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CP2-ES-0811/FR1

Pesticide and PCB Analyses Data Verification and Validation Paducah Gaseous Diffusion Plant, Paducah, Kentucky

FOUR RIVERS NUCLEAR PARTNERSHIP, LLC

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Pesticide and PCB 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
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managing the
Deactivation and Remediation Project at the
Paducah Gaseous Diffusion Plant,
under Contract DE-EM0004895

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APPROVALS

Pesticide and PCB Analyses
Data Verification and Validation
Paducah Gaseous Diffusion Plant,
Paducah, Kentucky

CP2-ES-0811/FR1

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ACRONYMS

CCV	continuing calibration verification
CF	calibration factor
CLP	Contract Laboratory Program
COC	chain of custody
CRQL	contract required quantitation limit
DQO	data quality objective
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
EB	equipment blank
FB	field blank
GC/ECD	gas chromatograph/electron capture detector
GC/MS	gas chromatograph/mass spectrometer
GPC	gel permeation chromatography
INDA/INDB	individual standard mixture A/B
LCS	laboratory control sample
MB	method blank
MDL	method detection limit
MS/MSD	matrix spike/matrix spike duplicate
PB	preparation blank
PEM	performance evaluation mixture
QAPP	quality assurance project plan
QC	quality control
RCM	resolution check mixture
RPD	relative percent difference
RRF	relative response factor
RSD	relative standard deviation
RT	retention time
SCB	sulfur cleanup blank
SCP	single component pesticides
SDG	sample delivery group
SOW	statement of work
SMO	Sample Management Office
SQL	sample quantitation limit
%D	percent difference
%R	percent recovery

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DEFINITIONS

NOTE 1: Qualifier definitions are listed in Appendix A.

NOTE 2: In this plan, 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 plan, 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.

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

COUNTING BATCH—A counting batch is a group of sample aliquots analyzed together on the same instrument detector system.

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

DATA QUALITY OBJECTIVE 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 plan, is defined as the period of time between sample collection and sample activity determination.

LABORATORY CONTROL SAMPLE (LCS)—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—The matrix spike 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. 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.

MINIMUM DETECTABLE ACTIVITY (MDA)—The MDA is the amount of a radionuclide, which if present in a sample, would be detected with a probability of nondetection while accepting a probability of erroneously detecting that radionuclide in an appropriate blank sample. For this plan, the probabilities are both set at 0.05. As defined here, the MDA applies to the nominal concept of detection, (i.e., specific to an instrument, radioanalytical method and typical sample type).

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.

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—Relative standard deviation is the measure of precision between multiple values, defined as the standard deviation of multiple values divided by the mean of the values.

REPORTING BATCH—A reporting batch is a group of sample results reported together in a single data package. The reporting batch may be comprised of samples prepared and analyzed together in the same preparation and counting batches or samples prepared and analyzed in different preparation and counting batches.

REPORTING LIMIT (RL)—The RL 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 CRQLs 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 plan, is a numeric denotation of the concentration, amount, or activity of a specific analytical parameter uniquely associated with an aliquot of environmental media.

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.

SURROGATE—Nontarget standard compounds added to every blank, sample matrix spike, matrix spike duplicate and standard; used to evaluate analytical efficiency by measuring percent recovery.

TURNAROUND TIME—Turnaround time is specified contractually 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.

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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 pesticide and polychlorinated biphenyl (PCB) analyses data verification and validation processes for evaluating analytical data generated using gas chromatography (GC).

This plan provides requirements for developing and implementing a data validation methodology for pesticides and PCB Contract Laboratory Program (CLP) and SW-846 (8081 and 8082) 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 which this plan provides limited guidance (i.e., 40 *CFR* Part 136, *Protection of Environment*, Appendix A—"Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater"; or "Superfund Low Concentration Statement of Work" methods) may necessitate development of modified criteria from this plan; however, the general data validation strategy outlined in this document should be applicable to most GC analytical methods. In the absence of specific guidance contained herein, data validators are advised to seek guidance in the specific method employed and/or from other industry standards. Examples include the U.S. Environmental Protection Agency (EPA) CLP, National Functional Guidelines for Organic Review; EPA Regional Data Validation Guidance; and subject matter experts within the industry.

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 pesticide/PCB data verification and validation.

1.1.2 Scope and Application

This plan applies to pesticide and PCB data verification and validation activities performed by 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 pesticide and/or PCB 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
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

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

Report Elements to be Reviewed*	Level I	Level II	Level III	Level IV
(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
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 Sample and Data Management. The requirements of the Level III and Level IV review and validation efforts will be referred to as "Analytical Data Validation," and the review typically is performed by an entity external to the project. This can be an internal staff member who is not associated with the project, or it may be an independent third party external to the Paducah Site project. 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 data verification process is evaluated.

Data verification, at the project level, is conducted by a 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 some

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 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. 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 pesticide/PCB 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 (if required), batch quality control samples [e.g., laboratory control sample (LCS)], the identification and quantitation of target analytes, performance standards (e.g., surrogates, internal standards) and the effect quality control (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 validation requests and takes, as input, the data verification checklist (or equivalent) and the steps in this plan 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 plan 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 a SMO representative and communicated to the validation organization (for Level III and Level IV validation requests 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, initialing and dating, 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 data verifier's or data 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 VALIDATION STRATEGY AND SOW DEVELOPMENT

The project team, with input as needed from a quality assurance specialist and/or a representative of the Sample and Data Management group, 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. A 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 of any if 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 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), 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) cannot establish custody history, then 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 sample preservation and holding times for routine analyses generally determined by pesticide and PCB methods. The data verifier or data validator shall always follow the most current methodology guidance for sample holding time, temperature, and preservation requirements.

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 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 on the data verification checklist as noncorrectable.

5.3.4 Data Validation

5.3.4.1 Holding Times

The data validator shall review the COC forms and laboratory raw data to determine the elapsed time from sample collection through analysis. Holding times that are listed in hours from collection to analysis will always be calculated using the time collected to ensure the holding time in hours has not lapsed. Holding times that are listed in days will be calculated using dates only. 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 for deviations identified on the data verification checklist.

If samples have been analyzed within the prescribed holding time, no action is warranted.

If holding times are exceeded, qualify as follows:

- If the holding time has been exceeded by < 2, qualify detected results "J" and nondetected results as "UJ."
- If the holding time has been exceeded by > 2, qualify detected results "J" and nondetected results "R."

