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CP2-ES-0811/FR2

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

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

Date Issued—November 2025

U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

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

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APPROVALS

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

CP2-ES-0811/FR2

November 2025

Approved by:

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Date: 2025.11.25 08:54:57 -06'00'

Caleb Kline/Date
Director, Technical Services

DOE Approval Letter: N/A

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REVISION/CHANGE LOG				
Revision/ Change Letter	**Description of Changes**	**Pages Affected**	**Date of Revision/ Change**	**Approved By (signature on file)**
FR0	Bluesheet	All	11/14/2017	Signature on file
FR1	Nonintent Changes for Bluesheet Incorporation	All	12/13/2017	Signature on file
FR1	In accordance with the Corrective Action Plan for CAPA CA-003116, Action ItemAI-0004735 and CAPA CA-003086, ActionItem AI-0004709, the periodic review date for this procedure has been extended to December 13, 2022.	1	12/13/2017	Signature on file
FR1A	Periodic Review has been completed with no changes identified in procedure technical content. Nonintent changes have been incorporated per CP3-NS-2001. Date for review cycle has been reset.	All	12/13/2022	Signature on file
FR2	General revision to update plan according to DoD/DOE QSM 6.0 requirements to address CA-005369, AI-0008630.	All	11/25/2025	Signature on file

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CONTENTS

TABLES

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ACRONYMS

CCV	continuing calibration verification
CFR	*Code of Federal Regulations*
COC	chain-of-custody
CRDL	contract-required detection limit
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DQO	data quality objective
ECD	electron capture detector
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
ICV	initial calibration verification
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
N/A	not applicable
PCB	polychlorinated biphenyl
QAPP	quality assurance project plan
QC	quality control
QSM	quality systems manual
RL	reporting limit
RPD	relative percent difference
RRT	relative retention time
RT	retention time
SAEP	sampling analysis and event plan
SAP	sampling and analysis plan
SDG	sample delivery group
SMO	sample management office
SOW	statement of work
SQL	sample quantitation limit
%D	percent difference
%R	percent recovery
%RE	percent relative error
%RSD	percent relative standard deviation
%RSE	percent relative standard error

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DEFINITIONS

NOTE 1: Data validation code 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.

Affected Sample Result—A sample result is affected when it is significantly influenced by a quality deficiency and is qualified accordingly through analytical data validation.

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—The history of the transfer of samples from the time of sample acquisition through archival and disposal of samples. Chain-of-custody 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 the continued validity of the calibration curve.

Contract-Required Detection Limit—The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is > 0.

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

Data Quality Objective—Data quality objectives are qualitative and quantitative statements derived from the outputs of each step of the data quality objective process that specify the study objectives, domain, limitations, the most appropriate type of data to collect, and also specify the levels of decision error that will be acceptable for the decision.

Data Quality Objectives Process—The data quality objective 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 data quality objective 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.

Data Validation—Data validation is a systematic process that is 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.

Data Verification—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.

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

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

Laboratory Control Sample—The laboratory control sample is a control sample of a known composition. Aqueous and solid laboratory control samples 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.

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.

Method Detection Limit—The method detection limit is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

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

Practical Quantitation Limit—The practical quantitation limit is defined as the lowest concentration of a contaminant that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation limit is typically several times higher than the method detection limit.

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—Relative percent difference 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 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.

Required Detection Limit—The required detection limit is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

Reporting Limit—The reporting limit is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

Sample Delivery Group—A sample delivery group 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 sample delivery group.

Sample Quantitation Limit—Sample quantitation limits are detection limits based on the required detection limit, which 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—The validation statement of work is a document prepared to function as the mechanism by which validation requirements are communicated from the project to the validation organization.

Surrogate—A compound unlikely to be found in a sample, which is spiked into samples in a known amount before extraction or other processing and is quantitated with the same procedures used to quantify other sample components. Surrogates are added to every sample, blank, matrix spike, matrix spike duplicate, and standard. Surrogates are used to evaluate analytical efficiency by measuring percent recovery.

Turnaround Time—Turnaround time is contractually specified as the amount of time that elapses between laboratory receipt of the raw samples and subsequent data receipt by the client.

Validation Code—A validation code is an alphabetic character that is 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 statement of work is a document prepared to function as the mechanism by which data validation implementation requirements are communicated from the sample management office to the validation organization.

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1. INTRODUCTION

1.1 PURPOSE AND SCOPE

This plan provides guidance for the verification and validation of pesticide and polychlorinated biphenyl (PCB) analysis laboratory data performed by an external party. For the purpose of this guidance, external parties are defined as organizations (including governmental entities, contractors, or vendors) that conduct analytical data review, verification, and validation activities, and that are not part of the immediate laboratory that generates the subject analytical data (but are part of the overall project-specific data review process).

This document focuses on data generated by gas chromatography (GC)/electron capture detector (ECD) for organochlorine pesticides using SW-846 Method 8081, *Organochlorine Pesticides by Gas Chromatography*, and by GC for PCBs using SW-846 Method 8082, *Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, U.S. Environmental Protection Agency (EPA) Method 608.3, *Organochlorine Pesticides and PCBs by GC/HSD*, or other applicable GC methods. When applicable, this plan incorporates requirements that are defined in the U.S. Department of Defense (DoD) and U.S. Department of Energy (DOE) Quality Systems Manual (QSM) for Environmental Laboratories Version 6.0; however, data validators should reference the most current version of the DoD/DOE QSM when validating data (DoD and DOE 2023). Data produced by analytical methods for which this plan provides limited guidance (i.e., 40 *CFR* Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants*, Appendix A—"Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," or "Superfund Low Concentration Statement of Work" methods) may necessitate the development of modified criteria from this plan; however, the general validation strategy outlined in this plan should be applicable. In the absence of specific guidance, data validators are advised to seek guidance in the specific method employed and/or from other industry standards. Examples include the National Functional Guidelines for Organic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

1.2 APPLICABILITY

Data verification and validation is a systematic process, which is performed externally from the data generator that applies a defined set of performance-based criteria to a body of data that can result in the application of validation codes to the data. The project team, with input as needed from a quality assurance specialist and/or representative of the sample management office (SMO), shall develop a data validation strategy based on inputs identified through the data quality objective (DQO) process. The project-specific sampling and analysis plan (SAP), sampling analysis and event plan (SAEP), or quality assurance project plan (QAPP) will define the DQOs and framework for performing data validation.

Data verification is the process of checking data for completeness, correctness, consistency, and contract compliance. These requirements are contained in the analytical laboratory statement of work (SOW) and/or project-specific planning documents (e.g., SAP, SAEP, QAPP). The data verification process compares the laboratory data package to requirements associated with the project. The data verification process can identify deficiencies in the laboratory data package that can be addressed by obtaining additional information from the laboratory.

Data validation is the process of examining a laboratory data package to provide a level of confidence in the reported analyte's identification, concentration (including detectability), and associated measurement uncertainty. The data validation process begins with a review of the laboratory data package to screen the areas of strength and weakness of the data. The data validation process continues with assessing the data against standardized procedures and criteria to confirm the presence or absence of an analyte and to evaluate the uncertainty of the quantification for the analyte. Each data point is then qualified as to its integrity and dependability in the context of the project requirements based on all available laboratory data.

