SMO will direct the laboratory to complete the analysis in accordance with the SOW.

Recovery (Internal) Standards				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Were all samples, blanks, and QC samples fortified with recovery (internal) standard spikes?				*	*
2. Were %Rs for the recovery (internal) standard compounds within acceptance criteria?				J	N/A

*Qualify only if the deviation indicates an adverse effect on data quality.

5.10 MATRIX SPIKE/MATRIX SPIKE DUPLICATES (MS/MSD)

Matrix spike (MS)/matrix spike duplicate (MSD) data are generated to determine long-term precision and accuracy of the analytical method on various matrices. If recovery criteria are not satisfied, there is difficulty in assessing whether the cause was the method or matrix-related interferences. To address this issue, LCSs/laboratory control sample duplicates (LCSDs) also analyzed to verify whether the method results themselves are satisfactory. If only the MS/MSD are affected, a matrix effect is likely. Qualification, therefore, is not applied to sample data based on MS/MSD alone, but is used in conjunction with other QC parameters in judging data usability.

NOTE: For a MS that does not meet the technical criteria, apply the action to all samples of the same matrix, if the data validator considers the samples sufficiently similar. The data validator will need to exercise professional judgment in determining sample similarity. The data validator should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and laboratory data for other parameters (e.g., total suspended solids, total dissolved solids, total organic carbon, alkalinity or buffering capacity, reactive sulfide, anions) in determining similarity. The data validator should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the data package. The data validator may determine that only some of the samples in the data package are similar to the MS sample, and that only these samples should be qualified. Or, the data validator may determine that no samples are sufficiently similar to the sample used for the MS, and thus that only the field sample used to prepare the MS sample should be qualified.

5.10.1 Deliverables

- CLP 3A or 3B or equivalent (dioxin/furan MS/MSD recovery)
- Raw data (required for confirmation)

5.10.2 Frequency

MS/MSD must be analyzed at a frequency of at least one MS/MSD pair per 20 field samples of similar matrix.

5.10.3 Criteria

For method 8290A: The MS/MSD solution contains all unlabeled analytes listed in Table 5 of the method. Results obtained from the MS/MSD samples (concentrations of PCDDs/PCDFs) should recover

within the laboratory's established acceptable range and agree within 20% relative percent difference (RPD).

For method 1613B: In the absence of specific criteria for this method, use project-specified limits or a recovery range of 60-140% with a maximum RPD of 50.

5.10.4 Data Verification

Verify the presence of required reporting forms. If they are not provided, contact the contract laboratory and request the information be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.10.5 Data Validation

Verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. If any criteria have not been met, or if information is omitted from the analytical laboratory report, request the missing information from the laboratory. If the omission is the result of a technical issue or due to an omitted analytical requirement, a member of the SMO will direct the laboratory to complete the analysis in accordance with the SOW.

The data validator shall determine to what extent that noncompliant MS/MSD data has on other sample data in regard to the MS/MSD sample itself as well as specific compounds in samples associated with the MS/MSD. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, the qualification should be limited to that sample alone. It may be determined that the laboratory is having a systematic problem in the analysis of one or more compound which affects all associated samples. Positive results of nonspiked compounds may be qualified "J," as appropriate. Nondetected results of nonspiked compounds may be qualified "UJ," as appropriate.

Recalculate one MS recovery from raw data for confirmation. Table 8 presents information on MS/MSD qualification. Equation C.1 in Appendix C is used to calculate MS % recovery.

Table 8. MS/MSD Qualification

Criteria	Action	
	Detected Compounds	**Nondetected Compounds**
%R or RPD > upper acceptance limit	J	No Qualification
20% < %R < lower acceptance limit	J	UJ
%R < 20%	J	Professional Judgment
Lower acceptance limit ≤ %R ≤ upper acceptance limit	No Qualification	

Matrix Spike/Matrix Spike Duplicate				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the MS/MSD analyzed at the appropriate frequency?				*	*
2. Are all MS/MSD compounds within control criteria?				**	**
3. Are all MS/MSD RPD within control criteria?				**	**

*Qualify only if the deviation indicates an adverse effect on data quality.
**Qualify only after evaluating other QC data in the SDG.