Table 2. Holding Time and Preservation Criteria

Sample Type	Sample Matrix	Container	Preservative[1]	Holding Time[2]
Pesticides	Aqueous samples with no residual chlorine present	4 × 1-L amber glass container with PTFE-lined (Teflon™) lid, or other size, as appropriate to allow use of entire sample for analysis	0–6°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction
	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.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
	Solid samples (e.g., soils, sediments, sludges, ash)	250 mL wide-mouth glass container with PTFE-lined lid	0–6°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction
PCBs	Aqueous samples with no 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	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

[1] 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 still are attainable.

[2] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage, and analyses performed outside the recommended holding times.

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 and method specific requirements.

Data may be qualified "R" if the data validator determines the effect of holding time has been grossly exceeded; however, detected organochlorine compounds generally are not rejected for soil/solid matrices based solely on holding time criteria due to their relative stability in these matrices. If samples have not been preserved and the holding time has been exceeded, use professional judgment when qualifying the data.

5.3.4.2 Temperature/Preservation

The data validator shall review laboratory receiving records to determine if samples were received at the appropriate temperature and that proper preservative addition (if required) has resulted in the appropriate pH adjustment(s). If records demonstrate samples were received 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 (Table 2), qualify detected analytes "J" and nondetects "UJ."

If samples are received at elevated temperature (6°C < sample temperature < 10°C) but have received the proper pH adjustment, qualify detected analytes "J" and nondetects "UJ." 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 proper preservation has not been followed (pH adjustment), qualify all affected sample results "R" rejected.

Data may be qualified "R" if the reviewer determines the temperature exceedance has had a significant effect on the accuracy of reported sample results. Justification of "R" qualifiers must be provided in the data validation report.

If samples have not been preserved properly in the field or have been stored improperly, qualify those sample results < RL "UJ" and sample results > RL "J."

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

*If samples are received without the proper pH adjustment, or 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."

5.4 GC/ECD INSTRUMENT PERFORMANCE CHECK (REQUIRED FOR CLP METHOD)

5.4.1 Deliverables

- CLP Form IV PEST-4,5; CLP Form VII PEST-1; CLP Form VIII PEST
- Raw data (required for confirmation)

5.4.2 Frequency

The resolution check mixture (RCM) is analyzed at the beginning of every initial calibration sequence, on each GC column and instrument used for analysis. The RCM contains the following pesticides and surrogates in Table 3.

Table 3. Resolution Check Mixture Compounds

Compounds	
gamma-Chlordane	Endrin ketone
Endosulfan I	Methoxychlor
4,4'-DDE	Endosulfan II
Dieldrin	Heptachlor-epoxide
Endosulfan sulfate	alpha-Chlordane
alpha-BHC	4,4'-DDD
beta-BHC	4,4'-DDT
delta-BHC	Endrin
gamma-BHC	Endrin aldehyde
Aldrin	Tetrachloro-m-xylene (surrogate)
Heptachlor	Decachlorobiphenyl (surrogate)

The performance evaluation mixture (PEM) is analyzed at the beginning (following the RCM) and at the end of the initial calibration sequence. The PEM analysis must bracket one end of each 12-hour analytical period. The PEM contains the following pesticides and surrogates in Table 4.

Table 4. Performance Evaluation Mixture Compounds

Compounds	
gamma-BHC	Endrin
alpha-BHC	Methoxychlor
4,4'-DDT	Tetrachloro-m-xylene (surrogate)
beta-BHC	Decachlorobiphenyl (surrogate)

5.4.3 Criteria

- For the RCM, the resolution between two adjacent peaks in the RCM must be ≥ 80% for all analytes for the primary column and ≥ 50% for the confirmation column in order to use one individual standards mixture (C). If two individual standard mixtures (A and B) are to be used, the resolution between two adjacent peaks in the RCM must be ≥ 60%.

- For the PEM, the resolution between any two adjacent peaks in the initial calibration and continuing calibration verification PEMs must be ≥ 90% on each GC column.

Retention time (RT) must be within RT windows, centered around the mean RTs determined from the three-point initial calibration using the individual standard mixtures [i.e., individual standard mixture A/B (INDA and INDB)].

- Relative percent difference (RPD) between the calculated amount and the amount added for each single component pesticide and surrogate in the PEM analyses must be within ± 25%.

- Percent breakdown of 4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT) and endrin in each PEM must be ≤ 20%. Combined percent breakdown must be ≤ 30%.

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 laboratory and request that 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 in the data.

The data verifier shall 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, the data verifier shall contact the laboratory and request that the missing information be provided. If the omission is the result of a technical issue or due to an omitted analytical requirement, direct the issue to the SMO. The SMO will direct the laboratory to complete the analysis in accordance with the SOW.

5.4.5 Data Validation

The data validator shall qualify only if the deviation indicates an adverse effect on data quality.

- RCM

  If resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may also be questionable if coelution exists. Qualify detects for target compounds that were not adequately resolved "NJ." Qualify nondetects unusable "R."

- PEM

  If PEM analysis is not performed at the required frequency, qualify all associated sample and blank results as unusable "R."

  If PEM resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may be questionable if coelution exists. Qualify detects "NJ." Qualify nondetects as unusable "R."

  If 4,4'-DDT breakdown is > 20%, qualify detects for 4,4'-DDT "J" and qualify detects for 4,4'-dichlorodiphenyldichloroethane [4,4'-DDD and/or 4,4'-dichlorodiphenyldichloroethylene (4,4'-DDE) "J"]. If 4,4'-DDT was not detected but 4,4'-DDD and/or 4,4'-DDE were detected, qualify nondetects for 4,4'-DDT as unusable "R," and qualify detects for 4,4'-DDD and/or 4,4'-DDE as presumptively present at an approximated quantity as "NJ."

  If endrin breakdown is > 20%, qualify detects for endrin "J" and qualify detects for endrin aldehyde and/or endrin ketone "J." If endrin was not detected, but endrin aldehyde and/or endrin ketone were detected, qualify the nondetects for endrin as unusable "R," and qualify detects for endrin aldehyde and/or endrin ketone as presumptively present at an approximated quantity "NJ."

  If mid-point individual standard mixture analysis is not performed at the required frequency, or if mid-point INDA/INDB or individual standard mixture (C) resolution criteria are not met, qualify detected target compounds that were not adequately resolved "NJ" and qualify nondetects as unusable "R."

GC/ECD (gas chromatograph/electron capture detector) instrument performance check validations are listed in Table 5.