2. RESPONSIBILITIES

Table 1 summarizes the responsibilities of data validator and the SMO.

Table 1. Responsibilities for Data Validator and SMO

Performer	Responsibilities
Data Validator	• Determines if all required information is presented in the laboratory data package. • Makes objective judgments and decisions about the data quality and defensibility. • Assigns data validation codes to the results. The data validation codes indicate the validity and usability of the data and the limitations on its end use. • Produces a data validation report.
SMO	• Reviews each data validation report. • Adds data validation codes to data in the project environmental measurements system. • Distributes the data validation report to the appropriate personnel.

3. GENERAL INFORMATION

3.1 LEVELS OF LABORATORY DATA DELIVERABLES

Laboratory data deliverables consist of a combination of forms and raw data. Depending upon the required laboratory report elements included, the deliverable can range from Level I to a Level IV laboratory data package. Level IV laboratory data packages are typically used for data validation purposes. The elements included in a laboratory data package for each level are provided in Table 2.

Table 2. Required Laboratory Report Elements

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
Cover/Signature Page/Executive Summary	✓	✓	✓	✓
Table of Contents	✓	✓	✓	✓
Laboratory Report Narrative	✓	✓	✓	✓
Method Summary		✓	✓	✓
Sample Summary/Sample Data Sheets	✓	✓	✓	✓
Shipping and Receiving Documents	✓	✓	✓	✓
Client Chain-of-Custody (COC)	✓	✓	✓	✓

Table 2. Required Laboratory Report Elements (Continued)

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
Sample Receipt Checklist	✓	✓	✓	✓
Interlab COC (where applicable)	✓	✓	✓	✓
Subcontract Laboratory COC (if required)	✓	✓	✓	✓
Glossary of Abbreviations and Laboratory Definitions	✓	✓	✓	✓
Quality Control (QC) Association Summary/Sample Traceability	✓	✓	✓	✓
Analysis Run Log			✓	✓
Surrogate and/or Tracer and Carrier Recovery Report	✓	✓	✓	✓
Method Blank (MB) Reports		✓	✓	✓
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD) Summary		✓	✓	✓
Matrix Spike (MS)/Matrix Spike Duplicate (MSD) Summary		✓	✓	✓
Duplicate Sample Summary		✓	✓	✓
Instrument Performance Check Summary			✓	✓
Calibration Data			✓	✓
Internal Standard Area and Retention Time (RT) Summary			✓	✓
Continuing Calibration [Initial Calibration Verification (ICV)/Continuing Calibration Verification (CCV)] Summary Report			✓	✓
Instrument Blank Report			✓	✓
Detection Limits Summary			✓	✓
Gas Chromatography Dual Column Identification Summary			✓	✓
Linear Ranges			✓	✓
Preparation Batch Log			✓	✓
Interference Check Standard Summary			✓	✓
Serial Dilution Summary			✓	✓
Cleanup Log			✓	✓
Standard/Reagent Traceability Log			✓	✓
Accreditation/Certification Summary			✓	✓
Raw Sample Data			✓	✓
Raw QC Data			✓	✓
Manual Integration Summary			✓	✓

*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 laboratory data package.

3.2 STAGES OF VALIDATION

For the purposes of this plan, the following terminology is recommended for use to describe the stages (extent) and processes that are used to validate laboratory analytical data packages, whether the validation is performed by a manual process, electronic process, or combination of both.

NOTE: The following lists of required activities per each stage of validation is not considered an “all-inclusive” list or applicable to every method that is validated.

- **Stage 1 Validation**: A verification and validation based only on completeness and compliance of sample receipt condition checks. Client sample IDs and target analytes are verified against the COCs for completeness; sample conditions upon arrival at laboratory noted; sample preservation was appropriate and verified by the laboratory; holding times were met; concentrations and units were appropriate; trip blanks, field blanks, and equipment blanks, and field duplicates met the project requirements for frequency and field QC.

- **Stage 2A Validation**: A verification and validation based on completeness and compliance checks of sample receipt conditions and **ONLY** sample-related QC results. MBs, LCSs, MSs, laboratory duplicates (LCSD, MSD, laboratory duplicate), surrogates (organics), serial dilutions, post digestion spikes (as appropriate to the method) and any preparatory batch cleanup QC to assure that project requirements for analyte spike list, frequency, and QC limits are met.

- **Stage 2B Validation**: A verification and validation based on completeness and compliance checks of sample receipt conditions and **BOTH** sample-related and instrument-related QC results.

- **Stage 3 Validation**: A verification and validation based on completeness and compliance checks of sample receipt conditions, both sample-related and instrument-related QC results, **AND** recalculation checks.

- **Stage 4 Validation:** A verification and validation based on completeness and compliance of sample receipt conditions, both sample-related and instrument-related QC, recalculation checks **AND** the review of actual instrument outputs.

The stage of validation required is generally defined at the program or project level. Validation parameters to be reviewed depending on the stage of validation can include instrument calibrations, calibration verification checks, QC sample results, analytical yields, holding times, and sample preservation. It is not the role of data validation to determine if project goals are met or to provide the decisions to be made. Data validation provides the overall appraisal of a data set and the project team should use this appraisal along with their own judgment to make their own decisions.

3.3 DATA ASSESSMENT REVIEW

The data assessment review includes the following.

- Data verification/contractual screen
- Data validation (if requested)
- Data assessment
- Data usability assessment

The data assessment review is comparable to a Stage 1 and Stage 2A validation (depending on analyte and method). As required by project-specific requirements, a Stage 2B, Stage 3, or Stage 4 validation of the data package **MAY** be requested. See CP3-ES-5003, *Quality Assured Data* for more information about the data assessment review process.

3.3.1 Data Verification/Contractual Screen

Data verification is the first step of the data assessment review process. The preferred method for performing verification is electronic. Verification criteria are documented using CP3-ES-5003-F01, “Data Assessment Review Checklist and Comment Form,” and CP3-ES-5003-F05, “Data Verification/Validation Checklist” (if Stage 2B, Stage 3, or Stage 4 data validation is required). Data verification is performed on 100% of data.

3.3.2 Data Validation

Data validation (if requested) follows data verification in the data assessment review process when requested by the project team. Stage 3 and Stage 4 validations must be performed by a third party. Third-party data validation is defined as validation that is performed by persons independent from the sampling, laboratory, and decision making for the project (i.e., not the project reviewer). Data validation is documented in a formal deliverable from the data validator. The stage and frequency that are chosen for validation is based on project requirements and the following considerations.

- Regulatory drivers/requirements
- End-user of data
- Future applicability of the data (other users such as regulatory agencies, risk assessment personnel, internal users, etc.)
- Legal ramifications and defensibility of data
- Confidence in laboratory (DOE Consolidated Audit Program-approved laboratory)

The project team determines if the data set requires validation. The project team also determines the stage and frequency of data validation.

When data validation is requested by the project, a validation SOW is prepared by the SMO to communicate data verification and validation requirements to the external party performing the data validation. Along with the validation SOW, full copies of the laboratory data packages, as well as an electronic data deliverable in the form of a Microsoft Excel file are sent to the data validators performing the validation. CP3-ES-5003-F05 is provided to the validator from the SMO and must be completed for every laboratory sample delivery group (SDG) being validated.

