PESTICIDE/PCB DATA VALIDATION FUNCTIONAL GUIDELINES - PART III

The requirements to be checked in validation are listed below. "CCS" indicates that the contractual requirements for these items will also be checked by Contract Compliance Screening (CCS). CCS requirements are not always the same as data validation criteria.

Appendices

I. PRESERVATION AND TECHNICAL HOLDING TIMES

A.   OBJECTIVE

The objective is to ascertain the validity of the analytical results based on the preservation techniques which were used and the holding time of the sample from <u>time of collection</u> to time of sample preparation and sample analysis, as appropriate.

B.   CRITERIA

The <u>Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses</u> should be used to validate all Region I Organic data. The CLP-Pesticide/PCB method QC acceptance criteria listed in Appendix F should be used as the default criteria when none exist for the Pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method-specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site-specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1.   <u>REGION I PRESERVATION CRITERIA</u>

SAMPLE TYPE	. PRESERVATION CODE
Pesticide/PCB Aqueous [a]	1,2,3
Pesticide/PCB Soil/Sediment [b]	1,3
Pesticide/PCB Sludge [b]	1,3
Oily Waste [b]	1,3
Biological Tissue [d]	3,4
Pest/PCB Air (PUF, Filters) [c]	3,5
Pest/PCB Wipes [c]	1,3
Pest/PCB Fly Ash [b]	1,3

Preservation Code:

1. Cool @ 4°C (± 2°)
2. Adjust to a pH range of 5.0 to 9.0 with NaOH or H_2SO_4
   if the sample will not be extracted within 72 hours
3. Protect from light
4. Freeze at <-20°C
5. Room Temperature (Avoid excessive heat)

2.   REGION I TECHNICAL HOLDING TIME CRITERIA

SAMPLE TYPE	CRITERIA
Pesticide/PCB Aqueous[a]	Extraction of properly preserved aqueous samples by liquid-liquid procedures must be completed within 7 days of sample collection. Extraction of properly preserved aqueous samples by separatory funnel or solid phase extraction (SPE) must be completed within 7 days of sample collection. Extracts must be analyzed within 40 days following sample extraction.
Pesticide/PCB Soil/Sediment [b]	Extraction of properly preserved soil/sediment samples by sonication or soxhlet procedures must be completed within 14 days of sample collection. Extracts must be analyzed within 40 days following sample extraction.
Pesticide/PCB Sludge [b]	Extraction of properly preserved soil/sediment samples by sonication or soxhlet procedures must be completed within 14 days of sample collection. Extracts must be analyzed within 40 days following sample extraction.
Pesticide/PCB Oily Waste [b]	Extraction of properly preserved oily waste samples by sonication or soxhlet procedures must be completed within 14 days of sample collection. Extracts must be analyzed within 40 days following sample extraction.
Pesticide/PCB Biological Tissue [d]	If the samples are not frozen, extraction of tissue samples must be completed within 14 days of sample collection. Frozen samples ($\leq$-20°C) may be held for up to one year if stored at $\leq$-20°C. The tissue must remain frozen prior to and during homogenization. Extracts must be analyzed within 40 days following sample extraction.
Pesticide/PCB Air [c]	Analyses of properly preserved air samples must be completed within 14 days of sample collection. Pre-cleaned and certified air collection devices, i.e., PUFs, Florisil cartridges, and filters, must be utilized for sample collection within the method-specified time frame.

SAMPLE TYPE	CRITERIA
Pesticide/PCB Wipes [c]	Extraction of properly preserved wipe samples by sonication or soxhlet procedures must be completed within 14 days of sample collection. Extracts must be analyzed within 40 days following sample extraction.
Pesticide/PCB Fly Ash [b]	Extraction of properly preserved fly ash samples by sonication or soxhlet procedures must be completed within 14 days of sample collection. Extracts must be analyzed within 40 days following sample extraction.

C.   EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from preservation and/or holding time anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum.
1. Preservation Examine the sample records (EPA Traffic Reports and/or COC Forms), Sample Receipt forms (DC-1 Form) laboratory tracking/storage forms, and the data package narrative to verify that samples were properly preserved by the sampler and the laboratory maintained preservation according to the preservation criteria on page Pest/PCB-I-1. If adequate documentation on field sample preservation is not present in the data package, then the validator must contact the sampler and/or laboratory to obtain the missing information.	1. Preservation If the sampler cannot be contacted or cannot produce adequate preservation documentation, then the validator should assume that the samples were not preserved and should document on the holding time worksheet the date that sampler contact was attempted and/or established. If the laboratory cannot provide adequate sample preservation information, then the validator should use professional judgment to accept, qualify or reject the sample data. If the samples were not preserved properly in the field and/or if the laboratory failed to properly maintain sample preservation, then the validator should take the following actions:

C.	EVALUATION	D.	ACTION
1 a.	Verify that samples were refrigerated or frozen (as required) and protected from light according to Region I preservation criteria.	1. a.	If samples for aqueous and soil/sediment matrices were not refrigerated and/or protected from light according to Region I preservation criteria on page Pest/PCB-I-1, then the validator should estimate (J) positive detects and estimate (UJ) non-detects for the affected samples, regardless of whether or not technical holding time criteria were met.
			For other matrices, the validator should estimate (J) positive detects and should use professional judgment to qualify or reject non-detects when temperature and light protection preservation criteria were not met.
			Professional judgment should be used when the laboratory has reported transportation cooler temperatures that slightly exceed the upper limits of the preservation criteria (>+6°C). In this case, the laboratory procedure for monitoring cooler temperature may be in question. In this event, the validator should document all justifications for qualifying data or not qualifying data in the Data Validation Memorandum.
2.	Technical Holding Times	2.	Technical Holding Times
a.	Verify that pesticide/PCB samples were extracted within technical holding time criteria. Establish extraction holding times by comparing sampling dates reported on the EPA Traffic Reports (TRs) and/or Chain of Custody (COC) Forms with dates of extraction reported on tabulated result forms.	a.	If aqueous and soil/sediment pesticide/PCB samples were properly preserved, but the technical extraction holding time criteria were exceeded, then the validator should estimate (J) positive detects and estimate (UJ) non-detects.
i.	Verify that liquid-liquid extractions for pesticide/PCB aqueous samples were begun within 7 days of sample collection.		For other matrices, the validator should estimate (J) positive detects and should use professional judgment to qualify or reject non-detects when technical holding times are exceeded.
ii.	Verify that aqueous pesticide/PCB extractions by separatory funnel were completed within 7 days of sample collection.		For all matrices except frozen biological tissue, if pesticide/PCB extraction holding time criteria were grossly exceeded (> 28 days), then the validator should estimate (J) positive detects and use professional judgment to qualify (UJ) or reject (R) non-detects. The validator should take into account the environmental stability of Aroclors when validating the sample data.
iii.	Verify that aqueous pesticide/PCB extractions by solid phase extraction (SPE) or other extraction technique were completed within 7 days of sample collection.		

C.	EVALUATION	D.	ACTION
	iv. Verify that pesticide/PCB soil/sediment sample extractions by sonication or soxhlet procedures were completed within 14 days of sample collection. v. Verify that samples of other matrices, i.e., wipes, biological tissue were extracted within the Region I holding time criteria.		
2. b. Verify that pesticide/PCB samples and/or extracts (as required) were analyzed within technical holding time criteria for analysis. Establish analytical holding times by comparing collection and/or extraction dates (as required) and analysis dates reported on tabulated result forms.		2. b. If aqueous and soil/sediment pesticide/PCB samples were properly preserved, but the technical analytical holding time criteria were exceeded, then the validator should estimate (J) positive detects and estimate (UJ) non-detects. For other matrices, the validator should estimate (J) positive detects and should use professional judgment to qualify or reject non-detects when technical holding times are exceeded. For all matrices, if pesticide/PCB analytical holding time criteria were grossly exceeded (> 60 days), then the validator should estimate (J) positive detects and use professional judgment to qualify (UJ) or reject (R) non-detects. The validator should take into account the environmental stability of Aroclors and pesticides when validating the sample data.	
* c. Check the raw data including extraction and instrument run logs to verify reported sample extraction and analysis dates.		c. If discrepancies between the raw data and reported data are found, then the validator should contact the laboratory to obtain corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.	

*   **Note:**   **The following subsections are applicable only to a Tier III data validation:**
        C.2.c

Table Pest/PCB-I-1:

QUALIFICATION OF PESTICIDE/PCB ANALYTES BASED ON
PRESERVATION & TECHNICAL HOLDING TIMES

PRESERVATION		TECHNICAL HOLDING TIMES		
Matrix	Refrig.& Light Protected	Extracted and/or Analyzed Within H.T.	Extracted and/or Analyzed Outside H.T.	If Extraction HT > 28 days and/or Analytical HT > 60 days
AQ and S/S	Yes	A - acceptable results	J - detects UJ - non-detects	J - detects Professional Judgment to either UJ or R - non-detects*
AQ and S/S	No	J - detects UJ - non-detects	J - detects UJ - non-detects	J - detects Professional Judgment to either UJ or R - non-detects*

Note: AQ = Aqueous, S/S = Soil/Sediment

*   The validator may use professional judgment to qualify or reject non-detected pesticides and multicomponent analytes based on their environmental stability.

For other matrices, the validator should estimate (J) positive detects and use professional judgment to qualify (UJ) or reject (R) the non-detects when Region I preservation and/or technical holding time criteria are not met. The results are acceptable (A) when the criteria are met.