Table 5. GC/ECD Instrument Performance Check Validation

Criteria (INDA/INDB)	Criteria [Individual Standard Mixture (C)] Action	Validation
Resolution Check Mixture % Resolution < 60%	Resolution Check Mixture % Resolution < 80% (primary column) % Resolution < 50% (secondary column)	Detects: NJ Nondetects: R
PEM % Resolution < 90%		Detects: NJ Nondetects: UJ
PEM: 4,4'-DDT % Breakdown < 20% and 4,4'-DDT is detected		Detects for 4,4'-DDT: J Detects for 4,4'-DDD: J Detects for 4,4'-DDE: J
PEM: 4,4'-DDT % Breakdown > 20% and 4,4'-DDT is not detected		Nondetects for 4,4'-DDT: R Detects for 4,4'-DDD: NJ Detects for 4,4'-DDE: NJ
PEM: endrin % Breakdown > 20% and endrin is not detected		Detects for endrin: J Detects for endrin aldehyde: J Detects for endrin ketone: J
PEM: Combined % Breakdown > 30%		Nondetects for endrin: R Detects for endrin aldehyde: NJ Detects for endrin ketone: NJ
Mid-point INDA/INDB % Resolution < 90%	Mid-point individual standard mixture (C) % Resolution < 80% (primary column) Mid-point individual standard mixture (c) % Resolution < 50 (secondary column)	Detects: NJ Nondetects: R
PEM analysis not performed at the required frequency		All results: R
Mid-point individual standard mixtures analysis not performed at the required frequency		All results: R

5.5 INITIAL CALIBRATION

Initial calibration is performed prior to analysis of samples to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide and PCB compounds on the target compound list.

5.5.1 Deliverables

- CLP Form IV PEST 1,2,3; CLP Form VII PEST 2
- Raw data (required for confirmation)

5.5.2 Frequency

Initial calibration must be performed before any samples are analyzed on the GC/ECD or gas chromatograph/electrolyte conductivity detector system.

5.5.3 Criteria

- Pesticides

  Individual standard mixture must be analyzed at five concentration levels during the initial calibration. The mean RTs of each of the single component pesticides (SCP) and surrogates are determined from the five-point initial calibration. An RT window must be calculated for each single component analyte and surrogate.

  Mean calibration factor (CF) must be calculated for each single component analyte and surrogate over the initial calibration range. The percent relative standard deviation (%RSD) of the CFs for each of the single component target compounds must be ≤ 20%, except for alpha-BHC and delta-BHC, which must be ≤ 25%. The %RSD of the CFs for the two surrogates (tetrachloro-m-xylene and decachlorobiphenyl) must be ≤ 30%.

  Toxaphene must be analyzed separately at a minimum of five different concentration levels during the initial calibration sequence. The peaks chosen must not share the same RT window as any SCP. A CF must be determined for each peak and the RT window is calculated. The %RSD of the CFs for each of the toxaphene peaks must be ≤ 30%. The %RSD of the CFs for the two surrogates [tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB)] must be ≤ 30%. The RT window should be ± 0.07 minutes of the absolute RTs.

- PCBs

  An initial five-point calibration is performed using Aroclors 1016 and 1260. These Aroclors may be analyzed in a single standard mixture. The RT of each of the three to five major peaks of Aroclors 1016 and 1260 and the RT of the surrogates are determined from the five-point calibration. For the other seven Aroclors, the RTs of each of the three to five major peaks and the RT of the surrogates are determined from the single-point standard initial calibration.

  An RT window must be calculated as ± 0.07 for each of the three to five Aroclor peaks and ± 0.05 and ± 0.10 for the surrogates TCMX and DCB, respectively. At least one Aroclor standard must yield peaks that give recorder deflections between 50–100% of full scale.

  Percent relative standard deviation of CFs for the three to five major peaks of each of the Aroclor compounds must be ≤ 20%. The %RSD of the CFs for the two surrogates must be ≤ 20%.

  When SW-846 methods are analyzed, a linear calibration curve may be generated as an alternate calibration to the %RSD method. When a linear calibration is used, the correlation coefficient should be > 0.99.

5.5.4 Data Verification

The data verifier shall verify the presence of required report forms. If they are not provided, contact the laboratory and request that they be provided.

The data verifier shall verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. Verify that the correct standards and standard concentrations were used to calibrate the instrument. If any criteria have not been met, or if information is omitted from the laboratory report, the data verifier shall contact the laboratory and request that the missing information be provided. If the omission is the result of a technical issue or due to an omitted analytical requirement, direct the

issue to the SMO. If issues cannot be resolved with the laboratory such that the occurrences are considered noncorrectable, indicate this on the data verification checklist and transmit it to the data validator.

5.5.5 Data Validation

The data validator shall qualify only if the deviation indicates an adverse effect on the data quality. If any initial calibration performance criteria are not met, the data validator shall use professional judgment to determine if the deviation affects the data usability. If the %RSD or linear calibration criteria are not met, the data validator shall qualify detects as "J" and apply professional judgment to nondetected target compounds.

Following is criteria for %RSD and linear calibrations for target compounds and surrogates:

- < 20% for single component target compounds except alpha-BHC and delta-BHC
- < 25% for alpha-BHC and delta-BHC
- < 30% for toxaphene peaks and surrogates (TCMX and DCB)
- < 20% for Aroclors and surrogates (TCMX and DCB)
- > 0.99 correlation coefficient for linear calibrations

For raw data confirmation, the data validator shall evaluate recorder deflections for peaks from at least one chromatogram that must be > 50% of full scale. If this criterion is not satisfied, qualify samples only if the peak heights or areas are small enough to preclude accurate quantitation of detected compounds.

Initial Calibration				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the initial calibration performed at the proper frequency?				*	*
2. Were the ISM (INDA and INDB) analyzed at low, middle and high levels during initial calibration? **(CLP Methods Only)**				*	*
3. Was the resolution of the midpoint INDA and INDB ≥ 90%? **(CLP Methods Only)**				J	R**
4. Is %RSD for single component pesticides within allowable limits? **(SW-846 Methods Only)**				J	UJ
5. Was the appropriate number of standards used? **(SW-846 Methods Only)**				*	*
6. Were the appropriate standard concentrations used? **(SW-846 Methods Only)**				J	R**
7. Is the correlation coefficient of the curve ≥ 0.99? **(SW-846 Methods Only)**				R**	R**
8. Do any of the samples exceed the linearity of the calibration and not diluted and reanalyzed?				J	**
9. Are printer/recorder deflections > 50% of full scale on at least one chromatogram from each INDA and INDB? **(CLP Methods and Level IV Data Validation only)**				See specific guidance in CP2-ES-0811	

*Use professional judgment and qualify only if the deviation indicates an adverse effect on the 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 IV-PEST 6,7; CLP Form VII-PEST 1,2; CLP Form VIII-PEST
- Raw data (required for confirmation)

5.6.2 Frequency

Immediately following initial calibration, calibration verification for CLP methods must begin with the analysis of an instrument blank, PEM, and the INDA/INDB or individual standard mixture (C). Throughout the analytical run the blank, PEM, and midpoint standard must bracket each end of a 12-hour period. For SW-846 methods, a blank and a continuing calibration standard must be analyzed at the beginning of each 12-hour period and after each group of 20 samples (after every 10 is recommended).