5.11 DUPLICATES

A laboratory duplicate sample is analyzed for each matrix to evaluate the precision of the laboratory at the time of analysis. A field duplicate sample is collected and analyzed to evaluate the precision of both the sampling techniques as well as the laboratory methodology. A field duplicate also may provide information on the homogeneity of the sample. Nonhomogenous samples can impact the apparent method precision; however, aqueous/water samples are generally homogenous and most soil/sediment samples are homogenous within a factor of two or three.

5.11.1 Deliverables

- CLP Form VI or equivalent for SW-846 methods
- Raw data (required for confirmation)

5.11.2 Frequency

One laboratory duplicate shall be analyzed per each sample batch or once per 20 samples, whichever is more frequent.

5.11.3 Criteria

- Samples identified as field blanks must not be analyzed as laboratory duplicate.

- For sample concentrations > 2 × the instrument detection limit (IDL), the laboratory duplicate precision as measured by RPD must be within ± 20% for aqueous samples and 35% for solid matrices. If the sample values are < 25 × the IDL, RPD does not apply. Instead, the absolute difference between sample and duplicate must be either < 2 × the IDL or the RL, whichever is higher.

5.11.4 Data Verification

The data verifier shall verify that field blanks were not analyzed as laboratory duplicates. If a field blank has been used, the sample manager will be notified immediately to ensure timely corrective action. If reanalysis cannot be completed, this issue will be identified as noncorrectable in the data verification checklist.

The data verifier shall verify the presence of laboratory and/or field duplicate results. If results are not provided or if the required frequency of analysis is not demonstrated in the laboratory deliverable, the data verifier will seek to obtain the missing information from the laboratory. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If the missing information cannot be obtained from the analytical laboratory, it is considered a noncorrectable problem and shall be identified in this way in the data verification checklist. Because they are contract compliance related, all such occurrences shall be communicated to the SMO and to the validator in the data verification checklist.

5.11.5 Data Validation

- Examine the raw data (if provided) for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility, etc.).

- Verify that appropriate methods and amounts were used in preparing the samples for analysis.

- Verify that there are no transcriptions or reduction errors (e.g., dilutions, Percent Solids, sample weights, etc.) on one or more samples.
- Verify that results fall within the linear range(s) of the instrument, if applicable.

See Table 9 for qualification instructions.

Table 9. Duplicate Qualification

Duplicate Type	Matrix	RPD	Sample Results	Qualification Instructions
Laboratory Duplicate	Aqueous	> 25%	Sample and dup > 5 × RL	Qualify results > RL "J" Qualify nondetects "UJ"
	Solid	> 35%		
	Aqueous	> 25%	Sample and dup < 5 × RL	Absolute difference > RL "J" Absolute difference < RL no action
	Solid	> 35%		
Field Duplicate	Aqueous	> 25%	Sample and dup > 5 × RL	Qualify results > RL "J" Qualify nondetects "UJ"
	Solid	> 35%		
	Aqueous	> 25%	Sample and dup < 5 × RL	Absolute difference > RL "J" Absolute difference < RL no action
	Solid	> 35%		

The above control limits are method requirements for matrix-specific duplicate samples. It should be noted that laboratory variability arising from the subsampling of nonhomogeneous matrices is a common occurrence; therefore, for technical review purposes only, regional policy or project DQOs may allow the use of less restrictive criteria (e.g., 35% RPD, 2 × the CRDL) to be used in assessing nonhomogeneous matrices. When project-specific DQOs mandate broader precision requirements, this information will be provided to the data validators as part of the validation SOW.

Duplicate				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have the Duplicate results been included in the data package?				----	----
2. Was the Duplicate analyzed at the appropriate frequency?*				----	----
3. Was the duplicate RPDs within control criteria?**				J	UJ

*Qualify only if the deviation indicates an adverse effect on data quality.
**Qualify only if other QC data in the SDG is outside established criteria.

5.12 LABORATORY CONTROL SAMPLE

An LCS (QC check standard) is analyzed to provide accuracy of the analytical method.

5.12.1 Deliverables

- LCS recovery form or equivalent
- Raw data (required for confirmation)

5.12.2 Frequency

The LCS must be analyzed at a frequency of at least one per 20 field samples of similar matrix.

5.12.3 Criteria

LCS %R should fall within laboratory specified limits based on the method used for sample analysis. If laboratory limits are not available, the data validator should follow advisory limits below from the EPA

National Functional Guidelines for PCCDs and PCDFs. Acceptance criteria for LCSs is provided in Table 10.