E.   EXAMPLES

Example #1: (Proper preservation; Extraction holding times grossly exceeded)

PCB soil sample SAA44 was collected on 12/1/95 and received at the laboratory on 12/2/95. Upon examination of the Traffic Report, laboratory receipt information, and sample tracking records, the validator determines that the sample was properly preserved at 4°C and was light protected. The validator examines the sample extraction log sheet and discovers that the sample was extracted by the soxhlet procedure on 12/30/95, 29 days after sample collection. The validator estimates (J) the positive Aroclor 1260 detect in sample SAA44 and uses professional judgment to estimate (UJ) the Aroclor non-detects on the Data Summary Tables due to the grossly exceeded extraction holding times. The validator discusses these qualifications in the Data Validation Memorandum.

Example #2: (Proper preservation; Analytical holding times exceeded)

Pesticide soil sample SAA34 was analyzed by routine analysis following CLP SOW OLM04.3. This sample was received by the laboratory on 4/10/95. Review of the Traffic Report, the extraction log sheet and the run log sheet revealed that the sample was collected on 3/29/95, was extracted on 4/11/95, and was analyzed on 6/9/95. The laboratory documentation indicates that the sample was properly preserved at 4°C and protected from light. Only 4,4'DDT and dieldrin were detected. Although the analytical holding time exceeded the 40 day criteria, it was not "grossly exceeded" and was analyzed within 60 days of extraction. Therefore, the validator estimates (J) the positive detects for 4,4'-DDT and dieldrin and uses professional judgment to estimate (UJ) the non-detects. The validator discusses these qualifications in the Data Validation Memorandum.

Example #3: (Improper preservation; Holding times met)

Pesticide/PCB water samples SAA99 - SAA106 were analyzed by routine analysis following CLP SOW OLM04.3. The validator examines the Traffic Report and the sample log-in sheets contained in the data package. The sampler properly preserved and shipped the samples at 4°C, however, the laboratory notes in the data package narrative that the samples were removed from the cooler and left in a hood for 36 hours after sample receipt due to a misunderstanding between shifts.

The validator reviews the chain-of-custody form, the extraction log and the run log data. The sampling date for samples SAA99 - SAA106 was 12/1/95, the extraction date was 12/5/95 and the analysis date was 12/15/95. Since all holding time criteria were met, but preservation criteria were not, the validator estimates (J) the positive pesticide and PCB detects and estimates (UJ) the pesticide and PCB non-detects on the Data Summary Table and discusses these qualifications in the Data Validation Memorandum.

REFERENCES

[a] **40 CFR, Part 136, Appendix A, 600 Series**

[b] **SW 846, 8000 Series**

[c] **Region I policy**

[d] **Evaluation of Dredged Material for Discharge in Waters of the U.S. - Testing Manual, EPA 823-B-97-001, February 1997, and QA/QC Guidance for Sampling and Analysis of Sediments, Waters, and Tissue for Dredged Material Evaluations, Chemical Evaluation, EPA 823-B-95-001, April 1995.**

II. GC/ECD INSTRUMENT PERFORMANCE CHECK

A.   OBJECTIVE

Performance checks on the gas chromatograph/electron capture detector (GC/ECD) system are performed to ensure adequate chromatographic resolution, column performance and to check the accuracy of the initial calibration. The Resolution Check Mixture (RCM) is analyzed at the beginning of the initial calibration sequence to ensure that the GC column can adequately resolve target analytes. The Performance Evaluation Mixture (PEM) is analyzed at the beginning (following the RCM) and at the end of the initial calibration sequence and is also analyzed during the continuing calibration verification. The PEM is analyzed to assess chromatographic resolution, pesticide degradation, and to check the accuracy of the initial calibration for the analytes in the PEM.

B.   CRITERIA

GC/ECD Instrument Performance criteria are not sample specific. Since conformance is determined using standard materials, these criteria should be met under all circumstances. The following validation criteria are based on the CLP-Pesticide/PCB method QC acceptance criteria as listed in Appendix F. These criteria should be used as the default criteria when none exist for the Pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method. Any deviations, modifications or non-CLP method-specific QC acceptance criteria must be explicitly defined in tabular format in the site-specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1.   a.   Adequate chromatographic resolution of GC peaks must be determined by analyzing a Resolution Check Mixture (RCM) and the Performance Evaluation Mixture (PEM) at the frequency, concentration, and composition stated in the method.

      b.   The chromatographic resolution between any two adjacent peaks in the RCM must be greater than or equal to 60.0 percent. The chromatographic resolution between any two adjacent peaks in the PEM must be greater than or equal to 90.0 percent on each column.

2.   Retention times of each of the single component pesticides and surrogates in the Resolution Check Mixture and Performance Evaluation Mixture standards must be within the calculated retention time windows.

3.   The percent difference (%D) between the calculated amount and the nominal amount (amount added) for each of the single component pesticides and surrogates in the Performance Evaluation Mixture (PEM) must not exceed ± 25.0 percent for both GC columns.

4.   The degree of pesticide degradation must be determined for each column used to analyze field samples. The percent breakdown is the amount of decomposition that 4,4'-DDT and endrin undergo when the PEM is analyzed on the GC column.

      a.   For 4,4'-DDT, the percent breakdown is determined by the presence of 4,4'-DDD and/or 4,4'-DDE in the GC chromatogram.

            i.   The percent breakdown for 4,4'-DDT in each PEM must be less than or equal to 20.0 percent for both GC columns.

        b.   For endrin, the percent breakdown is determined by the presence of endrin aldehyde and/or endrin ketone in the GC chromatogram.

              ii.   The percent breakdown for endrin in each PEM must be less than or equal to 20.0 percent for both GC columns.

        c.   Total breakdown for 4,4'-DDT and endrin is determined by adding these results.

              iii.   The combined percent breakdown for 4,4'-DDT and endrin in each PEM must be less than or equal to 30.0 percent for both GC columns.

5.   The criteria mentioned above apply to the results from both chromatographic columns. In the event that one GC column meets criteria and the other does not, the validator may use professional judgement to evaluate the effect of the noncompliance on the associated samples. The validator may choose to accept a sample result reported from the compliant GC column. The validator must consider if the noncompliant GC column criteria were grossly exceeded and whether or not false negative or false positive results may be present.

        The equations used to verify these calculations are provided in Appendix F.

Note: CLP SOW-OLM04.3 does not require the analysis of a multicomponent analyte performance check standard. If a multicomponent analyte performance check standard is required by a non-CLP method, then the above retention time criteria, resolution criteria, and % Difference criteria used to evaluate single component pesticides should be used to evaluate instrument performance for multicomponent analytes.

C.   EVALUATION/ D. ACTION

The following evaluation procedures and actions are specific to CLP-SOW OLM 04.3 data and can be modified for use in evaluating and qualifying non-CLP data.

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from GC/ECD instrument performance anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum.
1. **RESOLUTION CHECK** If resolution acceptance criteria are not achieved, quantitative and qualitative results may not be accurate due to coelution problems. Resolution Check Mixture: a. Verify from Form VI PEST-4 that the Resolution Check Mixture (RCM) contained the required analytes and that the resolution between two adjacent peaks is greater than or equal to 60.0% on both GC columns. The required analytes are listed in Appendix F-1, Section II. b. Verify from Form VIII PEST that the RCM was analyzed at the beginning of the initial calibration sequence on each GC column and instrument used for analysis.	1. **RESOLUTION CHECK - Worksheet Pest/PCB-II-A** Resolution Check Mixture: a. If the Resolution Check Mixture does not contain the correct analytes and/or they were not adequately resolved, then the validator should use professional judgment to accept, qualify or reject sample data taking into consideration the resolution results of the IND A/B standards and the PEMs analyzed in association with the samples. b. If the RCM was not analyzed in the correct sequence and at the proper frequency, then the validator should use professional judgment to determine the effect on the sample data.

C. EVALUATION	D. ACTION
1. **RESOLUTION CHECK - continued**	1. **RESOLUTION CHECK - continued**
* c. Examine the RCM chromatograms and raw data to verify that the resolution between two adjacent peaks for the required analytes is greater than or equal to 60.0% on both GC columns. Using equations found in Appendix F, recalculate the resolution between two RCM analytes to verify correct resolution calculations.	c. If any transcription and/or calculation errors are detected, perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used must be documented in the Data Validation Memorandum.
Performance Evaluation Mixture:	Performance Evaluation Mixture:
d. Verify from the Form VII PEST-1 that the Performance Evaluation Mixture (PEM) contained the proper analytes at the required concentrations. The analytes are listed in Appendix F-2, Section II.	d. If the PEM does not contain the correct analytes at the required concentrations and/or was not analyzed in the required sequence at the proper frequency, then the validator should use professional judgment to determine the effect on the sample data.
e. Verify from Form VIII PEST that the PEM was analyzed after the RCM in the initial calibration sequence and at the proper frequency throughout the analytical sequence.	e. If the PEM was not analyzed in the required sequence and at the proper frequency, then the validator should use professional judgment to determine the effect on the sample data.