5.6.3 Criteria

5.6.3.1 Resolution criteria

Resolution between any two adjacent peaks in the midpoint concentration in individual standard mixtures must be $\geq$ 90%.

5.6.3.2 Retention time windows

The absolute RT for each SCP and surrogate in the midpoint concentration of individual standard mixtures must be within the RT windows determined from initial calibration. If a continuing calibration verification is required for toxaphene because of its detection in a sample, the absolute RT for each toxaphene peak must be within the RT windows determined from the initial calibration. All samples injected after the last in-control standard potentially are affected.

5.6.3.3 RPD limits

- Pesticides

  For CLP methods, RPD between the calculated amount and true amount for each of the single component pesticides and surrogates in the midpoint concentration in individual standard mixtures must not exceed ± 25%. For Method 8081, the percent difference (%D) between response factors for the initial and continuing calibration must be within ± 20%.

- PCBs

  The RPD between the CF and each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration of the Aroclor standards and the CF from the initial calibration must be within ± 15%.

5.6.4 Data Verification

The data verifier shall verify the presence of required report forms. If they are not provided, contact the laboratory and request that they be provided.

The data verifier shall verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. Verify that the correct standards and standard concentrations were used. If any criteria have not been met, or if information is omitted from the laboratory report the data verifier shall contact the laboratory and request that the missing information be provided. If the omission is the result of a technical issue or due to an omitted analytical requirement, direct the issue to the SMO. If issues cannot be resolved with the laboratory, such that the occurrences are considered noncorrectable, indicate this on the data verification checklist and transmit it to the data validator.

5.6.5 Data Validation

The data validator shall qualify only if the deviation indicates an adverse effect on the data quality. If the RT criteria are not met or time elapsed is greater than acceptable limits, then professional judgment should be applied.

- Pesticides

  If percent difference (%D) > 25% for CLP methods or > 15% for SW-846 methods, qualify affected detected target compounds as "J" and nondetects as "UJ."

- PCBs

  If %D > ± 15%, qualify affected detected target compounds as "J" and nondetects as "UJ."

A summary of continuing calibration validation qualifications is found in Table 6.

Table 6. Continuing Calibration Validation

		Action	
Sample Type	**Criteria**	**Detected Associated Compounds**	**Nondetected Associated Compounds**
Pesticides	RT out of RT window	Use Professional Judgment	
	%D not within ±	J	UJ
	Time elapsed > acceptable limits	R	
PCBs	RT out of RT window	No Qualification	
	%D not within ± 15%	Use Professional Judgment	
	Time elapsed > acceptable limits	J	UJ
	RT, %D, time elapsed are within acceptable limits	No Qualification	

Continuing Calibration				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the continuing calibration performed at the proper frequency?				*	*
2. Was the resolution of the midpoint INDA and INDB ≥ 90%? **(CLP Methods Only)**				J	R**
Is the RPD between the true and calculated amount for single component compounds < 20% or ≤ 25%? **(CLP Methods Only)**				J	UJ
3. Are response factors within ± 15% of the initial calibration? **(SW-846 Methods Only)**				J	UJ

*Use professional judgment and qualify only if the deviation indicates an adverse effect on the data quality.
**Qualify as appropriate

5.7 BLANKS

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. Initial calibration blanks 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 carefully evaluated to determine whether a systematic problem affecting greater than one sample exists or whether the contamination is an isolated occurrence.

Additionally, the project team may elect to collect and analyze 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 (FB) 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 blank provides an indication as to whether or not nondedicated sampling equipment has been decontaminated properly, and what, if any, carry over may arise between sampled locations. It has been EPA Region 4 data validation policy to evaluate the FBs and equipment rinseate blanks as part of the validation process, but not to qualify the data based on these field samples.

5.7.1 Deliverables

- Method blank: CLP Form I, or equivalent for SW-846
- Instrument blank: CLP Form IV-PEST and CLP Form VIII-PEST
- 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.

- For CLP methods, an acceptable instrument blank must be analyzed at least once in each 12-hour period immediately prior to the analysis of either the PEM or INDA and INDB, depending on the position in the analysis sequence.

- For CLP methods, an instrument blank must be analyzed immediately after a sample containing compound(s) at high concentration(s) for carryover.

- For SW-846 methods, where practical, samples with unusually high concentrations of analytes should be followed by a solvent blank or by analysis of organic-free reagent water to check for cross-contamination.

NOTE: When the analysis of such blanks is not possible, such as when an unattended autosampler is employed, the analyst should review the results for at least the next two samples after the high-concentration sample. If analytes in the high concentration sample are not present in the subsequent samples, then the lack of carryover has been demonstrated. If evidence suggests that carryover may have occurred, then the samples should be reanalyzed.

- The sulfur cleanup blank (SCB) must be analyzed whenever part of a set of samples extracted together requires sulfur cleanup. If the entire set of samples associated with a method blank is subjected to sulfur cleanup, the MB will suffice as a SCB, and no separate SCB is required.

5.7.3 Criteria

Compounds detected in blanks analyzed under CLP must be at levels less than the RL. Blank performance criteria are not specified for SW-846 methods. For the purposes of data validation, blank contamination shall be evaluated against CLP guidelines.

5.7.4 Data Verification

The data verifier shall verify the presence of the pertinent deliverables for blank analyses. If the required information is not present in the laboratory report, or if the frequency of analysis is not satisfied, the data verifier will contact the laboratory to obtain the omitted information. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If the information cannot be obtained, these occurrences are considered noncorrectable problems and will be identified as such on the data verification checklist. As this is a contract compliance issue, the occurrence should be communicated to the SMO and the data validator on the data verification checklist.

5.7.5 Data Validation

Verify that results for the method blank and instrument blanks (if required) are reported accurately on the laboratory summary form from the raw data (Level IV only). The data validator shall qualify only if the deviation indicates an adverse effect on data quality.

All laboratory blanks associated with the batch must be evaluated against the sample results in the batch. However, qualification should be applied only to those samples directly related to the affected blank (if more than one blank is used per batch). Sample results are not qualified based on FB samples (FBs or equipment rinseate blanks), but the data validation report can address FB contamination if it is present.

Any analyte that is reported in both blank and sample must be evaluated; however, if the same analyte is reported in the sample(s) and more than one blank, the sample(s) should be evaluated against the blank with the highest concentration of the analyte.