Table 10. Acceptance Criteria for Laboratory Control Samples

PCDD/PCDF	Test Conc (ng/mL)	LCS % Recovery
2,3,7,8-TCDD	10	67–158%
2,3,7,8-TCDF	10	75–158%
1,2,3,7,8-PeCDD	50	70–142%
1,2,3,7,8-PeCDF	50	80–134%
2,3,4,7,8-PeCDF	50	68–160%
1,2,3,4,7,8-HxCDD	50	70–164%
1,2,3,6,7,8-HxCDD	50	76–134%
1,2,3,7,8,9-HxCDD	50	64–162%
1,2,3,4,7,8-HxCDF	50	72–134%
1,2,3,6,7,8-HxCDF	50	84–130%
1,2,3,7,8,9-HxCDF	50	78–130%
2,3,4,6,7,8-HxCDF	50	70–156%
1,2,3,4,6,7,8-HpCDD	50	70–140%
1,2,3,4,6,7,8-HpCDF	50	82–132%
1,2,3,4,7,8,9-HpCDF	50	78–138%
OCDD	100	78–144%
OCDF	100	63–170%

5.12.4 Data Verification

Verify the presence of required reporting forms. If they are not provided, contact the SMO and request that they be provided. If these occurrences cannot be resolved with the laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist.

5.12.5 Data Validation

If LCS recovery results are outside of the recovery limits, the data validator shall qualify affected results as "J" and nondetected results as "UJ" when it is a low recovery.

If LCS results are < 10%, qualify all affected results as "R."

Laboratory Control Sample (SW-846 Methods Only)				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the LCS analyzed at the proper frequency?				*	*
2. Was the LCS prepared and analyzed?				*	*
3. Were the %R of the reported compounds within acceptance criteria?				J	UJ/R
4. Was the LCS of the same matrix as the analyzed samples?				*	*

*Qualify only if the deviation indicates an adverse effect on data quality.

5.13 ESTIMATED MAXIMUM POSSIBLE CONCENTRATION

For method 8290A: When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a signal-to-noise ratio in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in the method, an estimated maximum possible concentration (EMPC) is calculated.

For method 1613B: For a peak that does not meet ion abundance criteria, the concentration of the EMPC is reported as the detection limit. There are many reasons that a peak might not meet ion abundance criteria including, but not limited to, coelution, poor peak integration, and low strength.

5.13.1 Data Validation

Review any dibenzodioxin or dibenzofuran peak reported as an EMPC and associated blank results to determine if the compound is also reported in the blank. If the compound reported as an EMPC is also reported in an associated blank and the concentration reported in the sample is $< 5 \times$ the blank concentration, report the compound as not detected at the reporting limit. All compounds reported as an EMPC shall be qualified as "J."

5.14 CLEANUP STANDARD

Cleanup is performed to remove matrix interferences from sample extracts prior to analysis. After sample extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process.

5.14.1 Deliverables

- Cleanup standard percent recoveries
- Raw data (required for confirmation)

5.14.2 Frequency

For method 1613B, the cleanup standard is added to all extracts prior to cleanup to measure the efficiency of the cleanup process. The cleanup standard is prepared by adding $^{37}Cl_4$-labeled 2,3,7,8-TCDD in nonane at the concentration shown in Table 3 of the method.

The cleanup standard is not required by method 8290A.

5.14.3 Criteria

$^{37}Cl_4$-labeled 2,3,7,8-TCDD must be present and detected in the sample.

5.14.4 Data Validation

Place reason code "V04" on the affected data if noncorrectable deliverable deficiencies have occurred. Qualify only if the deviation indicates an adverse effect on data quality.

Use professional judgment when qualifying sample results based on cleanup standard recoveries. If no recovery was reported for the cleanup standard, qualify all results for that sample as "J" or "UJ," as appropriate.

Cleanup Standard				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. For method 1613B, has a cleanup standard been added to all sample extracts?				--	--
2. The following checks are applicable to % recovery:					
Cleanup standard results have been evaluated.					
%R is < 0%				J	UJ

5.15 TARGET COMPOUND IDENTIFICATION, QUANTITATION, AND DETECTION LIMITS

An individual PCDD/PCDF is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of the authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. The non-2,3,7,8 substituted isomers and congeners are identified when retention times and ion-abundance ratios agree within predefined limits. Isomer specificity for 2,3,7,8-TCDD and 2,3,7,8-TCDF is achieved using GC columns that resolve these isomers from the other tetra-isomers.