C.			EVALUATION	D.			ACTION
1.	f.		Verify from Form VI PEST-5 that the resolution of all single component pesticide and surrogate peaks is greater than or equal to 90.0% on both GC columns.	1.	f.	i.	If PEM analytes were not adequately resolved on <u>both</u> GC columns, then the validator should estimate all affected analytes positive (J) and non-detected (UJ) results.
						ii.	If PEM analytes were not adequately resolved on <u>one</u> of the GC columns, then qualification may be necessary. If a tentatively identified positive result from the compliant column must be confirmed on the second but non-compliant column, then the positive result should be estimated (J).
							If resolution issues are noted in the PEM, qualification of positive results may not be necessary if only one analyte of the unresolved pair is present <u>and</u> if the positive result is reported from the compliant GC column.
							Professional judgment must be applied to evaluate whether or not data are acceptable, estimated (J) or rejected (R).
*	g.		Review the PEM raw data from the initial calibrations to verify that the resolution between adjacent peaks is greater than or equal to 90.0% on both GC columns. Using equations in Appendix C, recalculate the resolution between two PEM analytes to verify correct resolution calculations.		g.		If any transcription and/or calculation errors are detected, perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
*	h.		Review the Pesticide Standards Preparation Log entries to verify that the RCM solutions and PEM solutions contained the method required analytes at the required concentrations. The required concentrations are listed in Appendix F.		h.		If the RCMs and PEMs did not contain the proper analytes at the required concentrations, then the validator should use professional judgment to determine the effect on the sample data.

C. EVALUATION	D. ACTION
2. **RETENTION TIME CHECK**	2. **RETENTION TIME CHECK - Worksheet Pest/PCB-II-B**
a. Check Form VII PEST-1 to verify that the absolute retention times for the PEM analytes in both PEM analyses in the initial calibration are within the calculated retention time windows based on the mean RT from the three-point initial calibration on each column. The retention time windows are from Table App. F.III-3 and page F-5 in the Appendix.	a. Retention time windows are used in qualitative identification. If the retention times of the pesticides in the PEM do not fall within the established retention time windows, then the associated sample results should be carefully evaluated for the possibility of false positives and false negatives. All samples injected after the last <u>in-control</u> standard are potentially affected and a Tier III level of validation should be performed to assess the impact on sample results.
* b. Review the raw data for samples analyzed after the last compliant PEM to assess the possibility of false positives and false negatives. Evaluate whether or not the sample chromatograms have any peaks which are close to any target pesticides retention time windows. These peaks could indicate qualitative inaccuracies.	b. If no peaks are present either within or close to expected retention time windows of a target pesticide, then non-detected values can be considered valid.

If sample chromatograms contain peaks either close to or within the expected retention time window of target pesticides, then two options are available to the validator to determine the impact on the data:

Option 1 - In some cases, additional effort by the validator may be necessary to determine if sample peaks represent the pesticides of interest. For example:

i.   The validator should examine the data package for the presence of three or more standards containing the pesticides of interest that were run within a 72-hour period during which that sample was analyzed.

ii. If three or more such standards are present, revised retention time windows may be created by utilizing the mean retention time as an absolute retention time, and using the windows listed in Table App.F.III-3, or using 3x the standard deviation calculated from the retention times in the standards, as appropriate for the analytical run conditions. |

C.	EVALUATION	D.	ACTION
2. b. Continued from above.		**Option 1** - Continued from above.	
		iii. If all standards, surrogates, and matrix spikes fall within the revised window, then the validity of the positive or non-detected sample results can be re-evaluated using the revised retention time window.	
		iv. The Data Validation Memorandum must describe the data validation procedures performed by the validator and the impact on data usability. In addition, the supporting documentation should contain all calculations and comparisons generated by the validator.	
		Option 2 - If the validator cannot resolve the retention time problems at issue with the available data, then all positive detects and the sample quantitation limits for non-detects should be rejected (R).	
* c. Check the PEM raw data from the initial calibrations to verify that the correct absolute retention times for the PEM analytes in each PEM analysis have been transcribed correctly and are within the calculated retention time windows based on the mean RT from the three-point initial calibration using the values shown in Table App. F.III-3.		c. If transcription and/or calculation errors are extensive, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used must be documented in the Data Validation Memorandum.	

C. **EVALUATION**	**D.** **ACTION**
3. **ACCURACY (%D) CHECK**	3. **ACCURACY (%D) CHECK - Worksheet Pest/PCB-II-C**

a. Verify from Form VII PEST-1 that the %D between the calculated amount and the nominal amount for each of the single component pesticides (and, if applicable, multicomponent standards) in both PEMs in the initial calibration sequence does not exceed ± 25.0 % on each GC column.	a. i. If %D criteria are not met on <u>both</u> columns, then the validator should:
	
	      ● Estimate (J) associated positive detects for the affected analyte for all samples associated with the unacceptable PEM.
	
	      ● Estimate (UJ) sample quantitation limits for non-detects in samples associated with the non-compliant PEM.
	
	    ii. If %D criteria are not met on only <u>one</u> of the columns, then the validator may choose to accept the non-detects and positive detects if they are reported from the GC column with the compliant %D.
	
	The validator should use professional judgement to estimate (J) and/or reject (R) sample data if %D criteria were grossly exceeded on one or both columns and considering the possibility of false negatives or false positives.

* b. Check and recalculate 10% of the PEM percent difference data. Verify that the recalculated values agree within 10% of the laboratory reported values.	b. If more than 10% of the calculations are in error, then the validator should perform a more comprehensive review to determine the extent of the problem. If the problem is extensive, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C. **EVALUATION**	D. **ACTION**
4. PESTICIDE DEGRADATION CHECK a. Verify from Form VII PEST-1 that the individual breakdown for 4,4'-DDT in both PEM analyses in the initial calibration sequence is less than or equal to 20.0%.	**4. PESTICIDE DEGRADATION CHECK - Worksheet Pest/PCB-II-D** a. If 4,4'-DDT breakdown is greater than 20.0%, then the validator should: **4,4'-DDT Detected** i. Estimate (J) DDT, DDD, DDE positive detects and accept DDD and DDE non-detects for samples associated with the unacceptable PEM. **4,4'-DDT Not Detected** ii. Reject (R) DDT non-detects as unusable, accept DDD, DDE non-detects, and estimate (J) DDD, DDE positive detects and note the potential high bias for these two analytes. If the results from a second, compliant GC column are available, evaluate these results to determine to what extent DDD and DDE positive detects are due to DDT breakdown and use professional judgement to accept, estimate (J), or reject (R) results.
b. Verify from Form VII PEST-1 that the individual breakdown for endrin in both PEM analyses in the initial calibration sequence is less than or equal to 20.0%.	b. If endrin breakdown is greater than 20.0%, then the validator should: **Endrin Detected** i. Estimate (J) endrin, endrin ketone, endrin aldehyde positive detects, and accept endrin ketone, endrin aldehyde non-detects for samples associated with the unacceptable PEM. **Endrin Not Detected** ii. Reject (R) endrin non-detects, accept endrin ketone, endrin aldehyde non-detects, and estimate (J) endrin ketone endrin aldehyde positive detects and note the potential high bias for these two analytes. If the results from a second, compliant GC column are available, evaluate these results to determine to what extent endrin ketone and endrin aldehyde positive detects are the due to endrin breakdown and use professional judgement to accept, estimate (J), or reject (R) results.

C.	**EVALUATION**	**D.**	**ACTION**
4. c.	Verify from Form VII PEST-1 that the combined breakdown for 4,4'-DDT and endrin in both PEM analyses is less than or equal to 30.0%.	4. c.	If the combined 4,4'-DDT and endrin breakdown is greater than 30.0%, then the validator should:
			4,4'-DDT Detected
			i. Estimate (J) DDT, DDD, DDE positive detects and accept DDD and DDE non-detects for samples associated with the unacceptable PEM.
			4,4'-DDT Not Detected
			ii. Reject (R) DDT non-detects as unusable, accept DDD, DDE non-detects, and estimate (J) DDD, DDE positive detects and note the potential high bias for these two analytes.
			Endrin Detected
			iii. Estimate (J) endrin, endrin ketone, endrin aldehyde positive detects, and accept endrin ketone, endrin aldehyde non-detects for samples associated with the unacceptable PEM.
			Endrin Not Detected
			iv. Reject (R) endrin non-detects, accept endrin ketone, endrin aldehyde non-detects, and estimate (J) endrin ketone endrin aldehyde positive detects and note the potential high bias for these two analytes.
			If the results from a second, compliant GC column are available, evaluate these results to determine to what extent DDD, DDE, endrin ketone, and endrin aldehyde positive detects are the due to DDT and endrin breakdown and use professional judgement to accept, estimate (J), or reject (R) results.