NOTE: Sample results must not be modified by subtracting blank values from sample concentrations.

- If sample concentration is > RL and > 5 × blank concentration, no qualification of result is necessary.
- If sample concentration is > RL and < 5 × blank concentration, qualify the reported result as "U."
- If sample concentration is < RL and < 5 × blank concentration, qualify the reported result as "U."
- 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."
- Raw data confirmation—Verify that results for the method blank and instrument blanks (if required) are reported accurately on the laboratory summary form from the raw data.

Blanks				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have method blanks been analyzed at the proper frequency?				*	*
2. Are sample results > RL and > 5 × blank result (if blank contamination is present)?					
• Sample result is > RL and < 5 × the blank result				U	NA
• Sample result is < RL and < 5 × the blank result				U	NA
• Gross contamination				R	**
3. Have instrument blanks been analyzed after samples showing high concentrations?				See specific guidance in CP2-ES-0811.	

*Use professional judgment and qualify only if the deviation indicates an adverse effect on the data quality.
**Qualify as appropriate.

5.8 SURROGATE STANDARDS

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample extraction. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

5.8.1 Deliverables

- CLP Form II PEST-1 and 2 or equivalent for SW-846
- Raw data (required for confirmation)

5.8.2 Frequency

All samples, standard mixtures, PEMs, blanks, and matrix spikes are fortified with two surrogates: TCMX and DCB. The surrogates also are added to all the standards to monitor retention times.

5.8.3 Criteria

Performance criteria are not specified for SW-846 methods 8081 and 8082 for surrogate standard recovery, retention time, or RPD. For purposes of data validation, sample results should be evaluated against the laboratory's established acceptable limits. In the absence of laboratory defined limits, surrogate performance shall be evaluated against CLP guidelines.

- The CLP advisory percent recovery (%R) limits for the surrogates are 30–150% for both water and soil matrices. Consideration must be given to the fraction to which the surrogate is applied. For CLP analysis, the pesticide fraction should be compared to TCMX and the PCB fraction should be compared to DCB. For method 8081, the surrogates DCB and TCMX are recommended. For 8082, DCB is used when PCBs are determined as Aroclors and TCMX is used for PCB congener analysis.

- The surrogates must fall within the RT windows from the initial calibration (TCMX ± 0.05 minutes; DCB ± 0.10 minutes).

5.8.4 Data Verification

The data verifier shall verify the presence of required report forms. If they are not provided, contact the laboratory and request that they be provided.

The data verifier shall 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, the data verifier shall contact the laboratory and request that the missing information be provided. If the omission is the result of a technical issue or due to an omitted analytical requirement, direct the issue to the SMO. If issues cannot be resolved with the laboratory so that the occurrences are considered noncorrectable, indicate this on the verification checklist and transmit it to the data validator.

5.8.5 Data Validation

If either surrogate spike recovery is outside the acceptance limits, the reviewer must consider the existence of coelution and interference in the raw data and use professional judgment to qualify data, as surrogate recovery problems may not directly apply to target analytes.

If laboratory-generated control limits are provided, qualify as follows:

- If surrogate %R is within laboratory control limits, no qualifications are necessary.

- If any surrogate %R exceeds the laboratory upper control limit, then qualify detected results as "J". Nondetected results require no qualification.

- If any surrogate %R is between 10% and the laboratory lower control limit, then qualify detected results as "J" and nondetected results as "UJ."

- If any surrogate %R < 10%, then qualify detected results as "J" and nondetected results as "R," unless dilution is a factor in the %R then use professional judgment.

If laboratory-generated control limits are not provided, qualify as follows:

- If surrogate %R = 150–200%, qualify detected compounds "J." Nondetects are not qualified.
- If the surrogate %R > 200%, qualify detected compounds "J," and use professional judgment to qualify nondetects.
- If surrogate %R = 10–30%, qualify detected compounds "J," and nondetects "UJ."
- If surrogate %R = 0–10%, qualify detected compounds "J," and nondetects "R," unless dilution is a factor in the %R then use professional judgment.

If surrogates are detected outside the RT windows, the possibility of false negatives exists. The data validator must employ professional judgment to determine the effect of the RT window shift on reported target compounds. Data validators also are advised to consult other industry standard references and/or subject matter experts to aid in the evaluation. If the RT window has only a minor impact on the reported values, qualify detections "J" and nondetects "UJ." If the shift does not allow for proper quantitation, qualify all affected results as rejected "R." The data validation report will contain the technical basis for assignment of qualifiers relative to RT window shifts and their effect on the data.

For raw data confirmation, recalculate one surrogate recovery from raw data. Equation C.6 in Appendix C is used for calculating surrogate %R.

Surrogate Standards				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have surrogate standards been analyzed at the proper frequency??				*	*
2. Are all surrogate %Rs within established limits?					
• Is %R = 0–10%?				J	R*
• Is %R = 10–30%?				J	UJ
• Is %R = 150-200%?				J	NA
• Is %R > 200%?				J	*
3. Are surrogate standards within the appropriate retention time windows?				J	J/R
4. Confirm from raw data that compounds reported in the method blank are detected above the RL (applies to Level IV validation only)					

*Use professional judgment in qualifying data as surrogate recovery problems may not directly apply to target analytes.

5.9 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

Matrix spike/matrix spike duplicate (MS/MSD) data are generated to determine precision and accuracy of the analytical method on the sample matrices being quantified. Qualification must not be applied to sample data based on MS/MSD data alone, but should be used in conjunction with other QC parameters in judging data usability and the need for data qualification.

NOTE: For a matrix spike 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 matrix spike 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 matrix spike, and that only the field sample used to prepare the matrix spike sample should be qualified.

5.9.1 Deliverables

- MS/MSD results
- Sample preparation log
- CLP Form III PEST-1 and 2 ; CLP Form III ARO-1, 2
- Raw data (required for confirmation)

5.9.2 Frequency

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

5.9.3 Criteria

Inspect the %R of the MS/MSD and ensure that the recoveries and RPD are within laboratory limits. If no laboratory limits are specified, then use the following advisory limits in Table 7.