The detection limits and quantitation levels are usually dependent on the level of interferences rather than instrumental limitations. Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCDDs/PCDFs. The most frequently encountered interferences are chlorinated biphenyls, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides.

5.15.1 Deliverables

- CLP Form I or equivalent (dioxin/furan analysis data sheet)
- Raw data

5.15.2 Criteria

For method 8290A:

- For a GC peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria listed in Section 11.0 In addition, the retention time identification criterion described in Section 11.0 applies for congeners for which a carbon-labeled

analogue is available in the sample extract; however, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT.

- If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds exceeds the upper method calibration limits, the linear range of response versus concentration may have been exceeded, and a second analysis of the sample (using a one-tenth aliquot) should be taken.

- The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present.

For method 1613B, PCDD/PCDF compounds are identified when all of the following criteria are met:

- The signals for the two exact m/z in Table 8 of the method must be present and must maximize within the same two seconds.

- The S/N ratio for the GC peak at each exact m/z must be ≥ 2.5 for each PCDD or PCDF detected in the sample extract and >10 for all PCDDs/PCDFs in the calibration standard.

- The ratio of the integrated areas of the two exact m/z's specified in Table 8 of the method must be within the limit in Table 9 (see method), or within ± 10% of the ration in the midpoint calibration or calibration verification, whichever is most recent.

- The RRT of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limit in Table 2 of the method. The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in Section 10.3 of the method.

5.16 MANUAL RECALCULATION OF ANALYTICAL RESULTS

The accuracy and consistency of sample result calculation by the laboratory can be addressed using two different techniques. The application of each strategy depends on the laboratory's ability to minimize transcription during reporting, and how familiar the project is with the performance of the laboratory. If sample results are produced primarily through software processing and minimal transcription is performed in the laboratory, the data system(s) can be evaluated during an audit or surveillance by performing two different tests on the software (1) supply the data system a consistent set of input designed to provide a consistent set of output, and (2) supply the data system a set of nonconforming data to test the error detection routines. An additional evaluation of the laboratory's software configuration control and security is also necessary. Through this technique, a high level of confidence can be gained in the laboratory's reporting techniques and will result in a minimal need for manual recalculation of sample results.

If the laboratory has a high rate of manual transcription in generation of sample results, the project may choose to manually recalculate sample results at a determined frequency. If sample results cannot be reproduced through manual calculation, contacting the laboratory may be necessary to resolve the problem. Data may be qualified "R" as a last resort if no actions can reproduce reported values.

Calculations for compound quantitation and rounding rules can be found in Appendix C.

5.17 TOXICITY EQUIVALENCE

If requested by the data user, the laboratory may be required to calculate the 2,3,7,8-TCDD toxicity equivalents of PCDDs and PCDFs present in the samples. Toxicity equivalents are calculated according to the method recommended by the EPA Chlorinated Dioxins Workgroup and the Centers for Disease Control. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs and to OCDD and OCDF cited in the method. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times the concentration for each of the compounds or groups of compounds.

If TEFs are required to be reported, ensure that this information has been provided by the laboratory.

6. RECORDS

Generate and maintain all records in accordance with CP3-RD-0010, *Records Management Process.*

- Data Verification Checklist (Level II, III, and IV validation only)
- Data Validation Report (for Level III and Level IV validation only)
- Copies of qualified or unqualified results reports (if applicable)

7. REFERENCES

NOTE: The most current versions of the references listed below should be utilized when using this procedure for the data review, verification and validation process.

DOE/LX/07-1269&D2/R2, *Paducah Gaseous Diffusion Plant Programmatic Quality Assurance Project Plan.*

EPA/240/B-06/001, February 2006, *Guidance on Systematic Planning Using the Data Quality Objective Process.*

EPA-540/R-99/008, January 2010, *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review.*

EPA-540/R-11-016, September 2011, *USEPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review.*

EPA-OLM04.2, May 1999, *USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Multi-media, Multi-Concentration.*

CP3-ES-5003, *Quality Assured Data.*

Method 8290A, Revision 1, February 2007, *Final Update IV to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.*

Telliard, W.A., United States EPA Method 1613b, *Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS*, US EPA Office of Water, Washington, DC, (1994).