3.3.3 Data Assessment

Data assessment follows data verification and data validation (if requested) in the data assessment review process. Data assessment is performed by data reviewers who have been trained to evaluate laboratory quality assurance/QC requirements. Data assessment is performed on 100% of data.

3.3.4 Data Usability Assessment

Data usability assessment is the last review step of the data assessment review process prior to release of the data from the project team. Data usability assessment is an integration of all information collected about a result. Data verification and validation can ensure that analyses are correct; however, data usability assessment must be performed to evaluate the data usability. This includes a review of the data itself, the results of all previous reviews of the data, checking data for trends, and an evaluation against the intended purpose for data collected. Data usability assessment must be performed for all data collection activities and documented using CP3-ES-5003-F01. Data usability assessment is required prior to use of the data, or data release into the final data repository (i.e., Oak Ridge Environmental Information System). Data usability assessment is performed on 100% of data.

4. DATA VERIFICATION AND VALIDATION INSTRUCTIONS

NOTE 1: Data verifier and data validator may be the same individual. CP3-ES-5003-F05 is only completed for Stage 2B, Stage 3 and Stage 4 validations. Appendix B has qualification tables for multiple quality deficiencies.

NOTE 2: If data reviewers use this plan as a guide for qualifying data during data assessment, they should apply equivalent data assessment codes in place of the data validation codes referenced in this plan.

4.1 SAMPLE RECEIPT CONDITIONS

4.1.1 Chain-of-Custody

The 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 the 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 that the sample truly has been in custody from the field to the final result), an evaluation of field notes from sample data forms, laboratory records, and the COCs provide the best available indicator of sample traceability. A sample is defined as being under proper custody if any of the following conditions are met:

- The sample is within the possession of an authorized person (e.g., field personnel, laboratory personnel);
- 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: 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 identity of each sample. When custody problems cannot be resolved, they will affect the defensibility of the sample.

4.1.1.1 Data verification

Trace custody of all samples in the reporting batch from field sampling through receipt at the laboratory by reviewing the COC forms. 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), then indicate the problem on the data verification/validation checklist.

4.1.1.2 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 apply an "R" validation code to associated results.

4.1.2 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 re-extraction and analysis, the result must have been generated within the prescribed holding time in order for the result to be considered definitive.

4.1.2.1 Deliverables

The following are deliverables.

- Sample data forms
- COCs
- Laboratory sample receipt checklist
- Laboratory reports and/or raw data containing the following: dates of collection, preparation, and analysis for all samples, dilutions, and re-extractions

4.1.2.2 Criteria

Table 3 provides current industry-accepted standards for sample preservation and hold times for routine analyses generally determined by pesticide and PCB methods. In all cases, the data verifier or validator shall always follow the most current methodology guidance for sample holding time, temperature, and preservation requirements.

Table 3. Holding Time and Sample Preservation Criteria

Parameters	Matrix	Preservatives[a]	Holding Times[b]
Pesticides	Aqueous samples with no residual chlorine present	0–6°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction
	Aqueous samples with residual chlorine present	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, 0–6°C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction
	Solid samples (e.g., soils, sediments, sludges, ash)	0–6°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction

Table 3. Holding Time and Sample Preservation Criteria (Continued)

Parameters	Matrix	Preservatives[a]	Holding Times[b]
PCBs[c,d]	Aqueous samples with no residual chlorine present	0–6°C	Not applicable (N/A)[d,e]
	Aqueous samples with residual chlorine present	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, 0–6°C.	N/A[e]
	Solid samples (e.g., soils, sediments, sludges, ash)	0–6°C	N/A

[a] 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 DQOs for a project-specific application still are attainable.

[b] 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.

[c] EPA Method 608.3 says to extract all samples within seven days of collection and to analyze within 40 days of extraction.

[d] Aqueous samples for PCBs are collected in amber glass bottles.

[e] Some analytical laboratories use 1 year holding time for PCBs as a best management practice.

4.1.2.3 Data verification

Verify the presence of the pertinent COC forms in laboratory data packages. **If** COC forms are not provided, then contact the SMO to have the laboratory provide the missing information. **If** missing information cannot be obtained or reconstructed from field notes, COC forms, etc., **then** the data verifier will note the omitted information on the data verification/validation checklist as a noncorrectable problem.

4.1.2.4 Data validation

Holding Times

Review the data verification/validation checklist for holding times to confirm that all holding times have been met. Holding times that are listed in hours from collection to analysis always will be calculated using the time collected to ensure that 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 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/validation checklist.

If the elapsed time falls within the prescribed holding time, **then NO** actions will be taken and **NO** validation code applied.

If the holding time is exceeded, **then** apply validation codes to data as follows.

- **If** the holding time is exceeded by a factor of < 2, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the holding time is grossly exceeded by a factor ≥ 2, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

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.

Temperature/Preservation

Review the laboratory receiving records to determine **if** samples were received at the appropriate temperature **and if** proper preservative addition occurred. **If** records demonstrate that samples were received by the laboratory at the proper temperature with proper preservation, **then NO** action will be taken and **NO** validation code will be applied.

If sample receipt temperatures are exceeded and/or proper preservation was not followed, **then** apply validation codes to data as follows.

- **If** sample temperature upon receipt is elevated (6°C < sample temperature ≤ 10°C), **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** sample temperature upon receipt > 10°C, **then** the data validator must evaluate the integrity of the reported concentrations and the data may require an application of an "R" validation code.

- **If** samples are received at an elevated temperature and proper preservation has not been followed (i.e., pH adjustment), **then** professional judgment should be applied to determine the usability of the data.

- **If** samples have not been preserved properly in the field, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

Table 4 summarizes data validation qualification guidance for samples with holding time exceedances and temperature and/or preservation issues.

Table 4. Holding Times and Temperature/Preservation Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. Samples extracted and/or analyzed outside the appropriate holding time (< 2× holding time).	J	UJ
2. Samples extracted and/or analyzed outside grossly exceed holding time (≥ 2× holding time).	J	R
3. Samples received at elevated temperature (≤ 10°C) with correct preservative (if applicable).	J	UJ
4. Samples received at elevated temperature (> 10°C) with correct preservative (if applicable).	*	*
5. Samples preserved improperly.	J	UJ

*Use professional judgment.

4.2 SAMPLE-RELATED QUALITY CONTROL RESULTS

4.2.1 Blanks

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. All blanks should be processed using the same sample preparation and cleanup steps applicable to the analytical method. It has been the EPA Region 4 data validation policy to evaluate trip blanks, field blanks, and equipment rinsate blanks as part of the validation process, but not to apply validation codes to the data based on field sample results.

Instrument Blank

Initial calibration blanks and continuing calibration blanks are used to ensure a stable instrument baseline before analysis of analytical samples.

Method Blank

An MB is used to assess the level of contamination that is introduced to the analytical samples throughout the sample preparation and analysis process. **If** contamination is found in any blank, **then** all associated data must be carefully evaluated to determine whether there is a systemic problem affecting greater than one sample or if the contamination is an isolated occurrence.