Table 7. Matrix Spike Recovery and RPD Validation

Sample Type	Compound	% Recovery Water	RPD Water	% Recovery Soil	RPD Soil
Pesticides	gamma-BHC (Lindane)	56–123	0–15	46–127	0–50
	Heptachlor	40–131	0–20	35–130	0–31
	Aldrin	40–120	0–22	34–132	0–43
	Dieldrin	52–126	0–18	31–134	0–38
	Endrin	56–121	0–21	42–139	0–45
	4,4'-DDT	38–127	0–27	23–134	0–50
PCBs	Aroclor 1016	29–135	0–15	29–135	0–15
	Aroclor 1260	29–135	0–20	29–135	0–20

5.9.4 Data Verification

The data verifier shall verify that MS/MSD samples were analyzed at the required frequency and that results are provided for each sample. If results are omitted from the laboratory report, the data verifier will contact the laboratory to obtain the omitted information. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If results cannot be obtained or the frequency of analysis is not satisfied, these occurrences are considered noncorrectable problems and will be identified as such on the data verification checklist. As this is a contract compliance issue, the occurrence will be communicated to the SMO and data validator on the data verification checklist.

5.9.5 Data Validation

The data validator shall qualify only if the deviation indicates an adverse effect on data quality. Data validation of samples and sample groups using the MS/MSD should be conducted in conjunction with other quality control indicators for pesticides and PCBs. These generally include initial and continuing calibration checks, LCS, and surrogate standards.

When poor MS/MSD performance is the only difficulty associated with a sample group, the data validator is advised that only under special circumstances should qualification be applied (see below). For more routine occurrences of MS/MSD recovery difficulties, the data validator will evaluate MS/MSD performance in conjunction with key indicators to determine if matrix-specific or instrumental problems are the cause of poor performance. Only when other indicator(s) have shown similar difficulties (e.g., low MS recovery coupled with low surrogate recovery) should qualification be assigned.

A determination shall be made concerning 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, then qualification should be limited to that sample alone. However, it may be determined that the laboratory is having a systematic problem in the analysis of one or more compounds which affects all associated samples. Positive results of non-spiked compounds may be qualified "J" as appropriate. For any %R $\geq$ 20% and < the lower acceptance limit qualify nondetected target compounds as approximated "UJ." For any %R < 20% qualify detected target compounds as a "J" and use professional judgment for nondetected target compounds.

For raw data confirmation, recalculate one matrix spike recovery from raw data. Equation C.1 in Appendix C is used to calculate matrix spike %R.

Matrix Spike/Matrix Spike Duplicate				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the MS/MSD performed at the proper frequency?				*	*
2. Are all MS/MSD compounds within control criteria?				J**	UJ**
• Is %R or RPD > upper acceptance limit?				J	--
• Is %R < lower acceptance limit and %R $\geq$ 20%?				J	UJ
• Is %R < 20%?				J	*
3. Are all MS/MSD RPD results within control criteria?				J**	**

*Use professional judgment and qualify only if the deviation indicates an adverse effect on the data quality.
**Qualify as appropriate.

5.10 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. Nonhomogeneous samples can impact the apparent method precision; however, aqueous/water samples are generally homogeneous and most soil/sediment samples are homogeneous within a factor of two or three.

5.10.1 Deliverables

- Sample preparation log
- CLP Form III PEST-1 and 2; CLP Form III ARO-1, 2
- Raw data (required for confirmation)

5.10.2 Frequency

One laboratory duplicate shall be analyzed in accordance with the sample methodology used. Typically, a laboratory duplicate is analyzed per each sample batch or once per 20 samples, whichever is more frequent. Field duplicates are collected at a frequency identified in associated project planning documents (e.g., QAPPs).

5.10.3 Criteria

- Samples identified as FBs must not be analyzed as laboratory duplicate.

- For sample concentrations > 5 × the RL, the laboratory duplicate precision for aqueous samples as measured by RPD must be within ± 25% (lab duplicate and field duplicate). For solid matrices the RPD must be within ± 25% (lab duplicate) or ± 35% (field duplicate). If the sample values are < 5 × the RL, RPD does not apply. Instead, the absolute difference between sample and duplicate must be either < 5 × the RL.

5.10.4 Data Verification

The data verifier shall verify that FBs were not analyzed as laboratory duplicates. If an FB has been used, the SMO will be notified immediately to ensure timely corrective action. If reanalysis cannot be completed, this issue will be identified as noncorrectable on 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 noncorrectable problems and shall be identified in this way on the data verification checklist. Because they are contract-compliance related, all such occurrences shall be communicated to the SMO and to the data validator on the data verification checklist.

5.10.5 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.

Table 8. Laboratory and Field Duplicate Qualification

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

5.11 LABORATORY CONTROL SAMPLE

The LCS is not required for the CLP methods, but is required for SW-846 methods 8081 and 8082. It is stressed that this standard must be the same matrix as the analytical samples (especially for aqueous samples) and prepared and analyzed to demonstrate initial proficiency of the method. The LCS is prepared from an addition of a LCS concentrate into the appropriate clean matrix, extracted, and analyzed.

5.11.1 Deliverables

- Report summary of all analytes in the LCS
- Raw data (required for confirmation)

5.11.2 Frequency

The LCS shall be prepared and analyzed with each analytical batch or every group of 20 samples (of similar matrix) to demonstrate initial proficiency of the method. The LCS must be reanalyzed when significant changes in instrumentation are made or when LCS performance falls outside of laboratory or method specified limits or the advisory limits provided below.

5.11.3 Criteria

The LCS must fall within limits established by the laboratory for each determinative method. If no limits are specified, then use the following advisory limits in Table 9 when evaluating results.

5.11.4 Data Verification

The data verifier shall verify the presence of LCS results. If results are omitted from the laboratory report, the data verifier will contact the laboratory to obtain the omitted information. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If LCS analysis was required but not performed, this is considered a noncorrectable problem and shall be indicated on the data verification checklist. As this is a contract compliance issue, the occurrence should be communicated to the SMO and the data validator on the data verification checklist.

Table 9. LCS Recovery Validation

Sample Type	LCS Spike Compound	Recovery Limits (%)	LCS Spike Compound	Recovery Limits (%)
Pesticides	gamma-BHC	50–120	Endosulfan sulfate	50–120
	Heptachlor epoxide	50–150	gamma-Chlordane	30–130
	Dieldrin	30–130	Tetrachloro-m-xylene (surrogate)	30–150
	4,4'-DDE	50–150	Decachlorobiphenyl (surrogate)	30–150
	endrin	50–120		
PCBs	Aroclor 1016	50–150	Tetrachloro-m-xylene (surrogate)	30–150
	Aroclor 1260	50–150	Decachlorobiphenyl (surrogate)	30–150

5.11.5 Data Validation

If the LCS criteria are not met, laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data for which the associated LCS does not meet the required criteria.

- The data validator shall verify that the LCS was prepared and analyzed in the same fashion as the sample it accompanies. If the LCS was analyzed only (i.e., not prepared), it will provide limited value for method accuracy. Qualification should be applied only if the LCS and other QC data within the batch indicate that the accuracy of reported compounds has been affected.