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APPENDIX A

DATA VALIDATION QUALIFIERS AND QUALIFICATION CODES

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DATA VALIDATION QUALIFIERS AND QUALIFICATION CODES

Data Validation Qualifiers

U—Analyte compound or nuclide considered not detected above the reported detection limit.
J—Analyte compound or nuclide identified; the associated numerical value is approximated.
UJ—Analyte compound or nuclide not detected above the reported detection limit, and the reported detection limit is approximated due to quality deficiency.
NJ—Presumptively present at an estimated quantity (use with TICs only).
R—Result is not usable for its intended purpose.
= – "Equals" sign, indicates that no qualifier is necessary.

Data Validation Qualification Codes

Blanks
B01—Sample concentration was ≤ RDL and < 5 × the blank concentration (10 × for common contaminants).
B02—Sample concentration was > RDL and < 5 × the blank concentration (10 × for common contaminants).
B03—Gross contamination exists; blank result impacted associated analyte data quality.
B04—Negative blank result impacted associated analyte data quality.
B05—Blanks were not analyzed at appropriate frequency.
B06—Sample not significantly different than radiochemical method blank.
B07—Blank data not reported.
B08—Instrument blank not analyzed after high level sample.
B09—Other (describe in comments)
B10—Method blanks not extracted at appropriate frequency.
B11—Sample results were corrected for blank contamination.
B12—Blank was not the same matrix as the analytical samples.
B13—Concentration of target compound detected in sample affected by carryover.

Calibration
C01—Initial calibration average RRF was < 0.05
C02—Initial calibration %RSD was exceeded
C03—Initial calibration sequence was not follows as appropriate
C04—Continuing calibration RRF was < 0.05
C05—Continuing calibration %D was exceeded
C06—Calibration or performance check was not performed at the appropriate frequency
C07—Calibration data not reported
C08—Calibration not performed
C09—Chemical resolution criteria were not satisfied
C10—Calibration standard matrix not the same as sample matrix
C11—Compounds quantitated against inappropriate standard or standard concentration level
C12—Compound quantitated against inappropriate ion
C13—Calibration factor RSD criteria were not satisfied
C14—Retention time of compound outside window
C15—Initial calibration % R was below lower acceptance limit
C16—Initial calibration % R was above upper acceptance limit
C17—Initial calibration curve fit was < 0.995
C18—Inappropriate standard concentrations

C19—Continuing calibration R was below the lower acceptance limit
C20—Continuing calibration %R was above the upper acceptance limit
C21—CRI %R was below the lower acceptance limit
C22—CRI %R was above the upper acceptance limit
C24—Standard curve was established with fewer than the appropriate number of standards
C27—Calibration verification efficiency outside control criteria
C28—Calibration verification background outside control criteria
C29—Calibration verification energy outside control criteria
C30—Calibration verification peak resolution outside control criteria
C31—Chromatogram does not show adequate gain setting
C32—Other (describe in comments)

Laboratory Duplicate/Dual Column Sample Confirmation
D01—Significant difference between sample and duplicate
D02—Laboratory duplicate was not analyzed at the appropriate frequency
D03—Laboratory duplicate exceeds RPD criteria
D04—Laboratory duplicate data not reported
D05—Other (describe in comments)
D06—%D between primary and secondary column confirmation exceeds acceptance criteria

Evidentiary Concerns
E01—Custody of sample in question
E02—Standard not traceable
E03—Other (describe in comments)

Interference Check Samples (ICS)
F01—ICS recovery below lower control limit or advisory limit
F02—ICS recovery above upper control limit or advisory limit

General
G01—Professional judgment was used to qualify the data
G02—Other (describe in comments)

Holding Times/Preservation
H01—Extraction holding times were exceeded
H02—Extraction holding times were grossly exceeded
H03—Analysis holding times were exceeded
H04—Analysis holding times were grossly exceeded
H05—Samples were not preserved properly
H06—Sample preservation cannot be confirmed
H07—Sample temperature exceeded criteria prior to preparation
H08—Other (describe in comments)

Internal Standards
I01—Area count was above upper control limits
I02—Area count was below lower control limits
I03—Extremely low area counts or performance was exhibited by a major drop off
I04—Internal standard retention time varied by more than 30 seconds
I05—Inappropriate internal standard used
I06—Inappropriate internal standard concentration(s) used

I07—Internal standard data not reported
I08—Other (describe in comments)