Field Blank

The project team may elect to collect and analyze a field blank to evaluate the existence and magnitude of contamination that may arise as a result of field-level activities. The field blank provides an indication of ambient conditions during the sampling activities, as well as an indication that the source of decontamination water is free of targeted analytes.

Equipment Rinsate Blank

The equipment rinsate blank provides an indication as to whether nondedicated sampling equipment has been properly decontaminated, and what, if any, carryover may arise between sampled locations.

4.2.1.1 Deliverables

The following are deliverables.

- MB report for each MB
- Instrument blank report
- Raw data (required for confirmation)

4.2.1.2 Frequency

The MB should be analyzed at a frequency of one per batch of 20 samples or less. MBs **must** be extracted for each batch of 20 or less samples of similar matrix in each SDG **or** whenever a sample extraction procedure is performed. 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.

4.2.1.3 Criteria

A blank **shall** be considered contaminated if one of the following occurs:

- The concentration of any target analyte in the blank exceeds one-half of the reporting limit (RL) **or** one-tenth the amount measured in any associated sample, whichever is greater; or

- The concentration of any target analyte identified as a common laboratory contaminant in the MB exceeds the RL **or** one-tenth the amount measured in any associated samples, whichever is greater.

4.2.1.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a “B07” validation reason code to the affected data if a noncorrectable problem has occurred and the problem has an adverse effect on data quality.

4.2.1.5 Data validation

Verify that results for the MB and instrument blanks (if required) are reported accurately on the laboratory summary form from the raw data (Stage 3 and Stage 4 Validation 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).

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, **then** 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 a blank was not analyzed with reported samples **or** analyzed of a different matrix than the reported samples, **then** apply an “R” validation code to detected results.

If a compound was detected in the blank, **then** apply validation codes to data as follows.

- **If** sample concentration is greater than the RL and > 5× blank concentration, **then** no qualification of the data is necessary.

- **If** sample concentration is greater than the RL and ≤ 5× blank concentration, **then** apply a “J” validation code to detected results.

- **If** both blank concentration and sample concentration are greater than the method detection limit (MDL) and less than or equal to RL, **then** apply a “U” validation code to detected results.

- **If** gross contamination (saturated peaks in blank) is present, **then** apply an "R" validation code to detected results.

If an instrument blank is not analyzed immediately after a sample showing compound(s) at high concentration(s), **then** the data validator must evaluate the analyses following the saturated sample analysis for carryover. Apply a "J" validation code to reported compounds significantly affected by instrument carryover.

For Stage 4 validation only, conduct the raw data confirmation by determining from raw data whether compounds reported in the blanks are detected above the MDL.

Table 5 summarizes data validation qualification guidance for issues with the blanks.

Table 5. Blanks Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. Blanks **NOT** analyzed at the appropriate frequency.	R	N/A
2. Blanks **NOT** the same matrix as the samples.	R	N/A
3. Sample result greater than RL and > 5× blank result.	N/A	N/A
4. Sample result greater than RL and ≤ 5× blank result.	J	N/A
5. Sample and blank results > MDL and ≤ RL.	U	N/A
6. Gross contamination.	R*	N/A
7. Instrument blank **NOT** analyzed after sample shows high concentration.	J*	N/A

***Use professional judgment in qualifying data.**

4.2.2 Laboratory Control Sample/Laboratory Control Sample Duplicate

An LCS is analyzed to provide accuracy of the analytical method.

4.2.2.1 Deliverables

- LCS/LCSD percent recovery (%R) summary
- Raw data (required for confirmation)

4.2.2.2 Frequency

The LCS **shall** be prepared **and** analyzed with each analytical batch to demonstrate proficiency of the analytical method. The LCS **must** be reanalyzed when significant changes in instrumentation are made.

4.2.2.3 Criteria

The LCS **must** be analyzed and the LCS %R **must** fall within the DoD/DOE QSM limits. It is recommended that this standard be the same matrix as the analytical samples. Unless prepared with the analytical samples, the LCS will not provide a representation of method accuracy. The LCS is prepared from the addition of an LCS concentrate into the appropriate clean matrix, extracted if applicable, and analyzed. All reported analytes **must** be spiked in the LCS and LCSD (if applicable), with the exception of PCBs. DoD/DOE QSM allows for the LCS and/or LCSD to be spiked per the method (i.e., only PCB-1016 and PCB-1260 to be spiked).

4.2.2.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a "L05" validation reason code to the affected data if a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.2.5 Data validation

If the LCS criteria are not met, **then** laboratory performance and method accuracy are in question. The data validator **shall** verify that the LCS and/or LCSD were prepared and analyzed in the same fashion as the sample it accompanies. 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. Professional judgment should be used to determine if the data should be qualified. The following guidance is suggested for qualifying sample data for which the associated LCS and/or LCSD does not meet the required criteria.

- **If** the LCS %R for an analyte is greater than the DoD/DOE QSM upper acceptance limit, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.
- **If** the LCS %R for an analyte is ≥ 20% and less than the DoD/DOE QSM lower acceptance limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** the LCS %R for an analyte < 20%, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.
- **If** an LCSD is included with the analyses and the calculated relative percent difference (RPD) between the LCS and LCSD results is > 30%, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.
- **If** an analyte is not spiked in the LCS and/or LCSD, **then** apply an "R" validation code to detected and nondetected results. See Section 4.2.2.3 for PCBs exception.

Table 6. LCS Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. LCS **NOT** analyzed at the proper frequency.	J	UJ
2. LCS **NOT** prepared and analyzed.	R	R
3. LCS %R > DoD/DOE QSM upper acceptance limit.	J	N/A
4. LCS %R ≥ 20% and < DoD/DOE QSM lower acceptance limit.	J	UJ
5. LCS %R < 20%.	J	R
6. LCS and LCSD RPD > 30%.	J	N/A
7. Analyte **NOT** spiked in LCS/LCSD.	R*	R*

* See exception for PCBs in Section 4.2.2.3.

4.2.3 Matrix Spike/Matrix Spike Duplicate

The purpose of the MS/MSD is to determine whether the sample matrix contributes bias to the analytical results. **If** the MS/MSD %R criteria are not satisfied, **then** there is difficulty in assessing whether the cause was due to method performance or matrix. To address this issue, LCS and/or LCSD are analyzed to verify method accuracy. **If** only the MS/MSD are affected, **then** a matrix effect is likely.

The data validator may determine that only some of the samples in the data package are similar to the MS sample, and that only these samples should be qualified. The data validator may determine that **NO** samples are sufficiently similar to the sample used for the MS, **and** that only the field sample used to prepare the MS sample should be qualified.

4.2.3.1 Deliverables

The following are deliverables for evaluating MS/MSD.

- MS/MSD recovery summary
- Raw data (required for confirmation)

4.2.3.2 Frequency

MS/MSD are analyzed at a frequency of once per 20 samples of similar matrix and concurrently with the samples in the SDG, unless a MS/MSD analysis is **NOT** required.

4.2.3.3 Criteria

The MS/MSD %R should fall within DoD/DOE QSM limits. In the absence of DoD/DOE QSM limits, MS/MSD %R **shall** be evaluated against laboratory defined limits. **If** the MS/MSD results fall outside the acceptable limits, **then** the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. The full target analyte list **must** be spiked in the MS/MSD pair(s), with the exception of PCBs. DoD/DOE QSM allows for the MS/MSD to be spiked per the method (i.e., only PCB-1016 and PCB-1260 to be spiked).