C.	EVALUATION	D.	ACTION
*4. d.	Check and recalculate 10% of the DDT and endrin breakdown data. Verify that the recalculated values agree within 10% of the laboratory values.	4. d.	If more than 10% of the calculations are in error, then the validator should perform a more comprehensive review to determine the extent of the problem. If the problem is extensive, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

*   Note: The following subsections are applicable only to a Tier III data validation:

C.1.b, C.1.c, C.1.g, C.1.h, C.2.b, C.2.c, C.3.b, C.4.d

Table Pest/PCB-II-1:

<u>**QUALIFICATION OF PESTICIDE/PCB ANALYTES**</u>
<u>**BASED ON THE RESOLUTION CHECK MIXTURE (RCM) - Resolution Check**</u>

Sample Results	Resolution ≥ 60.0%	Resolution < 60.0%
Detects	A	Professional Judgment
Non-Detects	A	Professional Judgment

Table Pest/PCB-II-2:

<u>**QUALIFICATION OF PESTICIDE/PCB ANALYTES**</u>
<u>**BASED ON THE PERFORMANCE EVALUATION MIXTURE (PEM) - Resolution Check**</u>

Sample Results	Resolution ≥ 90.0%	Resolution < 90.0%
Detects	A	J
Non-detects	A	Professional Judgment

Table Pest/PCB-II-3:

<u>**QUALIFICATION OF PESTICIDE/PCB ANALYTES BASED ON THE**</u>
<u>**PERFORMANCE EVALUATION MIXTURE (PEM) - CALIBRATION CHECK - Accuracy Check**</u>

Sample Results	%D ≤ ±25.0%	%D > ±25.0%	One column meets criteria but the other exceeds
Detects	A	J	Professional judgement
Non-Detects	A	UJ	Professional judgement

Table Pest/PCB-II-4:

QUALIFICATION OF PESTICIDE/PCB ANALYTES BASED ON 4,4'-DDT/ENDRIN BREAKDOWN - PESTICIDE DEGRADATION CHECK

Sample Results	4,4'-DDT Breakdown ≤ 20.0%	4,4'-DDT Breakdown > 20.0% and 4,4'-DDT detected	4,4'-DDT Breakdown > 20.0% and 4,4'-DDT not detected	Endrin Breakdown ≤ 20.0%	Endrin Breakdown > 20.0% and Endrin detected	Endrin Breakdown > 20.0% and Endrin not detected	Combined Breakdown ≤ 30.0%	Combined Breakdown > 30.0% and 4,4'-DDT and/or Endrin detected	Combined Breakdown > 30.0% and 4,4'-DDT and/or Endrin not detected
4,4'-DDT	A	J	R (NDs)	N/A	N/A	N/A	A	J	R (NDs)
DDD	A	J (detects) A (NDs)	J (detects) A (NDs)	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)
DDE	A	J (detects) A (NDs)	J (detects) A (NDs)	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)
Endrin	N/A	N/A	N/A	A	J	R (NDs)	A	J	R (NDs)
Endrin Aldehyde	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)	A	J (detects) A (NDs)	J (detects) A (NDs)
Endrin Ketone	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)	A	J (detects) A (NDs)	J (detects) A (NDs)

N/A   =   Not Applicable
J   =   Estimate result
R (NDs)   =   Reject non-detects
A (NDs)   =   Accept non-detects

Note: The validator must always discuss negative and positive bias in sample data in the Data Validation Memorandum.

E.   EXAMPLES

Example #1: Resolution (Non-compliant RCM; Compliant PEM)

The resolution between 4,4'-DDE and dieldrin is 59.0% in the RCM. The validator reviews the PEM results, which were analyzed following the RCM to determine if the resolution problem is specific to the RCM analysis or to the entire analytical sequence run. The resolution between the PEM analytes was found to be acceptable and the validator uses professional judgment to accept the sample data associated with the RCM.

Example #2: (Retention Time Evaluation)

Historically heptachlor has been found at Site X and is a contaminant of concern. The RPM requested a Tier II validation and was concerned that heptachlor was not identified in any of the field samples. A Tier III validation was subsequently requested to verify that heptachlor was not present in the samples. The retention time window for heptachlor is 13.30 - 13.40, and a peak that elutes during that retention time window may be considered to be a positive detect for heptachlor if confirmed by second column analysis. A positive identification for heptachlor is obtained on the first column but not on the second. The validator reviews the second column chromatograms and computer print-outs to check if a peak eluted just prior to or after the retention time window on the secondary column (15.30 - 15.40). The validator notes that there is a peak at retention time 15.28 in many of the field samples which he suspects may be heptachlor. To investigate this, the validator reviews the standards and PEMs which were analyzed during the same time period as the samples in question. The mean and standard deviation of the retention time window are re-evaluated. All the standards and matrix spikes fall within the revised windows, and the validator redetermines sample results using these revised windows and reports the presence of heptachlor in the field samples. The validator documents all extra efforts and calculations in the Data Validation Memorandum.

Example #3: (Non-compliant %D)

The validator reviews the initial calibration data and notes that on one column the PEMs analyzed before and after the initial three point calibration standard analyses had %Ds for endrin of 36.0% and 41.0%, respectively. The validator reviews the subsequent continuing calibration Individual Standards A and B data analyzed 12 hours later and determines that endrin had a %D of 25.0% and was compliant. The validator estimates (J) the positive endrin detects and estimates (UJ) the endrin non-detects on the Data Summary Table for the samples analyzed following the non-compliant initial calibration PEMs and before the compliant Individual Standards A and B.

E.   EXAMPLES

Example #4: (Pesticide Degradation)

The validator reviews the DDT/Endrin breakdown data and notes that the DDT breakdown in the PEM, which was analyzed after the 3 point calibration Individual Standards A and B curve, is 45.0%. The validator then reviews the subsequent PEM analyzed 12 hours later and notes that the DDT breakdown is less than 20.0% and is acceptable. For samples that have positive DDT detects; the validator estimates (J) the DDT detects, and estimates (J) positive DDD and DDE detects and accepts DDD and DDE non-detects for all samples analyzed following the non-compliant PEM and before the compliant PEM. For samples that have DDT non-detects; the validator rejects (R) the DDT non-detects and estimates (J) DDD and/or DDE detects and accepts DDD and DDE non-detects. It is noted in the Data Validation Memorandum that when the breakdown for 4,4'-DDT is high, the values for 4,4'-DDT are potentially biased low and the values for 4,4'-DDD and 4,4'-DDE are potentially biased high.

III. INITIAL CALIBRATION

A.   OBJECTIVE

Compliance requirements for initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data.   Initial calibration data demonstrate that the instrument is capable of satisfactory performance at the beginning of the analytical sequence by producing a linear calibration curve.

B.   CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP-Pesticide/PCB method QC acceptance criteria listed in Appendix F should be used as the default criteria when none exist for the Pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method-specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site-specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1.   Single Component Pesticides

      a.   Calibration standard mixtures containing all of the single component pesticides and surrogates must be analyzed at low, mid, and high concentration levels during the initial calibration sequence, on each GC column and instrument used for analysis prior to the analysis of any field samples or blanks. If the continuing calibration method QC acceptance criteria are not achieved, an Initial Calibration must be performed.

          The low concentration standard must be at or below the quantitation level for each analyte; the midpoint concentration must be 4 times the low concentration standard; and the high concentration standard must be at least 16 times the low concentration standard, but a higher concentration may be chosen. See Appendix F, Table App. F. III-1.

      b.   The chromatographic resolution between any two adjacent peaks in the midpoint concentration of the calibration standard mixtures in the initial calibration must be greater than or equal to 90.0 percent on each column. See Appendix F-1, Section II.

      c.   The absolute retention times for each of the single component pesticides and surrogates are determined from an initial three point calibration. A list of the windows and an example for calculating retention time windows are provided in Appendix F, Table App. F.III-3.

      d.   Calibration factors for single component pesticides are calculated for each of the three standard concentrations. The midpoint calibration standard is used for sample quantitation. (The instrument linearity is checked by calculating the %RSD; see Appendix F-8, Section III. The calculation uses the mean calibration factor.) Calibration factors can be calculated using either peak area or peak height. However, the calculation procedure, peak height or area, must be consistent for field, QC, and blank sample calculations.

      e.   The Percent Relative Standard Deviation (%RSD) of the calibration factors for each of the single component pesticides in the initial calibration on both columns for the calibration standards mixtures must be less than or equal to 20.0 percent, except for alpha-BHC and delta-BHC which must be less than or equal to 25 percent. The %RSD of the calibration factors for the surrogates must be less than or equal to 30.0 percent.

f.   The chromatograms that result from the analyses of the Resolution Check Mixture, the PEM, and Individual Standard Mixtures A and B during the initial calibration sequence must display the single component analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.

g.   The chromatograms for at least one of the three analyses each of Individual Standard Mixtures A and B from the initial calibration sequence must display the single component analytes at greater than 50 percent and less than 100 percent of full scale.

h.   For any standard containing alpha-BHC, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

2.   Multicomponent Analytes

a.   The multicomponent analytes (the 7 Aroclors and Toxaphene) must each be analyzed separately (except Aroclors 1016 and 1260 which may be analyzed together in the same mixture) at a minimum of one concentration level during the initial calibration sequence on each GC column and instrument used for analysis prior to the analysis of any field samples or blanks. If the continuing calibration method QC acceptance criteria are not achieved an Initial Calibration must be performed (for concentrations, see Appendix F, Table App.F.III-2).   The pesticide surrogates must be analyzed along with the multicomponent target analytes.

b.   The absolute retention times for 3 to 5 peaks for each multicomponent analyte are determined from the initial calibration based on a minimum of at least one concentration point. A window of ±0.07 minutes is used to calculate the retention time windows for each of the 3 to 5 peaks from the multicomponent analyte standard.

c.   i.   Calibration factors for multicomponent analytes are calculated based on a one point standard concentration. Calibration factors can be calculated using either peak area or peak height. However, the calculation procedure, peak height or area, must be consistent for field, QC and blank sample calculations.

        ii.   Calibration factor data generated from the multicomponent analyte standard must be provided for each of the 3 to 5 peaks used to quantitate that multicomponent analyte in the field, QC and blank samples.

d.   If a multi-point calibration is analyzed for a multicomponent analyte (not required in CLP OLM04.3), then the %RSD of each of the 3 to 5 identifying peaks must be less than or equal to 25.0 percent on both columns. The %RSD of the calibration factors for the surrogates must be less than or equal to 30.0 percent.

e.   The chromatograms of the multicomponent analyte standards analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25 percent and less than 100 percent of full scale deflection.