- If the LCS %R > the upper acceptance limit, detected target compounds may be qualified as "J." Nondetected target compounds should not be qualified.

- If the LCS %R < the lower acceptance limit, qualify detected target compounds as "J" and nondetects estimated as "UJ" or rejected as "R" (use professional judgment).

- Professional judgment should be used to qualify data for compounds other than those compounds that are included in the LCS. Professional judgment to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in the performance of the LCS compound to the non-LCS compound.

Laboratory Control Sample (SW-846 Methods Only)				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Was the LCS performed 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
• %R > Upper Acceptance Limit?				J	No Qualification
• %R < Lower Acceptance Limit?				J	UJ/R*
4. Was the LCS of the same matrix as the analyzed samples?				*	*

*Use professional judgment.

5.12 PESTICIDE CLEANUP CHECK

Pesticide cleanup is performed to remove matrix interferences from sample extracts prior to analysis. Florisil® cleanup significantly reduces these interferences caused by polar compounds. Gel permeation chromatography (GPC) is used to remove high molecular weight contaminants that can interfere with the analysis of target compounds.

The pesticide cleanup procedures are checked by fortifying the cleanup columns and cartridges, and verifying the %R of pesticides that may be affected through the cleanup procedure.

5.12.1 Deliverables

- CLP Form IX, PEST-1 and 2
- Raw data (required for confirmation)

5.12.2 Frequency

- For CLP Methods, Florisil® cleanup is used on all sample extracts, and GPC is used for the cleanup of all soil extracts and for water sample extracts containing high molecular weight components that interfere with the analysis of the target compounds.

- For SW-846 Methods, the Florisil® cleanup procedure is required to be performed on all samples and QC samples in order to evaluate the cleanup procedure is functioning adequately. GPC is performed at the discretion of the analyst.

5.12.3 Criteria

- For CLP Methods, each lot number of Florisil® must be checked by spiking with 2,4,5-trichlorophenol and the midpoint concentration of INDA. Florisil® cartridges are considered acceptable for use if recoveries of 80–120% in INDA are reported, if %R of 2,4,5-trichlorophenol is < 5%, and if no peaks interfering with target compounds are detected.

- The calibration of the GPC unit must be checked at least once every seven days by injecting the GPC calibration verification solution. The GPC calibration is acceptable if the two UV traces meet the following requirements:

  — Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
  — Corn oil and the phthalate peaks should exhibit > 85% resolution.

— The phthalate and methoxychlor peaks should exhibit > 85% resolution.
— Methoxychlor and perylene peaks should exhibit > 85% resolution.
— Perylene and sulfur peaks must not be saturated and should exhibit > 90% baseline resolution.
— The RT shift is < 5% between UV traces for bis(2-ethylhexyl)phthalate and perylene.

- For SW-846 Methods, if QC samples show percent recoveries of surrogates that are outside criteria, evaluate whether the recovery may have been due to matrix effects or loss through extraction prior to qualification.

5.12.4 Data Verification

The data verifier shall verify the presence of required report forms. If they are not provided, contact the laboratory and request that they be provided.

The data verifier shall 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, the data verifier shall contact the laboratory and request that the missing information be provided. If the omission is the result of a technical issue or due to an omitted analytical requirement, direct the issue to the SMO. If issues cannot be resolved with the laboratory such that the occurrences are considered noncorrectable, indicate this on the data verification checklist and transmit it to the data validator.

5.12.5 Data Validation

The data validator shall qualify only if the deviation indicates an adverse effect on data quality.

If frequency requirements have not been satisfied, sample data should be qualified only if the deviation indicates an adverse effect on data quality.

- If %R < 10%, the data validator should qualify nondetects as "R." If %R of pesticide compounds is > 120%, professional judgment must be used in qualification of detected target compounds; nondetects need no qualification.

For raw data confirmation, if criteria are not satisfied, raw data should be examined for the presence of high molecular weight contaminants. If these contaminants are present and significantly preclude accurate quantitation of target compounds, affected detected compounds may be qualified as "J" and nondetects qualified as "R."

Pesticide Cleanup Check				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have the Florisil and/or GPC cleanup been analyzed at the proper frequency?				*	*
2. Are all %R within established limits?					
• Is %R < 10%?				**	R
• Is %R > 120%?				**	NA
3. For noncompliant cleanup analyses, have raw data been inspected for presence of high molecular weight compounds? (Level IV validation only)				See specific guidance in CP2-ES-0811	

*Use professional judgment and qualify only if the deviation indicates an adverse effect on data quality.
**Qualify as appropriate.

5.13 TARGET COMPOUND IDENTIFICATION

5.13.1 Deliverables

- CLP Form I or equivalent for SW-846 methods
- Raw data (if required)

5.13.2 Criteria

Retention times for both of the surrogates, matrix spikes, and reported compounds in each sample must be within the calculated RT windows on both columns. TCMX must elute within ± 0.05 minutes of the mean RT determined from initial calibration; and DCB must elute within ± 0.10 minutes of the mean RT determined from initial calibration.

5.13.3 Data Validation

- The data validator shall ensure that all detectable sample results have been analyzed on the two contract-required chromatographic columns.

- Check sample chromatogram for peaks close to the expected retention window of the pesticide or PCBs of interest. If no peaks are present either within or close to the RT window, nondetected values can be considered valid.

- If the affected sample chromatogram contains peaks > RL, and either close to or within the expected retention window of the pesticide of interest, the possibility of false negatives exists. Calibration RT windows should be consulted to determine appropriate window of elution; and the sample chromatogram should be inspected for occurrences of high concentration compounds or contaminants, or matrix interferences that may affect the RT window of the sample.

- Ensure that an instrument blank was analyzed immediately after a sample containing compound(s) at high concentration(s) for carryover.

- If RT criteria are not met, the possibility of false positives and false negatives exists. All target compounds reported as detected should be changed to nondetected status with the sample quantitation limit (SQL) reported instead of a detected value; use the following guidance when reporting SQL(s) instead of detected values:

  — If a misidentified peak was sufficiently outside the target pesticide RT window, the reported values may be false positive and should be replaced with the SQL value.

  — If a misidentified peak poses an interference with potential detection of a target peak, then the reported value should be qualified "R."

  — If multi-component target compounds exhibit marginal pattern-matching quality, professional judgment should be used to establish whether the differences are due to environmental "weathering" (degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of a multicomponent pesticide is strongly suggested, results should be reported "NJ."