4.2.3.4 Data Verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "M05" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.3.5 Data Validation

Review the MS/MSD results to determine **if** there is an overall bias to the sample. Data validation of samples and sample groups using the MS/MSD should be conducted in conjunction with other supporting QC data. These generally include initial and continuing calibration checks, LCS, and surrogate standards. The data validator will evaluate MS/MSD performance in conjunction with the other QC data to determine if matrix-specific or instrumental problems are the cause of poor performance. Professional judgment shall be used to determine the need for applying validation codes to reported compounds. The data validator **shall** qualify only if the deviation indicates an adverse effect on data quality.

If MS/MSD analysis was required, but **NOT** performed, **then** qualify data only **if** the deviation indicates an adverse effect on data quality. Occasionally, limited sample volumes prevent the preparation and analysis of MS/MSDs. In these cases, it is common practice for the laboratory SOW to allow for the analysis of an LCS/LCSD pair as a substitute to provide an evaluation of accuracy and precision in the measurable range of the method.

In the absence of either the MS/MSD or LCS/LCSD, it is unlikely that a complete evaluation of method precision and accuracy can be completed. In this case, at a minimum, sample results should be considered estimated quantities due to the inability to fully determine the quality of the reported results. Apply a “J” validation code to detected results and apply a “UJ” validation code to nondetected results unless other quality deficiencies are observed.

The laboratory may also include an MS/MSD analysis performed on a parent sample that is not from the sample set being reviewed in the laboratory data package. This is commonly called a “batch QC sample.” The data validator should consult with the SMO to determine whether the batch QC data is applicable to the sample set being validated.

A determination shall be made concerning what extent the noncompliant MS/MSD recoveries have on other sample data regarding the sample matrix effect 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 parent sample, then application of validation codes shall 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.

If the MS and/or MSD have been provided and recovery difficulties have been noted, **then** the following guidance shall be used for evaluating accuracy.

- **If** an analyte is not spiked in the MS/MSD pair, **then** apply an “R” validation code to detected and nondetected results for analyte not spiked. See Section 4.2.3.3 for PCBs exception.
- **If** poor spike recovery occurs in a sample whose concentration > 4× the spiked amount, **then** professional and technical judgment should be used in whether application of a validation code to data is warranted.
- **If** the MS %R for an analyte is greater than the DoD/DOE QSM upper acceptance limit, **then** apply a “J” validation code to detected results. No qualification is necessary for nondetected results.
- **If** the MS %R for an analyte is ≥ 20% and less than the DoD/DOE QSM lower acceptance limit, **then** apply a “J” validation code to detected results and apply a “UJ” validation code to nondetected results.
- **If** the MS %R for an analyte is < 20%, **then** apply a “J” validation code to detected results and apply an “R” validation code to nondetected results.

If poor MS/MSD precision is observed, **then** the following guidance shall be used.

- **If** the RPD for an MS/MSD pair is > 30%, **then** apply a “J” validation code to associated detected results. No qualification is necessary for nondetected results.

For raw data confirmation, recalculate one MS recovery from raw data. Equation C.4 in Appendix C is used to calculate MS %R.

Table 7 summarizes data validation qualification guidance for issues with the MS/MSD.

Table 7. MS/MSD Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. MS/MSD **NOT** analyzed at the appropriate frequency.	J[a]	UJ[a]
2. Analyte **NOT** spiked in MS/MSD.	R[b]	R[b]
3. MS %R > DoD/DOE QSM upper acceptance limit.	J	N/A
4. MS %R ≥ 20% and < DoD/DOE QSM lower acceptance limit.	J	UJ
5. MS %R < 20%.	J	R
6. MS/MSD RPD > 30%.	J	N/A

[a] In cases of insufficient sample volume, alternative QC may be used to evaluate precision and accuracy (i.e. LCS/LCSD and laboratory duplicate).

[b] See Section 4.2.3.3 for PCBs exception.

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

4.2.4 Duplicates

A laboratory duplicate sample may be 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.

4.2.4.1 Deliverables

The following are deliverables.

- Laboratory duplicate sample summary
- Raw data (required for confirmation)

4.2.4.2 Frequency

If analyzed, laboratory duplicates **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).

4.2.4.3 Criteria

The following are criteria for laboratory and field duplicates.

- Samples identified as field blanks or equipment rinsate blanks **must NOT** be analyzed as the laboratory duplicate.

- For sample concentrations > 5× the RL, the RPD precision criteria for aqueous and solid laboratory duplicate samples **must** be within ± 25%.

- For sample concentrations > 5× the RL, the RPD precision criteria for aqueous field duplicate samples **must** be within ± 25%. The RPD precision criteria for solid field duplicate samples **must** be within ± 40%.

- **If** the sample results < 5× the RL, **then** RPD does not apply. Instead, the absolute difference between the sample and duplicate results **must** be less than the RL.

4.2.4.4 Data Verification

Verify that field blanks and/or equipment rinsate blanks were **NOT** analyzed as laboratory duplicates. **If** a field blank or equipment rinsate blank has been used as the laboratory duplicate, **then** contact the SMO to have the laboratory address the issue. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem and **shall** be identified as such on the data verification/validation checklist.

Verify the presence of laboratory and field duplicate results. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem **and** shall be identified as such on the data verification/validation checklist.

4.2.4.5 Data Validation

The following are data validation steps to evaluate laboratory and/or field duplicates.

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

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

- Verify that there are **NO** transcription or reduction errors (e.g., dilutions, percent solids, sample weights) on one or more samples.

- Verify that results fall within the linear range(s) of the instrument, if applicable.

The following summarizes data qualification guidance for evaluating laboratory duplicates and field duplicates.

- For aqueous and solid matrix laboratory duplicates where sample concentrations ≥ 5× the RL **and** the RPD between sample and laboratory duplicate > 25%, apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- For aqueous matrix field duplicates where sample concentrations ≥ 5× the RL **and** the RPD between sample and field duplicate > 25%, apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- For solid matrix field duplicates where sample concentrations ≥ 5× the RL **and** the RPD between sample and field duplicate > 40%, apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- For aqueous and solid matrix laboratory and/or field duplicates where sample concentrations < 5× the RL and the calculated absolute difference between sample and duplicate is greater than the RL, apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

Table 8 summarizes data validation qualification guidance for issues with the laboratory and/or field duplicate.

Table 8. Laboratory and Field Duplicate Validation Qualification Guidance

				Validation Qualification Guidance	
Duplicate Type	**Matrix**	**RPD**	**Sample Results**	**Detects**	**Nondetects**
Laboratory Duplicate	Aqueous	> 25%	Sample and duplicate ≥ 5× RL	J	UJ
	Solid	> 25%			
	Aqueous	N/A (Absolute difference greater than RL)	Sample and duplicate < 5× RL	J	N/A
	Solid				
Field Duplicate	Aqueous	> 25%	Sample and duplicate ≥ 5× RL	J	UJ
	Solid	> 40%			
	Aqueous	N/A (Absolute difference greater than RL)	Sample and duplicate < 5× RL	J	N/A
	Solid				

NOTE: 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.