Laboratory Control Sample (QC Check Standard)
K01—QC Check Standard not analytically prepared but only analyzed
K02—Recovery of QC Check Standard was above upper control limits
K03—Recovery of QC Check Standard was below lower control limits
K04—QC Check Standard data not analyzed or not reported
K05—Other (describe in comments)

Laboratory Control Sample
L01—LCS recovery above upper control limit
L02—LCS recovery below lower control limit
L03—LCS was not analyzed at appropriate frequency
L04—LCS not the same matrix as the analytical samples
L05—LCS data not reported
L06—Other (describe in comments)

Matrix Spike and MS/MSD
M01—MS and/or MSD recovery above upper control limit
M02—MS and/or MSD recovery below lower control limit
M03—MS/MSD pair exceeds the RPD limit
M04—MS and/or MS/MSD not analyzed at the appropriate frequency
M05—MS and/or MS/MSD data not reported
M06—Other (describe in comments)

Instrument Performance
P01—High background levels or a shift in the energy calibration were observed
P02—Extraneous peaks were observed
P03—Loss of resolution was observed
P04—Peak tailing or peak splitting that may result in inaccurate quantitation were observed
P05—Instrument performance data not reported
P06—Instrument performance not analyzed at the appropriate frequency
P07—Other (describe in comments)
P08—Resolution Check Mixture (RCM) not analyzed at the beginning of the initial calibration sequence
P09—RCM criteria were not met
P10—RPD criteria in Performance Evaluation Mixture (PEM) was not met

Quantitation
Q01—Peak misidentified
Q02—Target analyte affected by interfering peak
Q03—Qualitative criteria were not satisfied
Q04—Cross contamination occurred
Q07—Analysis occurred outside 12 hour gas chromatography/mass spectrometry window
Q09—TIC result was not above 10 × the level found in the blank
Q10—TIC reported as detect in another fraction
Q11—Common artifact reported as a TIC
Q12—No raw data were provided to confirm quantitation
Q13—MDA > RDL
Q14—Inappropriate aliquot sizes were used
Q15—Sample result < MDA

Q16—Sample result < 2σ uncertainty
Q17—Negative result
Q18—Compounds were not adequately resolved
Q19—Sample geometry different from calibration geometry
Q20—Sample weight greater than greatest weight on mass attenuation curve
Q21—Isotopes of same radionuclide do not show equilibrium
Q22—Peak not within appropriate energy range
Q23—Counting uncertainty ≥ 80% of sample result
Q24—Raw data anomaly
Q25—Other (describe in comments)
Q26—RT outside calculated RT window
Q28—Neither CRQL or the SQL are reported for a nondetect result
Q29—SQL > RDL
Q30—Compound detected at < SQL and not qualified "J"
Q31—Presence of high molecular weight contaminants impacted sample quantitation

Surrogates
S01—Surrogate recovery was above the upper control limit
S02—Surrogate recovery was below the lower control limit
S03—Surrogate recovery was < 10%
S04—inappropriate surrogate standard used
S05—Inappropriate surrogate standard concentration(s) used
S06—Surrogate data not reported
S07—Surrogate outside retention window
S08—Other (describe in comments)

Instrument Tuning
T01—Mass calibration ion misassignment
T02—Mass calibration was not performed every 12 hours
T03—Mass calibration did not meet ion abundance criteria
T04—Mass calibration data was not reported
T05—Scans were not properly averaged
T06—Other (describe in comments)

Pesticide Sample Cleanup
U01—Florisil performance requirements not met
U02—GPC calibration not checked at required frequency
U03—GPC calibration criteria not met
U04—GPC blank not analyzed after GPC calibration
U05—GPC blank greater than half the CRQL for target compound

Cleanup
V01—10% recovery or less was obtained during either check
V02—Recoveries during either check were > 120%
V04—Cleanup data not reported
V05—Cleanup check not performed at the appropriate frequency
V06—Other (describe in comments)

Dilutions
X01—Serial dilution not analyzed at the appropriate frequency
X02—%D between the original sample and the diluted result (or serial dilution) exceeded acceptance criteria
X03—Reported results not corrected for dilution factor
X04—Other (describe in comments)

Radiochemical Yield
Y01—Radiochemical tracer yield was above the upper control limit
Y02—Radiochemical tracer yield was below the lower control limit
Y03—Radiochemical tracer yield was zero
Y04—Radiochemical yield data was not present
Y05—Other (describe in comments)

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APPENDIX B

QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

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QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

Guidance for Data Qualification Due to Multiple Quality Deficiencies

This appendix provides guidance in the qualification of data due to instances of multiple quality deficiencies. Quality deficiencies can be categorized based on potential effect on sample data. The effect of quality deficiencies may be applicable to only a single sample or to all samples within the reporting batch. A validation qualifier should not be placed on sample data until all quality deficiencies have been identified within the reporting batch.