3.   The criteria mentioned above apply to the results from both chromatographic columns. In the event that one GC column meets criteria and the other does not, the validator may use professional judgement to evaluate the effect of the noncompliance on the associated samples. The validator may choose to accept a sample result reported from the compliant GC column. The validator must consider whether the noncompliant GC column criteria were grossly exceeded, and the possibility of false negatives or false positives.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from initial calibration anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum.
1. Single Component Pesticides	1. Single Component Pesticides
a. i. Verify from Form VIII PEST that the Individual Standard Mixtures A and B were analyzed at the required frequency and in the proper sequence on each GC column and instrument used for analysis.	a. i. If Individual Standard Mixtures A and B were not analyzed at the required frequency and in the proper sequence on each GC column and instrument, then professional judgment must be used to evaluate the effect of the non-compliance on the sample data. This non-compliance should be noted in the Data Validation Memorandum (Worksheet Pest/PCB-III).
* ii. Review the raw data to verify that analysis times were accurately reported for the initial calibration standards on Form VIII PEST.	ii. If the laboratory has made transcription errors, then the validator should contact the laboratory to obtain corrected data and forms.
b. i. Verify from the Forms VI PEST-1 and PEST-2 that the low point standard concentrations correspond to the quantitation limit for each analyte; that the midpoint standard concentration is 4 times the low point; and that the high point is at least 16 times the low point.	b. i. If the Individual Standard Mixtures A and B were not analyzed at the required concentration levels, then the sample data may be adversely affected. The validator must use professional judgment to determine the severity of the effect on the linear range of the instrument and the resultant sample data and these data should be qualified accordingly (Worksheet Pest/PCB-III).

C. **EVALUATION**	**D.** **ACTION**
*1. b. ii. Review the raw data to verify that the low point standard concentrations, the midpoint standard concentrations, and the high point standard concentrations were accurately reported on Forms VI PEST-1 and PEST-2.	1. b. ii. If the laboratory has made transcription errors in the recording the concentrations of the standards, then the validator should have the laboratory resubmit all corrected raw data and forms.
iii. Verify from Forms VI PEST-1 and PEST-2 that all the required analytes are reported for the initial calibration from the Individual Standard Mixtures A and B.	iii. If errors are detected in the reporting of all the required analytes, then the validator should perform a more comprehensive review that includes the review of raw data as described in C.1.b.iv.
* iv. Review the raw data to verify that all the required analytes were analyzed in the standards and were accurately reported on Form VI PEST-1 and PEST-2.	iv. If the laboratory has made transcription errors, then the validator should have the laboratory resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be estimated (J) or rejected (R).

If the required analytes were not analyzed in the initial calibration, then the sample data may be adversely affected. The accuracy and quantitation of the affected analyte(s) are questionable. The sample data associated with the initial calibration should be rejected (R), unless an acceptable alternate method of quantitation or detection limit determination was used. The validator must use professional judgement to determine whether the sample data should be accepted (A), estimated (J) or rejected (R).

A discussion of the reasons for data qualification and the qualifiers used should be documented in the Data Validation Memorandum. |

C. EVALUATION	D. ACTION
1. c. i. Verify from Forms VI PEST-6 and -7 that resolution is greater than or equal to 90.0 percent for any two adjacent peaks in the mid-point concentration of the Individual Standard Mixtures A and B in the initial calibration on both columns.	1. c. i. If resolution criteria are not met, then the quantitative results may not be accurate due to peak overlap and inadequate resolution. Positive detects for analytes that were not adequately resolved should be estimated (J). Qualitative identifications may be questionable if coelution exists. Non-detects that elute in the region of coelution may not be valid depending upon the extent of the coelution problem and professional judgment should be used to accept (A), estimate (J), or reject (R) non-detects as unusable. Refer to Section II (GC/ECD Instrument Performance Check Criteria) and Section XII (Target Analyte Identification Criteria) of the Pesticide/PCB Functional Guidelines for additional guidance (Worksheets Pest/PCB-II-A and Pest/PCB-XII). A discussion of the reasons for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
* ii. Evaluate the raw data to verify that the reported resolution is correctly calculated and accurately transcribed for Individual Standard Mixtures A and B in the initial calibration on both columns. See Appendix F, Section II for the method of calculation.	ii. If the laboratory made calculation and/or transcription errors, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the reasons for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C.	EVALUATION	D.	ACTION
1. d. i.	Review Form VI PEST-1 to verify that retention time windows were reported for all single component pesticides.	1. d. i.	If the laboratory did not report retention time windows for all single component pesticides, then the validator should have the laboratory resubmit all corrected raw data and forms.
ii.	Review 10% of the tabulated mean RTs and retention time windows reported on Form VI PEST-1 to verify that they were calculated correctly. See Appendix F, Table App.F.III-3 for retention time windows.	ii.	If errors are detected in the calculations of the mean RTs or retention time windows, then the validator should perform a more comprehensive review that includes the review of raw data as described in d.iii.
* iii.	Review the Individual Standard Mixtures A and B raw retention time data for calculation and transcription errors.	iii.	If the laboratory made calculation and/or transcription errors, then the validator should contact the laboratory to obtain corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
e. i.	Review Form VI PEST-2 to verify that low, mid and high calibration factors were reported for each single component pesticide and surrogate on each column.	e. i.	If the laboratory did not report low, mid and high calibration factors for each single component pesticide and surrogate, then the validator should contact the laboratory to obtain omitted data and corrected forms.
ii.	Review 10% of the tabulated %RSD and Mean CF results reported on Form VI PEST-2 to verify that they were calculated correctly.	ii.	If an error rate of greater than 10% is detected in the calculations of the Mean CFs and %RSDs, then the validator should perform a more comprehensive review that includes the review of raw data as described in C.1.g.

C.	**EVALUATION**	**D.**	**ACTION**
1. f.	Review Form VI PEST-2 to verify that the %RSD for the calibration factors in each of the single component pesticides in the initial calibration analyses on both columns are in compliance with the linearity criteria as described in B.1.e.	1. f.	If the %RSD linearity criteria (Pest/PCB-III-12, Table Pest/PCB-III-1) are not met on one or both columns for the single component pesticides being quantified, then the validator should:
		i.	Estimate (J) positive detects for that affected analyte for all samples associated with the initial calibration.
		ii.	Estimate (UJ) non-detects for that affected analyte for all samples associated with the initial calibration.
		iii.	Use professional judgment if the %RSD is exceeded on one column and positive detects are quantified using CFs generated from a dissimilar column with a compliant initial calibration. The validator may choose to accept a sample result if the analyte was reported from the compliant GC column. However, qualification may be necessary if a tentative identification is made on the compliant GC column that requires confirmation on the noncompliant GC column. The validator should use professional judgement to estimate (J) and/or reject (R) sample data if %RSD criteria were grossly exceeded on one or both columns and the possibility of false negatives or false positives.
g.	Review Form VI PEST-2 to verify that the %RSD for the calibration factors for each of the surrogates in the initial calibration analyses on both columns are in compliance with the linearity criteria as described in B.1.e.	g.	If a surrogate analyte fails to meet %RSD criteria, then the % surrogate recoveries in the samples, QC samples and blanks associated with the initial calibration may be biased high or low. In this case, the validator should use professional judgment to assess the impact of surrogate analyte calibration data on the sample results.

C.	EVALUATION	D.	ACTION
*1. h.	Review the raw calibration factor data and recalculate the calibration factors and %RSD for one or more of the single component pesticides; verify that the recalculated values agree within 10% of the reported values.	1. h.	If errors of greater than 10% are detected in the calibration factor and %RSD calculations, then the validator should perform a more comprehensive review to determine the magnitude of the problem. This review should recalculate at least 20% of the calibration factors and %RSDs and should use the DQOs to decide which analytes to recalculate. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
* i.	Confirm from the Individual Standard Mixtures A and B chromatograms that at least one of the three analyses for each of Individual Standard Mixtures A and B from the initial calibration sequence displays the single component pesticides at greater than 50 percent and less than 100 percent of full scale.	i.	If none of the chromatograms for the initial calibration Individual Standard Mixtures A and B have peaks that are between 50 and 100 percent of full scale, then the validator should use professional judgment which may include that the laboratory should replot and resubmit corrected data and forms. The validator may use professional judgement to accept the data if it is determined that adequate standard chromatographic data are available to confirm positive analyte identifications and quantitation limits for non-detects.

C. EVALUATION	D. ACTION
2. Multicomponent Analytes	2. Multicomponent Analytes
a. i. Verify from Form VIII PEST that each multicomponent analyte standard was analyzed at the required frequency and in the proper sequence on each GC column and instrument used for analysis.	a. i. If the multicomponent analyte standards were not analyzed at the required frequency and in the proper sequence on each GC column and instrument, then the sample data may be adversely affected. The validator must use professional judgment to determine the severity of the non-compliance on the sample data and these data should be qualified accordingly.
* ii. Review the raw data to verify that analytical run times were accurately reported.	ii. If the laboratory has made transcription errors, then the validator should have the laboratory resubmit all corrected raw data and forms.
b. i. Verify from the Form VI PEST-3 that the multicomponent analytes and surrogates were analyzed at the required concentration.	b. i. If multicomponent analyte standards were not analyzed at the required concentration, then the sample data may be adversely affected. The validator must use professional judgment to determine the severity of the effect on the sample data and these data should be qualified accordingly.
* ii. Review the raw data to verify that the multicomponent analyte and surrogate concentrations were accurately reported.	ii. If the laboratory has made transcription errors, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms.