4.2.5 Surrogate Standards

Surrogate standards are nontarget compounds added to all analytical samples, blanks, and QC samples to assess the overall system performance. The evaluation of the surrogate recovery results is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Because 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.

4.2.5.1 Deliverables

The following are deliverables related to surrogate standards.

- Surrogate recovery reports for all samples, blanks, and QC samples
- Raw data (required for confirmation)

4.2.5.2 Frequency

Surrogate standards are added to all analytical samples, blanks, and QC samples. Surrogate standards are tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB). TCMX is also routinely referred to as 4cmx.

4.2.5.3 Criteria

The surrogate %Rs are evaluated against the laboratory determined limits. DoD/DOE QSM Appendix C provides acceptance criteria that can be used. The surrogates must fall within the RT windows from the initial calibration (TCMX ± 0.05 minutes; DCB ± 0.10 minutes).

4.2.5.4 Data Verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "S06" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.5.5 Data Validation

Evaluate surrogate %Rs that exceed the acceptance criteria. **If** either surrogate spike recovery is outside the acceptance limits, **then** the reviewer must consider the existence of coelution, dilution factors, and interference in the raw data and use professional judgment to qualify data, as surrogate recovery problems may not directly apply to target analytes.

The following summarizes data qualification guidance for evaluating surrogate standards.

- **If** surrogates are not spiked in sample, **then** apply a "J" validation code to detected results and apply a "R" validation code to nondetected results.

- **If** surrogate %R is greater than upper control limit, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

- **If** surrogate %R ≥ 10% and less than the lower control limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** any surrogate %R < 10%, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

- **If** surrogates are "diluted out," **then** the data validator must use professional judgment to determine if application of a validation code is necessary.

If surrogates are detected outside the RT windows, **then** 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. The data validation report **must** contain the technical basis for application of data validation codes relative to RT window shifts and their effect on the data.

- **If** the RT window shift has only a minor impact on the reported values, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the RT window shift does not allow for proper quantitation, **then** apply a "R" validation code to all affected results.

For raw data confirmation, recalculate one surrogate recovery from raw data (Stages 3 and 4 only). Equation C.11 in Appendix C is used for calculating surrogate %R.

Table 9 summarizes data validation qualification guidance for issues with surrogate standards.

Table 9. Surrogate Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. Surrogate standards **NOT** spiked in sample.	J	R
2. Surrogate %R > upper control limit.	J	N/A
3. Surrogate %R ≥ 10% and < lower control limit.	J	UJ
4. Surrogate %R < 10%.	J	R
5. Surrogates diluted out.	*	*
6. Surrogate standards outside appropriate RT windows with minor impact	J	UJ
7. Surrogate standards outside appropriate RT windows (proper quantitation not allowed)	R	R

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

4.3 INSTRUMENT-RELATED QUALITY CONTROL RESULTS

4.3.1 Gas Chromatography/Electron Capture Detector Instrument Performance Check

A GC/ECD instrument performance check is applicable to pesticides analysis only. The GC/ECD instrument performance check evaluates degradation problems by injecting a standard containing 4,4’-dichlorodiphenyltrichloroethane (4,4’-DDT) and endrin into the instrument and calculating a percent breakdown for DDT and endrin. Presence of 4,4’-dichlorodiphenyldichloroethylene (4,4’-DDE), 4,4’-dichlorodiphenyldichloroethane (4,4’-DDD), endrin ketone, or endrin aldehyde indicates breakdown.

4.3.1.1 Deliverables

The following are deliverables for the GC/ECD performance check.

- Instrument performance check summary
- Raw data (required for confirmation)

4.3.1.2 Frequency

The percent breakdown of 4,4’-DDT and endrin should be measured before sample analysis **and** at the beginning of each 12-hour shift, on each GC column and instrument used for analysis.

4.3.1.3 Criteria

Percent breakdown of 4,4’-DDT and endrin **must** be ≤ 15%.

4.3.1.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is a noncorrectable problem. Apply a “P05” validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.1.5 Data Validation

Verify the analysis frequency has been satisfied for all instruments used to quantify sample results. **If** the GC/ECD instrument performance check has **NOT** been performed at the proper frequency, **then** apply a "R" validation code to all associated results.

Evaluate the GC/ECD instrument performance check for percent breakdown of 4,4'-DDT and endrin. The data validator shall qualify only **if** the deviation indicates an adverse effect on data quality.

- **If** 4,4'-DDT % breakdown > 15%, **then** apply an "R" validation code to associated results for 4,4'-DDT, 4,4'-DDD and 4,4'-DDE. No qualification is necessary for other compounds.

- **If** endrin % breakdown > 15%, **then** apply an "R" validation code to associated results for endrin, endrin aldehyde, and endrin ketone. No qualification is necessary for other compounds.

Table 10 summarizes the GC/ECD instrument performance check validation qualification guidance.

Table 10. GC/ECD Instrument Performance Check Qualification

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. GC/ECD instrument performance check not performed at proper frequency.	R	R
2. 4,4'-DDT % breakdown > 15%.	R	R
3. Endrin % breakdown > 15%.	R	R

4.3.2 Initial Calibration

Compliance requirements for satisfactory instrument calibration ensure that the instrument can produce acceptable qualitative and quantitative data for pesticide and PCB compounds on the target compound list. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run.

4.3.2.1 Deliverable

The following are deliverables for evaluating initial calibration.

- Initial calibration summary
- Raw data (required for confirmation

4.3.2.2 Frequency

For pesticides analysis, initial calibration **must** be performed within 12 hours of the initial GC/ECD instrument performance check **and** prior to sample analysis. For PCB analysis, initial calibration **must** be performed prior to sample analysis.

4.3.2.3 Criteria

Individual standard mixture **must** be analyzed at a minimum of five concentration levels when using %RSD or linear regression and six levels for evaluation by quadratic regression during the initial calibration. The mean RTs of each of the single component pesticides and surrogates are determined from the initial calibration. An RT window **must** be calculated for each single component analyte and surrogate.

Multicomponent analytes such as Aroclors, toxaphene and chlordane **must** be analyzed separately at a minimum of five different concentration levels during the initial calibration sequence.

Average Response Evaluation: Mean calibration factor **must** be calculated for each single component analyte and surrogate over the initial calibration range. The percent relative standard deviation (%RSD) of the calibration factors for each of the single component target compounds **must** be ≤ 20%.

The coefficient of determination (r^2) for the linear and quadratic regression calibration curves should be ≥ 0.99 for each target analyte.

Linear and Quadratic Regression: The percent relative error (%RE) or percent relative standard error (%RSE) **must** be evaluated at or near the mid-range of the initial calibration **and** at less than or equal to the RL. The maximum allowable %RE at or near the mid-range and low level of the calibration **shall** be 20% and 50%, respectively. The maximum allowable %RSE **shall** be 30%.

Quantitation using internal standards are optional, and if used internal standards should be added to all samples, QC samples and calibration standards. Pentachloronitrobenzene is suggested as an internal standard for the single-column analysis, when it is not considered to be a target analyte. 1-bromo-2-nitrobenzene may also be used. **If** internal standards are used, **then** the measured area of the internal standard in the samples and QC standards **must** be **NO** more than ± 50% different from the average area calculated during initial calibration.