The following is a listing of data quality indicators and the probable effects on sample data.

Data Quality Indicator	Effect on Sample Data
Instrument Performance Check	Identification and quantitation
Initial Calibration RSD	Quantitation
Continuing Calibration	Quantitation
Method Blank	Positive bias
Internal Standard (Labeled Compound) Spike	Positive or negative bias
Laboratory Control Sample	Method bias
Matrix Spike/Matrix Spike Duplicate	Positive or negative bias and precision
Recovery (Internal) Standard	Positive or negative bias
Cleanup Standard	Quantitation

In the instance of multiple quality deficiencies the validation qualifier should be placed consistent with the acceptable level of uncertainty associated with the intended use of the data. The validation SOW should provide a summary of the intended use(s) of the data. (e.g., risk assessment, fate and transport modeling, waste management) to facilitate appropriate placement of validation qualifiers.

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APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

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RULES, CALCULATIONS, AND EQUATIONS

Rounding Rules

1. In a series of calculations, carry the extra digits through to the final result, and then round off.
2. If the digit to be removed is less than 5, the preceding digit stays the same.
3. If the digit to be removed is equal to or greater than 5, the preceding digit is increased by 1.

Calculations/Equations

C.1 MS % Recovery

$$\%R_{MS} = \frac{SSR - SR}{SA} \times 100$$

where:	SSR	=	Spiked sample result
	SR	=	Sample result
	SA	=	Spike added

C.2 Relative % Difference

$$RPD = \frac{|R1 - R2|}{\overline{X}_{(R1,R2)}} \times 100$$

where:	R1	=	Result 1
	R2	=	Result 2

C.3 Method 8290 – For gas chromatographic peaks that have met the criteria outlined in the method, calculate the concentration of the PCDD and PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RF_n}}$$

where:	C_x	=	Concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g
	A_x	=	Sum of the integrated ion abundances of the quantitation ions (Table 6 of method) for the unlabeled internal standards
	A_{is}	=	Sum of the integrated ion abundances of the quantitation ions (Table 6 of method) for the labeled internal standards
	Q_{is}	=	Quantity, in pg, of the internal standard added to the sample before extraction
	W	=	Weight in g of the sample (solid or organic liquid) or volume in mL of an aqueous sample
	RF_m	=	Calculated mean relative response factor for the analyte

C.4 Method 1613B – Isotope Dilution Quantitation: Relative response (RR) values are used in conjunction with the initial calibration data to determine concentrations directly, so long as labeled compound spiking levels are constant, using the following equation:

$$C_{ex}(ng/nL) = \frac{(A1_n + A2_n)C_l}{(A1_l + A2_l)RR}$$

where:

C_{ex}	=	Concentration of the PCDD/PCDF in the extract
$A1_n/A2_n$	=	Areas of the primary and secondary m/z's for the PCDD/PCDF
$A1_l/A2_l$	=	Areas of the primary and secondary m/z's for the labeled compound
C_l	=	Concentration of the labeled compound in the calibration standard
RR	=	Relative response

C.5 Method 8290 – Internal Standard % Recovery

$$\%R = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times RF_m} \times 100$$

where:

A_{is}	=	Sum of the integrated ion abundances of the quantitation ions (Table 6 of the method) for the labeled internal standard
A_{rs}	=	Sum of the integrated ion abundances of the quantitation ions (Table 6 of the method) for the labeled recovery standard
Q_{is}	=	Quantity, in pg, of the internal standard added to the sample before extraction
Q_{rs}	=	Quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis
RF_m	=	Calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard

C.6 Method 1613B: Relative response for isotope dilution calibration

$$RR = \frac{(A1_n + A2_n)C_l}{(A1_l + A2_l)C_n}$$

where:

$A1_n/A2_n$	=	Areas of the primary and secondary m/z's for the PCDD/PCDF
$A1_l/A2_l$	=	Areas of the primary and secondary m/z's for the labeled compound
C_l	=	Concentration of the labeled compound in the calibration standard
C_2	=	Concentration of the native compound in the calibration standard