C.	EVALUATION	D.	ACTION
2. c. i.	Review Form VI PEST-3 to verify that retention time windows were reported for at least 3 peaks for each multicomponent analyte.	2. c. i.	If the laboratory did not report retention time windows for at least three peaks, then the validator should have the laboratory resubmit all corrected raw data and forms.
ii.	Review 10% of the tabulated retention time windows reported on Form VI PEST-3 to verify that they were calculated correctly.	ii.	If errors were detected in the retention time window calculations, then the validator should perform a more comprehensive review that includes the review of raw data as described in C.2.c.iii.
* iii.	Review the multicomponent analyte raw retention time data for calculation and transcription errors.	iii.	If the laboratory made calculation and/or transcription errors, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
d.	Verify from Form VI PEST-3 that at least three peaks were used for the initial calibration and that calibration factor data are available for each peak.	d.	If at least three peaks were not used for quantitation, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms.

C. EVALUATION	D. ACTION
**2.e. If applicable, review tabulated results of %RSD for multicomponent analyte standards.	2. e. If the %RSD linearity criteria are not met for the multicomponent analytes being quantified, then the validator should:
	i. Estimate (J) positive detects for that affected analyte for all samples associated with the initial calibration.
	ii. Estimate (UJ) non-detects for that affected analyte for all samples associated with the initial calibration.
	iii. Use professional judgment if the %RSD is exceeded on one column and positive detects are quantified using CFs generated from a dissimilar column with a compliant initial calibration.
	The validator may choose to accept a sample result if the analyte was reported from the compliant GC column. However, qualification may be necessary if a tentative identification is made on the compliant GC column that requires confirmation on the noncompliant GC column.
	The validator should use professional judgement to estimate (J) and/or reject (R) sample data if %RSD criteria were grossly exceeded on one or both columns and the possibility of false negatives or false positives.
f. If applicable, review tabulated results of %RSD for surrogate analytes.	f. If any surrogate analyte fails to meet %RSD criteria of 30%, then the % surrogate recoveries in the samples, QC samples and blanks associated with the initial calibration may be biased high or low resulting in unacceptable surrogate recoveries. In this case the validator should use professional judgment to assess the impact of surrogate analyte calibration data on the sample results.

C.	EVALUATION	D.	ACTION
*2. g.	Review and recalculate the calibration factors (and %RSD if applicable) for one or more multicomponent analytes; verify that the recalculated values agree within 10% of the reported values.	2. g.	If errors greater than 10% are detected in the calibration factor and/or %RSD (if applicable to method) calculations, then the validator should perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
* h.	Confirm that the standard chromatogram peaks chosen for multicomponent analyte identification are greater than 25% and less than 100% of full scale deflection.	h.	If none of the chromatograms for the initial calibration multicomponent analytes have peaks that are between 25 and 100% of full scale, then the validator should use professional judgment to decide if the laboratory should be required to replot and resubmit corrected data and forms. The validator may determine that adequate standard chromatographic data are available to confirm positive analyte identification and quantitation limits for non-detected results.

C. EVALUATION	D. ACTION
3. Single and Multicomponent Analytes	3. Single and Multicomponent Analytes
* a. Review Standard Preparation Logs (if provided in the data package) to ensure that primary and secondary initial calibration standard concentrations are accurate and traceable to NIST standards.	a. If standards preparation data have not been submitted with the data package, then the validator should use professional judgment to determine if standards preparation data are necessary to facilitate the validation of sample data. If necessary, the validator should contact the laboratory to obtain standards information, including traceability information. If standards preparation data were submitted and found not to be NIST traceable, second source standards, PES, and other QC data should be evaluated. The validator must use professional judgement to accept (A), estimate (J), or reject (R) the sample data. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
* b. Review and recalculate the calculated initial calibration standard concentration for one single component and one multicomponent analyte (if standards preparation documentation was provided in the data package). Verify that the calculated values agree within 10% of the laboratory reported values.	b. If errors greater than 10% are detected in the standard concentration calculations, then the validator should perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

*   **Note: The following subsections are applicable only to a Tier III data validation:**

       C.1.a.ii, C.1.b.ii, C.1.b.iv, C.1.c.ii, C.1.d.iii, C.1.h, C.1.i, C.2.a.ii, C.2.b.ii, C.2.c.iii, C.2.g, C.2.h, C.3.a, C.3.b

**   **Not required in CLP-SOW OLM04.3**

Table Pest/PCB-III-1:

QUALIFICATION OF PESTICIDE/MULTICOMPONENT[*] ANALYTES BASED ON THE INITIAL CALIBRATION

Sample Results	%RSD $\leq$ 20.0% (alpha-BHC & delta-BHC %RSD $\leq$ 25.0%)	%RSD > 20.0% (alpha-BHC & delta-BHC %RSD > 25.0%)	If applicable, multicomponent analyte %RSD $\leq$ 25.0%	If applicable, multicomponent analyte %RSD > 25.0%	One column meets criteria but the other exceeds
Detects	A	J	A	J	Professional judgement
Non-detects	A	UJ	A	UJ	Professional judgement

*   OLM04.3 does not require analysis of more than one initial calibration standard concentration for multicomponent analytes.

E. **EXAMPLES**

Example #1: (High %RSD)

The Percent Relative Standard Deviation (%RSD) of the calibration factors for 4,4'-DDT is 80.0% on the reporting column. Due to erratic instrument performance, the validator estimates (J) all positive 4,4'-DDT detects and estimates (UJ) the 4,4'-DDT non-detects in the field samples associated with the initial calibration on the Data Summary Tables and discusses this in the Data Validation Report.

Example #2: (Non-compliant chromatographic scaling factors)

The validator cannot differentiate between Aroclor 1242 and Aroclor 1016 in the standards because the peaks are well below 25% of full scale. After examining the sample chromatograms, the presence of either Aroclors 1016 or 1242 is detected. The validator contacts the laboratory and requests that they replot and resubmit the standards data at full scale. The validator is able to differentiate the two Aroclors in the resubmitted data and completes the validation. Telephone logs of all communications between the validator and the laboratory are incorporated into the Data Validation Report.

Example #3: (Non-compliant standard concentrations)

The laboratory ran Individual Standard Mixtures A and B at concentrations higher than required by the analytical specifications. The reported quantitation limits are higher than the CRQLs. The Data Quality Objectives (DQOs) were designed to assess human health risks due to contamination at this site. The CRQLs were designated by the project specifications and the reported quantitation limits do not provide the required information to meet the DQOs. The validator apprises the EPA of the situation and payment is denied for the non-compliant analyses. All telephone logs between the validator and the laboratory and the validator and the EPA are incorporated into the Data Validation Report and the recommendation for non-payment.

IV. CALIBRATION VERIFICATION

A.   OBJECTIVE

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Successful completion of the calibration verification procedures ensure satisfactory instrument performance. Calibration verification is performed to confirm the accuracy of the calibration at designated intervals within the analytical sequence. Calibration verification procedures include the analysis of instrument blanks to verify the presence or absence of instrument contamination, and single component pesticide and multicomponent analyte calibration standards to verify the accuracy of the initial calibration. Also, a Performance Evaluation Mixture (PEM) is analyzed to verify that chromatographic resolution and pesticide degradation acceptance criteria are achieved.

B.   CRITERIA

The <u>Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses</u> should be used to validate all Region I Organic data. The CLP - Pesticide/PCB method QC acceptance criteria listed in Appendix F Section IV should be used as the default criteria when none exist for the pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method-specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site-specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1.   Calibration verification is performed once every 12 hours of sample analysis, on each GC column and instrument used for analysis. An instrument blank and the PEM must bracket one end of a 12-hour period during which sample data are collected, and a second instrument blank and the midpoint concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period. Samples may be injected for 12 hours from the injection of the instrument blank. The multicomponent analyte standard must be analyzed within 72 hours of that multicomponent analyte being detected in a sample chromatogram.

2.   The chromatographic resolution between any two adjacent peaks in the calibration verification midpoint single component pesticide calibration standard mixtures (Individual Standard Mixtures A & B) and the PEMs must be greater than or equal to 90.0 percent.

3.   The absolute retention time for each single component pesticide, surrogate and multicomponent analyte in the calibration verification standards and the PEM must be within the retention time windows determined from the initial calibration.

4.   The Percent Difference (%D) between the calculated amount and the nominal amount for each of the single component pesticides, multicomponent analytes and surrogates in the calibration verification standards and the PEM must not exceed ± 25.0 percent.

5.   The degree of pesticide degradation must be determined for each column used to analyze field samples. See Section II, GC/ECD Instrument Performance Check for additional information.
        a.   The percent breakdown for 4,4'-DDT in each PEM must be less than or equal to 20.0 percent for both GC columns.
        b.   The percent breakdown for endrin in each PEM must be less than or equal to 20.0 percent for both GC columns.

c.   The combined percent breakdown for 4,4'-DDT and endrin in each PEM must be less than or equal to 30.0 percent for both GC columns.

6.   The chromatograms that result from the analyses of the calibration verification PEMs, single component calibration standard mixtures, and multicomponent analyte standards must display the analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.

7.   The instrument blanks must meet all acceptance criteria as stated in Section V. Blanks.

8.   The criteria mentioned above apply to the results from both chromatographic columns. In the event that one GC column meets criteria and the other does not, the validator may use professional judgement to evaluate the effect of the noncompliance on the associated samples. The validator may choose to accept a sample result reported from the compliant GC column. The validator must consider whether the noncompliant GC column criteria were grossly exceeded, and the possibility of false negatives or false positives.

Note: CLP SOW-OLM04.3 does not require the analysis of a multicomponent analyte calibration verification. If a multicomponent analyte calibration verification standard is required by a non-CLP method, then the above frequency criteria, retention time criteria, and % Difference criteria used to evaluate single component pesticides should be used to evaluate calibration verification for multicomponent analytes.