Chromatographic Resolution: The height from the baseline to the valley between two peaks is less than or equal to 50% of the height of the shorter peak. **If** the required resolution cannot be achieved at initial calibration, **then** the compounds that are not resolved **shall** be reported as an aggregate of the compounds.

No Internal Standard: RT or relative retention time (RRT) **shall** be set using the midpoint standard of the initial calibration when initial calibration is performed **or** on days when initial calibration is not performed, the opening CCV for the batch **shall** be used. RT width is ± 3 times standard deviation for each analyte RT from the 72-hour study or 0.03 minutes, whichever is greater. For analytes reported across a RT range (e.g., TPH variations, chlordane), the RT window of the method defined marker compounds are established as stated above. The RT range is calculated based on the lower limit of the RT window for the first marker compound and the upper limit of the RT window for the last marker compound.

Internal Standard Used: RRT window width is ± 0.06 from the established RRT.

4.3.2.4 Data Verification

Verify the presence of required reporting forms. **If** they are not provided, contact the SMO to have the laboratory provide the missing information. **If** this issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a “C07” validation reason code to affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.2.5 Data Validation

If any initial calibration performance criteria are not met, **then** the data validator shall use professional judgment to determine **if** the deviation affects the data usability. The data validator **shall** qualify only **if** the deviation indicates an adverse effect on the data quality.

The following is data validation qualification guidance for issues related to the initial calibration.

- **If** initial calibration is **NOT** performed, **then** apply a "R" validation code to all results.
- **If** initial calibration does **NOT** have the appropriate number of standards used, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** the %RSD > 20% for a target analyte, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** the $r^2 \geq 0.90$ **and** $r^2 < 0.99$ for a target analyte, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** the $r^2 < 0.90$ for a target analyte, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.
- **If** the %RE > 20% near the mid-range of the calibration **or** 50% at the low level of the calibration, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** the %RSE > 30%, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** a concentration in a sample exceeds the calibration range, **then** the sample **must** be diluted to fall within the range. **If** the sample concentration is reported above the calibration range, **then** apply a "J" validation code to detected results.
- **If** the multicomponent target analytes were **NOT** calibrated properly, **then** apply a "J" validation code to detected results.

Table 11. Initial Calibration Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. Initial calibration **NOT** performed.	R	R
2. Appropriate number of standards **NOT** used.	J	UJ
3. %RSD > 20%.	J	UJ
4. $r^2 \geq 0.90$ and $r^2 < 0.99$.	J	UJ
5. $r^2 < 0.90$.	J	R
6. %RE > 20% (mid-range) or %RE > 50% (low level) of the calibration.	J	UJ
7. %RSE > 30%.	J	UJ
8. Sample(s) exceed the calibration range and **NOT** diluted/reanalyzed.	J	N/A
9. Multicomponent analytes **NOT** calibrated properly.	J	N/A

4.3.3 Initial and Continuing Calibration Verification

ICVs and CCVs ensure that the instrument is capable of consistently producing acceptable qualitative and quantitative data. The instrument is checked over specific time periods during the sample analysis.

4.3.3.1 Deliverables

The following are deliverables for evaluating ICVs and CCVs.

- Continuing calibration (ICV/CCV) summary report
- Raw data (required for confirmation)

4.3.3.2 Frequency

An ICV **must** be analyzed after the initial calibration. A CCV **must** be analyzed prior to sample analysis **and** after each group of 10 field samples. An opening CCV is **NOT** required if samples are analyzed immediately following an ICV.

4.3.3.3 Criteria

All reported analytes and surrogates **must** be within established RT windows. The percent difference (%D) between response factors for the ICV and CCV **must** be within ± 20%.

4.3.3.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a "C07" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.3.5 Data validation

Verify the correct standards and standard concentration were used in ICVs and CCVs. Check that all reported analytes and surrogates were within established RT windows. Review the %D between the response factors for ICV/CCVs.

The following is data validation qualification guidance for issues related to ICV/CCVs.

- **If** a target analyte is **NOT** within established RT window, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the ICV and/or CCV is **NOT** analyzed at the appropriate frequency for a target analyte, **then** apply an "R" validation code to detected and nondetected results.

- **If** the %D for a target analyte exceeds ±20% **and** does **NOT** exceed ± 50%, **then** apply a "J" validation code to affected detected target compound results and apply a "UJ" validation code to nondetected results.

- **If** the %D for a target analyte exceeds ± 50%, **then** apply an "R" validation code to detected and nondetected results.

Table 12 summarizes the validation qualification guidance for ICV/CCV issues.

Table 12. ICV/CCV Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Analyte in ICV/CCV RT **NOT** within established RT window.	J	UJ
2. ICV/CCV **NOT** analyzed at appropriate frequency.	R	R
3. The %D for ICV or CCV exceeds ± 20% **and** does **NOT** exceed ± 50%.	J	UJ
4. The %D for ICV or CCV exceeds ± 50%.	R	R

4.3.4 Target Compound Identification

Tentative identification of PCBs and pesticides is based on an agreement between the RTs of peaks in the sample chromatogram and the RT windows that are established through the analysis of standards of the target analytes. Compound identification based on single-column analysis should be confirmed on a second column or should be supported by at least one other qualitative technique. Multicomponent analytes present problems in measurement and identification.

4.3.4.1 Deliverables

The following are deliverables.

- Sample summary/sample data sheets
- Raw data (if required)

4.3.4.2 Criteria

For internal standard calibration, RRTs should be within ± 0.06 RRT units of the midpoint standard of the initial calibration curve or, on days when initial calibration is not performed, the opening CCV. When not employing internal standard calibration, the RT window width is determined at method set-up and is ± 3 times the standard deviation for each analyte RT from the 72-hour study or equal to 0.03 minutes, whichever is greater. The midpoint position is set using the midpoint standard of the initial calibration curve or, on days when initial calibration is not performed, the opening CCV.

If an analyte is detected, **then** the analyte should be confirmed using secondary column confirmation and the RPD between the results from the primary and secondary column should be ≤ 40%.

4.3.4.3 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved, **then** it is considered a noncorrectable problem and shall be noted as such on the data verification/validation checklist.

4.3.4.4 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 RT window of the pesticide or PCBs of interest. **If** overlapping peaks are present (e.g. PCB-1242 and PCB-1248), **then** apply a "J" validation code to detected results. **If** no peaks are present within or close to the RT window, then no qualification is necessary for nondetected results.

If the sample chromatogram contains peaks indicating concentrations greater than the RL, and close to or within the expected RT window of the target analyte, **then** the possibility of false negatives exists. Initial calibration and ICV/CCV RT windows should be consulted to determine the appropriate RT 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, **then** the possibility of false positives and false negatives exists. All target compounds should be evaluated, and professional judgment should be used to determine qualification applied to the data.

If multicomponent target compounds exhibit marginal pattern-matching quality, **then** professional judgment should be used to establish whether the differences are due to environmental “weathering” or degradation of the earlier eluting peaks relative to the later eluting peaks. **If** the presence of a multicomponent pesticide is strongly suggested, **then** apply a “NJ” validation code to detected results and apply a “UJ” to nondetected results.