- The data validator must verify that gas chromatograph/mass spectrometer (GC/MS) confirmation was run on samples if concentrations of any compound exceed 10 ng/µL. If the samples have been analyzed for the presence of volatiles or semivolatiles, a cross-reference should be made to the TICs in these fractions to determine the possible identify of artifacts detected in the pesticide/PCB fraction.

- If multi-component pesticides/PCBs exhibit marginal pattern-matching quality, professional judgment should be used to establish whether the differences are due to degradation of earlier eluting peaks relative to later eluting peaks. If the presence of a multi-component pesticide is strongly suggested, results should be reported "N." If a pattern matches more than one Aroclor, the best match should be chosen.

5.14 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.

First, supply the data system a consistent set of input designed to provide a consistent set of outputs. Next, 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, the laboratory shall be contacted to determine if omissions or other factors are contributing to calculation issues. If the problem cannot be corrected through correspondence with the laboratory, it may be necessary to qualify results. The data validator will use professional judgment to determine the effect of the calculation effort(s). If reported results can be reconstructed through other means, reported values will be changed manually during data validation to reflect corrected values. If results cannot be reproduced by the laboratory or the data validator, qualify affected results "R." Justification for the assignment of an "R" qualifier will be provided in the data validation report.

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

5.15 REPORTING LIMITS AND SAMPLE QUANTITATION LIMITS

RLs have been developed to enable the laboratory to meet realistic detection limit goals while accommodating many different types of project DQOs. Due to deviations from method-specified sample weights, soil percent moisture, extract volume, or due to dilution, RLs are modified accordingly and are termed SQLs.

5.15.1 Deliverables

- CLP Form I or equivalent for SW-846 methods for all samples

5.15.2 Frequency

RLs or SQLs are reported for all compounds that are not detected above the method detection limit.

5.15.3 Data Verification

- For all samples, the SQL must be ≤ RL, which is identified and communicated to the laboratory in the laboratory SOW. If the SQL > RL, this may indicate matrix-related problems or analytical conditions precluding RL achievement.

- All sample results shall be reviewed to determine RL compliance. In cases where the SQL > RL, the project may decide to request a reanalysis.

- The data verifier will correspond with the project and the laboratory to resolve SQL reporting issues and their effect on the project DQOs. If reanalysis is required, the issue will be addressed by the SMO and the laboratory.

- Verify that compounds detected at levels below the SQL have been qualified "J" by the laboratory.

5.15.4 Data Validation

- For one nondetected compound in each sample and blank, verify that RLs have been reported properly. No additional validation qualifiers are necessary for results detected below the SQL unless directed in other sections of this document.

- Quantitation limits effected by large off-scale peaks should be qualified "R."

- If single peak pesticide or Aroclors were detected on both GC columns, and the %D between the two results is > 25%, consider the potential for coelution and use professional judgment to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interfering compound is indicated, use professional judgment to determine how best to report, and if necessary, qualify the data.

- Equation C.3 for modifications to the RL can be found in Appendix C.

6. RECORDS

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

- Data Verification Checklist (for 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

"Contract Laboratory Program Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration," OLM04.2, U.S. Environmental Protection Agency, Washington, DC, May 1999.

"Test Methods for Evaluation Solid Waste, SW-846," Third Edition, Revisions through Update III, U.S. Environmental Protection Agency, Washington, DC, March 2009.

Contract Laboratory Program National Functional Guidelines for Organic Data Review, EPA-540/R-99/008, U.S. Environmental Protection Agency, Washington, DC, January 2010.

Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA/240/B-06/001, U.S. Environmental Protection Agency, Washington, DC, February 2006.

Paducah Gaseous Diffusion Plant Programmatic Quality Assurance Project Plan, DOE/LX/07-1269&D2/R2, U.S. Department of Energy, Paducah, KY, March 2015.

Quality Assured Data, CP3-ES-5003.

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.
NJ	Analyte compound or nuclide presumptively present at an estimated quantity.
UJ	Analyte compound or nuclide not detected above the reported detection limit, and the reported detection limit is approximated due to quality deficiency.
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 < the RL, and < 5× the blank concentration (10× for common contaminants).
B02	Sample concentration was > the RL, 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 relative standard deviation 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
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 GC/MS 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 > RL
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 RL or the SQL are reported for a nondetect result
Q29 SQL > RL
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 RL 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
GC performance check	identification and quantification
Initial calibration relative standard deviation	quantitation
Continuing calibration	quantitation
Method blank	positive bias
Surrogate standards	positive or negative bias
Matrix spike/matrix spike duplicate	positive or negative bias and precision
QC check standard	positive or negative bias
Florisil® cleanup	quantitation
GPC cleanup	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 Percent Recovery

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

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

C.2 Relative Percent Difference

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

R1 = Result 1
R2 = Result 2

C.3 Sample Quantitation Limit

$$SQL = RL_{SOW} \times DF \times S \times \frac{BW}{SW} \times \frac{BA}{SA} \times \frac{1}{\%S}$$

RL_{SOW} = required RL form the CLP SOW 3/90
DF = dilution factor
%S = percent solids (100–% moisture)/100
S = splitting factor (for sample volumes between column analyses)
BW = method blank weight
SW = sample weight
BA = method blank aliquot
SA = sample aliquot

C.4 Results for Waters

$$\mu g/L = \frac{A_X \times V_T \times D_F}{C_F \times V_O \times V_I}$$

A_x = area of measured compound peak
CF = calibration factor for midpoint concentration (area per ng)
V_o = volume of water extracted in mL
V_i = volume of extract injected in µL (use ½ volume if single injection is made onto two columns)
V_t = volume of the concentrated extracted (must be 10,000 µL)
D_t = dilution factor

C.5 Results for Soils/Sediments (dry weight basis)

$$\%R = \frac{A_X \times V_t \times D_f \times 2.0}{CF \times V_i \times W_s \times \%S}$$

A_x = area of measured compound peak
CF = calibration factor for midpoint concentration (area per ng)
V_i = volume of extract injected in µL (use ½ volume if single injection is made onto two columns)
V_t = volume of the concentrated extracted (must be 5,000 µL)
D_t = dilution factor
%S = (100–% moisture)/100
W_s = weight of sample extracted in grams

C.6 Surrogate Percent Recovery

$$\%R = \frac{S_{ng/g}}{\dfrac{(C_s V_s \times 1000 ng/\mu g)}{Wg \times \left(100 \times \dfrac{M}{100}\right)}} \times 100$$

$S_{ng/g}$ = surrogate concentration
V_s = volume of surrogate solution spiked into analytical sample (0.1 mL for waters; 0.2 mL for soils)
C_s = concentration of surrogate solution (2 µg/mL)
W_g = sample weight in grams
M = % moisture (for soils only)