C.   EVALUATION/ D. ACTION

C. **EVALUATION**	**D.** **ACTION**
	All potential and actual impacts on the sample data resulting from calibration verification anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum.
1. a. Review the Form VIII PEST to verify that the instrument blanks, PEMs, and Individual Standard Mixtures were analyzed at the required frequency on each GC column and instrument used for analysis and that no more than 12 hours elapsed between calibration verification brackets in an ongoing analytical sequence. Confirm that a multicomponent analyte standard was analyzed within 72 hours of that multicomponent analyte being detected in a sample chromatogram.	1. a. If the calibration verification sequence did not meet method requirements then professional judgment must be used to evaluate the effect of the non-compliance on the sample data. If the non-compliance affects the data, then the validator should use professional judgment to determine whether the associated sample data should be qualified or rejected.

C. **EVALUATION**	**D.** **ACTION**
*1. b. Review the raw data to verify that analytical run times are reported accurately by comparing the date and time of injection reported on the chromatograms with the date and time analyzed reported on Form VIII PEST.	1. b. If the laboratory has made transcription errors, then the validator should have the laboratory resubmit all corrected raw data and forms.
2. **RESOLUTION CHECK** a. Review Form VI PEST-5, Form VI PEST-6 and Form VI PEST-7 to verify that the resolution between any two adjacent peaks is greater than or equal to 90.0% in the PEMs and in the midpoint concentrations of Individual Standard Mixtures A and B. * b. Examine the chromatograms to verify that the reported peak resolution is correctly calculated and transcribed for the PEMs and the Individual Standard Mixtures A and B in the calibration verifications on both columns. See Appendix F, Section II for the method of calculations.	2. **RESOLUTION CHECK - Worksheet Pest/PCB-II-A** a. If the resolution QC criteria for the method are not met, then the quantitative results may not be accurate due to inadequate resolution. Estimate (J) positive detects for analytes that were not adequately resolved. Qualitative identifications may be questionable if coelution exists. Non-detects that elute in the region of coelution may not be valid depending upon the extent of the coelution problem. Before rejecting (R) any of the non-detects as unusable, proceed to the next section, C.2.b, and examine the chromatograms (Tier III level) to verify that the analytical results have been calculated and reported accurately. If the results have been calculated and reported accurately, then professional judgement should be used to reject (R) non-detects as unusable. b. If the laboratory made calculation and/or transcription errors, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to determine the more accurate value. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
3. **RETENTION TIME CHECK**	3. **RETENTION TIME CHECK - Worksheet Pest/PCB-II-B**
a. Review Form VII PEST-1 and Form VII PEST-2 to verify that the absolute retention times of the analytes in the PEMs and the Individual Standard Mixtures A and B are within the appropriate retention time window limits.	a. Retention time windows are used in qualitative identifications. If the retention times of the pesticides in the calibration verification standards or PEMs do not fall within the established retention time windows, then the associated sample results should be carefully evaluated for the possibility of false positives and false negatives. All samples injected after the last <u>in-control</u> standard are potentially affected and a Tier III level of validation should be performed to assess the impact on sample results.
* b. Review the raw data for samples analyzed after the last compliant calibration verification (either Individual Standard Mixtures A and B or PEM). Review the sample chromatograms to verify the presence or absence of peaks close to the expected retention time windows for any target pesticide.	b. If no peaks are present within or close to expected retention time windows for any target pesticide, then non-detected values can be considered valid. If sample chromatograms contain peaks close to or within the expected retention time window of target pesticides, then the validator should follow the guidelines provided in Section II.D.2.b Options 1 and 2 to determine the action to be taken.
* c. Review the retention time data for each of the single component pesticides and surrogates in the midpoint concentration of Individual Standard Mixtures A and B and PEMs to verify that the absolute retention times have been correctly calculated and reported and are within the appropriate retention time windows. Review the retention time data on the chromatograms for each of the multicomponent analytes analyzed in the calibration verification.	c. If the laboratory made calculation and/or transcription errors, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
4. **ACCURACY (%D) CHECK**	4. **ACCURACY (%D) CHECK - Worksheet Pest/PCB-IV**
a. Review Form VII PEST-1 and Form VII PEST-2 to verify that the %D between the calculated amount and the nominal amount for each of the single component pesticides and surrogates does not exceed ± 25.0% in either the Individual Standard Mixtures or the PEMs. If applicable, check any tabulated results for %Ds between the calculated amount and the nominal amount for each of the multicomponent analytes and surrogates to verify that the %Ds do not exceed ± 25.0%. See Appendix F, Section II for the method of calculating %D.	a. If the % D exceeds ± 25.0 % for the single component or multicomponent analytes being quantified, then the validator should:
	i. Estimate (J) positive detects for the affected analyte for all samples associated with the unacceptable PEM and/or Individual Standard Mixture. Note that the associated samples are the ones analyzed before and after the non-compliant PEM/Individual Standard and between compliant standards.
	ii. Estimate (UJ) non-detects for that affected analyte for all samples associated with the unacceptable PEM and/or Individual Standard Mixture.
	iii. If any surrogate analyte in the PEM and/or Individual Standard Mixture A or B fails to meet %D criteria, then the % surrogate recoveries in the samples, QC samples and blanks associated with the calibration verification may be biased high or low resulting in unacceptable surrogate recoveries. In this case, the validator should use professional judgment to assess the impact of surrogate analyte calibration data on the sample results.
	iv. Use professional judgment if the %D is exceeded on one column. The validator may choose to accept a sample result if the analyte was reported from the compliant GC column. However, qualification may be necessary if a tentative identification is made on the compliant GC column that requires confirmation on the noncompliant GC column.
	The validator should use professional judgement to estimate (J) and/or reject (R) sample data if %D criteria were grossly exceeded on one or both columns considering the possibility of false negatives or false positives.

C. EVALUATION	D. ACTION
4. a. Continued from above.	4. a. v. Before estimating (J, UJ) large amounts of data, professional judgement may be used to determine that a Tier III level of data validation is warranted. In this case, proceed to section C.4.b and verify that the %D results have been calculated and reported correctly.
* b. Review the raw data from the midpoint concentration of Individual Standard Mixtures A and B and the PEMs to verify that the % D has been correctly calculated and reported. If applicable, review the raw data for each of the multicomponent analytes analyzed in the calibration verification to verify that the %D has been correctly calculated and reported.	b. If the laboratory made calculation and/or transcription errors, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
c. Review the Form VII PEST-1 and VII PEST-2 to verify that the calibration verification standards were analyzed at the correct concentrations for each analyte.	c. If the calibration verification standards were not analyzed at the correct concentrations then professional judgment must be used to evaluate the effect of the non-compliance on the sample data. If the non-compliance affects the data, then the validator should use professional judgment to determine whether the associated sample data should be qualified or rejected.
* d. Review the raw data to verify that the concentrations reported on Form VII-PEST-1 and VII-PEST-2 were reported accurately.	d. If the laboratory has made transcription errors, then the validator should have the laboratory resubmit all corrected raw data and forms.

C. EVALUATION	D. ACTION
5. **PESTICIDE DEGRADATION CHECK** a. Verify from Form VII PEST-1 that the individual breakdown for 4,4'-DDT is less than or equal to 20.0% in the calibration verification PEM analyses.	5. **PESTICIDE DEGRADATION CHECK - Worksheet Pest/PCB-II-D** a. If 4,4'-DDT breakdown is greater than 20.0%, then the validator should: **4,4'-DDT Detected** i. Estimate (J) DDT, DDD, DDE positive detects and accept DDD and DDE non-detects for samples associated with the unacceptable PEM. **4,4'-DDT Not Detected** ii. Reject (R) DDT non-detects as unusable, accept DDD, DDE non-detects, and estimate (J) DDD, DDE positive detects and note the potential high bias for these two analytes. If the results from a second, compliant GC column are available, evaluate these results to determine to what extent DDD and DDE positive detects are due to DDT breakdown and use professional judgement to accept, estimate (J), or reject (R) results.

C.	EVALUATION	D.	ACTION
5. b.	Verify from Form VII PEST-1 that the individual breakdown for endrin is less than or equal to 20.0% in the calibration verification PEM analyses.	5. b.	If endrin breakdown is greater than 20.0%, then the validator should: **Endrin Detected** i. Estimate (J) endrin, endrin ketone, endrin aldehyde positive detects, and accept endrin ketone, endrin aldehyde non-detects for samples associated with the unacceptable PEM. **Endrin Not Detected** ii. Reject (R) endrin non-detects, accept endrin ketone, endrin aldehyde non-detects, and estimate (J) endrin ketone endrin aldehyde positive detects and note the potential high bias for these two analytes. If the results from a second, compliant GC column are available, evaluate these results to determine to what extent endrin ketone and endrin aldehyde positive detects are the due to endrin breakdown and use professional judgement to accept, estimate (J), or reject (R) results.

C. EVALUATION	D. ACTION
5. c. Verify from Form VII PEST-1 that the combined breakdown for 4,4'-DDT and endrin is less than or equal to 30.0% in the calibration verification PEM analyses.	5. c. If the combined 4,4'-DDT and endrin breakdown is greater than 30.0%, then the validator should: **4,4'-DDT Detected** i. Estimate (J) DDT, DDD, DDE positive detects and accept DDD and DDE non-detects for samples associated with the unacceptable PEM. **4,4'-DDT Not Detected** ii. Reject (R) DDT non-detects as unusable, accept DDD, DDE non-detects, and estimate (J) DDD, DDE positive detects and note the potential high bias for these two analytes. **Endrin Detected** iii. Estimate (J) endrin, endrin ketone, endrin aldehyde positive detects, and accept endrin ketone, endrin aldehyde non-detects for samples associated with the unacceptable PEM. **Endrin Not Detected** iv. Reject (R) endrin non-detects, accept endrin ketone, endrin aldehyde non-detects, and estimate (J) endrin ketone endrin aldehyde positive detects and note the potential high bias for these two analytes. If the results from a second, compliant GC column are available, evaluate these results to determine to what extent DDD, DDE, endrin ketone, and endrin aldehyde positive detects are the due to DDT and endrin breakdown and use professional judgement to accept, estimate (J), or reject (R) results.