When an analyte is detected and the RPD between the results from the primary and secondary column do not agree, **then** 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 analyte is detected and the RPD between the results from the primary and secondary column > 40%, **then** apply a “J” validation code to detected results. No qualification is necessary for nondetected results.

4.4 RECALCULATION CHECKS

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 the laboratory has a high rate of manual transcription in generation of sample results, **then** the project may choose to manually recalculate sample results at a determined frequency. **If** sample results **CANNOT** be reproduced through manual calculation, **then** contacting the laboratory may be necessary to resolve the problem. “R” validation codes may be applied to data as a last resort, **if NO** actions can reproduce reported values. For Stage 3 and Stage 4 validation only, **if** recalculations are performed, **then** recalculate one sample result from raw data for confirmation.

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

4.4.1 Reporting Limits/Sample Quantitation Limits

RLs have been developed to enable the laboratory to meet realistic detection limit goals. RLs should be greater than or equal to the lowest calibration standard used in the initial calibration.

Due to deviations from method-specified sample weights, extract volume or aliquot used in analysis or due to dilution or soil percent moisture, RLs are modified accordingly and are called sample quantitation limits (SQLs).

4.4.2 Deliverables

The following is a deliverable for evaluation of RLs and SQLs.

- Sample summary/sample data sheets

4.4.3 Frequency

RLs or SQLs are reported for all compounds.

4.4.4 Data Verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to request the forms be provided by the laboratory. **If** the missing information cannot be provided by the laboratory, **then** a noncorrectable problem exists.

4.4.5 Data Validation

For one nondetected compound in each sample blank, verify that RLs have been adjusted for deviations from the nominal preparation and analysis conditions, such as sample size and aliquot, **if** necessary.

Calculations for modifications to the RL can be found in Appendix C.

5. RECORDS

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

- Data verification/validation checklist (for Stage 2B, Stage 3, and Stage 4 validation)
- Data validation report (for Stage 2A, Stage 2B, Stage 3, and Stage 4 validation)

6. REFERENCES

NOTE: Use the most current version of the references that are listed below for data review, verification, and validation processes.

CP3-ES-5003, *Quality Assured Data*

EPA 2018. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium*, SW-846, Revisions through Update VI, U.S. Environmental Protection Agency, Washington, DC, December.

DoD and DOE (U.S. Department of Defense and U.S. Department of Energy) 2023. *Department of Defense and Department of Energy Quality Systems Manual for Environmental Laboratories Version 6.0*, U.S. Department of Defense Environmental Data Quality Workgroup and U.S. Department of Energy Consolidated Audit Program Data Quality Workgroup, Washington, DC, December.

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APPENDIX A

DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

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A.1. DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

Data Validation Codes

U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
NJ	Presumptively present at an estimated quantity [use with tentatively identified compounds (TICs) only].
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 rejected by validator.
=	Validated result, no additional qualifier necessary.
X	Not validated; Refer to the RSLTQUAL field for more information.

Data Validation Reason Codes

Blanks

B01	Sample concentration was less than the reporting limit (RL), and ≤ 5× the blank concentration (10× for common contaminants).
B02	Sample concentration was greater than 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 relative response factor (RRF) was < 0.05 or < 0.01 for poor response compounds
C02	Initial calibration percent relative standard deviation was exceeded
C03	Initial calibration sequence was not followed as appropriate
C04	Continuing calibration RRF was < 0.05 or < 0.01 for poor response compounds
C05	Continuing calibration percent difference (%D) was exceeded
C06	Calibration or performance check was not performed at the appropriate frequency
C07	Calibration data not reported
C08	Calibration not performed

Calibration (continued)

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 percent recovery (%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	Contract-required detection limit (CRDL) %R was below the lower acceptance limit
C22	CRDL %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 relative percent difference (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

Holding Times/Preservation (continued)

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 (LCS)

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 (MS) and Matrix Spike Duplicate (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 was not met

Quantitation

Q01	Peak misidentified
Q02	Target analyte affected by interfering peak
Q03	Qualitative criteria were not satisfied
Q04	Cross contamination occurred
Q07	Analysis occurred outside 12-hour gas chromatography/mass spectrometry window
Q09	TIC result was not above 10 × the level found in the blank
Q10	TIC reported as detect in another fraction
Q11	Common artifact reported as a TIC

Quantitation (continued)

Q12	No raw data were provided to confirm quantitation
Q13	Minimum detectable activity (MDA) greater than RL
Q14	Inappropriate aliquot sizes were used
Q15	Sample result less than MDA
Q16	Sample result less than 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 $\geq$ 80% of sample result
Q24	Raw data anomaly
Q25	Other (describe in comments)
Q26	Retention Time (RT) outside calculated RT window
Q28	Neither RL or the sample quantitation limit (SQL) are reported for a nondetect result
Q29	SQL greater than RL
Q30	Compound detected at less than 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	Gel permeation chromatography (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 appropriated frequency

Cleanup (continued)

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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B.1. QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

This appendix provides guidance in the application of validation codes to data due to instances of multiple quality deficiencies. Quality deficiencies can be categorized based on the 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 code should not be placed on sample data until all quality deficiencies have been identified within the reporting batch.

Table B.1 provides a listing of data quality indicators and the probable effects on sample data.

Table B.1 Data Quality Indicators and Effects on Sample Data

Data Quality Indicator	Effect on Sample Data
GC/ECD performance check	Identification and quantitation
Initial calibration RSD	Quantitation
ICV/CCVs	Quantitation
Method blank	Positive bias
Surrogate standards	Positive or negative bias
LCS/LSCD	Method bias and precision
MS/MSD	Positive or negative bias and precision
Florisil® cleanup	quantitation
Gel permeation chromatography cleanup	quantitation

In the instance of multiple quality deficiencies, the validation code 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 codes.

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APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

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C.1. 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 < 5, the preceding digit stays the same.
3. If the digit to be removed is ≥ 5, the preceding digit is increased by one.

Calculations/Equations

C.1 Calculation for CF

$$\text{CF} = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

C.2 Calculation for %RSD

where:
σ = Standard deviation of the five initial calibration relative response factors (per compound)
$X_{(R1,R2)}$ = Mean of the five initial calibration relative response factors (per compound)

C.3 LCS Percent Recovery

$$\%R = \frac{Measured}{Expected} x100$$

C.4 MS Percent Recovery

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

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

C.5 Relative Percent Difference

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

R1 = Result 1
R2 = Result 2

C.6 Sample Quantitation Limit

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

RL = instrument RL (lowest calibration standard)
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 = ample aliquot

C.7 Relative Error

$$\%RE = \frac{x' - x}{x} \times 100$$

where:
x = True value for the calibration standard
x’ = Measured concentration of calibration standard

C.8 Relative Standard Error

$$\%RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \div (n - p)}$$

where:
x_t = True value for the calibration standard
x_t’ = Measured concentration of calibration standard
p = Number of terms in the fitting equation (average = 1, linear = 2, quadratic = 3)
n = Number of calibration points

C.9 Results for Waters

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

where:
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.10 Results for Soils/Sediments (dry weight basis)

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

where:
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.11 Surrogate Percent Recovery

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

where:
$S_{ng/g}$ = 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)

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