C. **EVALUATION**	D. **ACTION**
*5. d. Review and recalculate 10% of the DDT and endrin breakdown data in the PEMs. Verify that the recalculated values agree within 10% of the laboratory values.	5. d. If errors greater than 10% are detected, then the validator should perform a more comprehensive review to determine the extent of the problem. If the problem is extensive, then the validator should have the laboratory recalculate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
*6. Review the raw data to verify that the chromatographic peaks of the single component pesticides and multicomponent analytes calibration standard mixtures are greater than 10% of full scale but less than 100% of full scale.	6. If none of the chromatograms for the calibration verification standards yield peaks that are between 10 and 100% of full scale, then the validator should use professional judgment to decide whether or not the laboratory should be required to replot and resubmit corrected data and forms. Alternatively, the validator may determine that adequate standard chromatographic data are available to confirm positive analyte identifications and non-detects.

C.	EVALUATION	D.	ACTION
*7. a.	Review Standard Preparation Logs (if provided in the data package) to ensure that primary and secondary calibration verification standard concentrations are accurate and traceable to NIST standards.	7. a.	If standards preparation data have not been submitted with the data package, then the validator should use professional judgment to determine whether or not standards preparation data are necessary to facilitate the validation of sample data. If necessary, the validator should contact the laboratory to obtain standards information including traceability information.
* b.	Review and recalculate the calibration verification standard concentration for one single component target analyte and one multicomponent target analyte (if standards preparation documentation was provided in the data package). Verify that the calculated values agree within 10% of the laboratory reported values.	b.	If errors greater than 10% are detected in the standard concentration calculations, then the validator should perform a more comprehensive review to determine the magnitude of the problem. If the problem is extensive, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

*   Note: The following subsections are applicable only to a Tier III data validation:

C.1.b, C.2.b, C.3.b, C.3.c, C.4.b, C.4.d, C.5.d, C.6, C.7.a, C.7.b

Table Pest/PCB-IV-1:

QUALIFICATION OF PESTICIDE/PCB ANALYTES BASED ON CALIBRATION VERIFICATION

Sample Results	%D $\leq \pm 25.0\%$	%D $> \pm 25.0\%$	One column meets criteria but the other exceeds
Detects	A	J	Professional judgement
Non-detects	A	UJ	Professional judgement

Table Pest/PCB-IV-2:

**QUALIFICATION OF PESTICIDE/PCB ANALYTES BASED ON
4,4'-DDT/ENDRIN BREAKDOWN - PESTICIDE DEGRADATION CHECK**

Sample Results	4,4'-DDT Breakdown ≤ 20.0%	4,4'-DDT Breakdown > 20.0% and 4,4'-DDT detected	4,4'-DDT Breakdown > 20.0% and 4,4'-DDT not detected	Endrin Breakdown ≤ 20.0%	Endrin Breakdown > 20.0% and Endrin detected	Endrin Breakdown > 20.0% and Endrin not detected	Combined Breakdown ≤ 30.0%	Combined Breakdown > 30.0% and 4,4'-DDT and/or Endrin detected	Combined Breakdown > 30.0% and 4,4'-DDT and/or Endrin not detected
4,4'-DDT	A	J	R (NDs)	N/A	N/A	N/A	A	J	R (NDs)
DDD	A	J (detects) A (NDs)	J (detects) A (NDs)	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)
DDE	A	J (detects) A (NDs)	J (detects) A (NDs)	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)
Endrin	N/A	N/A	N/A	A	J	R (NDs)	A	J	R (NDs)
Endrin Aldehyde	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)	A	J (detects) A (NDs)	J (detects) A (NDs)
Endrin Ketone	N/A	N/A	N/A	A	J (detects) A (NDs)	J (detects) A (NDs)	A	J (detects) A (NDs)	J (detects) A (NDs)

N/A   =   Not Applicable
J   =   Estimate result
R (NDs) =   Reject non-detects
A (NDs) =   Accept non-detects

Note: The validator must always discuss negative and positive bias in sample data in the Data Validation Memorandum.

E.   EXAMPLES

Example #1: (Non-compliant analytical sequence)

The validator checks Form VIII PEST and determines that 14 hours elapsed between calibration verification standard brackets in an ongoing analytical sequence. The validator examines the sample data and determines that all calibration criteria were met (retention times were within the required retention time windows and %Ds were within criteria. Using professional judgment the validator reports the sample results unqualified on the Data Summary Table and notes the non-compliance in the Data Validation Memorandum.

Example #2: (Non-compliant chromatographic resolution)

The validator checks Form VI PEST-6 to verify that the peak resolution criteria were met in Individual Mixture A. The resolution between endosulfan I and heptachlor is found to be 88.0% on column DB1701. The validator also reviews the previous and subsequent standard runs containing these analytes to assess the extent of non-compliance for these analytes. Since the resolution is only slightly out of criteria in one Individual Mixture A and the resolution between these analytes on column DB608 was met, the validator reports the sample results unqualified on the Data Summary Table and notes the non-compliance in the Data Validation Memorandum.

Example #3: (Non-compliant retention time)

The validator checks Form VII PEST-2 to verify that the retention time criteria were met. The retention time window for methoxychlor is from 11.64 to 11.78. The calibration verification retention time for methoxychlor in Individual Mixture A is 11.86. The validator examines the sample chromatograms and determines that no peaks are present either within or near the retention time window. The validator uses professional judgment to accept the methoxychlor non-detects and reports the methoxychlor quantitation limits unqualified on the Data Summary Table and notes the non-compliance in the Data Validation Memorandum.

Example #4: (Non-compliant %D)

The validator reviews Form VII PEST-2 to check percent differences between the calculated amount and the nominal amount. Gamma-Chlordane has a %D of 65.0% in Individual Mixture B. The validator checks the raw data and verifies that the %D has been properly calculated. The validator reviews the previous and subsequent standard runs containing gamma-chlordane to assess the extent of the non-compliance for this analyte. Due to variable instrument performance, the validator estimates (J) the positive gamma-chlordane detects and estimates (UJ) the gamma-chlordane non-detects for all samples associated with the non-compliant calibration verifications on the Data Summary Table. The validator discusses the sample qualification in the Data Validation Memorandum.

Example #5: (Pesticide Degradation)

The validator reviews the DDT/Endrin breakdown data and notes that the endrin breakdown in the PEM, which was analyzed as the calibration verification for this sequence, is 39.0%. The validator then reviews the subsequent PEMs that were analyzed 24 hours before and after and notes that the endrin breakdown is less than 20.0%. For samples that have positive endrin detects; the validator estimates (J) the endrin detects, and estimates (J) positive endrin ketone and endrin aldehyde detects and accepts endrin ketone and endrin aldehyde non-detects for all samples analyzed before and after the non-compliant PEM. For samples that have endrin non-detects; the validator rejects (R) the endrin non-detects and estimates (J) endrin ketone and/or endrin aldehyde detects and accepts endrin ketone and endrin aldehyde non-detects. It is noted in the Data Validation Memorandum that when the breakdown for endrin is high, the values for endrin are potentially biased low and the values for endrin ketone and endrin aldehyde are potentially biased high.

V. BLANKS

A. OBJECTIVE

The purpose of blank analyses is to determine the existence and magnitude of contamination problems resulting from laboratory and/or field activities and to subsequently assess their contribution to measurement error. The criteria for evaluation of laboratory blanks (method blanks, instrument blanks, and sulfur cleanup blanks) may be applied to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent measurement error associated with the entire data set, or if the problem is an isolated occurrence limited to specific samples.

B. CRITERIA

The Region I, EPA-NE Data Validation Functional Guidelines For Evaluating Environmental Analyses should be used to validate all Region I Organic data. The CLP - Pesticide/PCB method QC acceptance criteria listed in Appendix F should be used as the default criteria when none exist for the pesticide/PCB analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been specified. Deviations, modifications or non-CLP method specific QC acceptance criteria may be used but must be explicitly defined in tabular format in the site-specific EPA approved QAPP/SAP or amendment to the QAPP/SAP.

1. The frequency and types of blanks collected and analyzed must support the site-specific Data Quality Objectives (DQOs) as documented in the EPA approved QAPP or SAP. Different types of blanks may be used to identify the source of potential contamination resulting in analytical and/or sampling measurement error. The following table lists types of blanks, the environment of these blanks, and the possible sources of contamination associated with those blanks:

BLANK	**LABORATORY/FIELD**	**IDENTIFIES CONTAMINATION FROM**
Method Blank	Laboratory	Laboratory and Reagents
Instrument Blank	Laboratory	Instrumentation
Bottle Blank	Field	Sample Container
Equipment Blank (Rinsate)	Field	Sampling Equipment

Note: Aqueous equipment (rinsate) blank results and bottle blank results will be used to determine blank action levels for aqueous samples based on a volume of 1 liter of blank sample. Ideally soil/sediment blanks should be used to determine soil/sediment blank actions for soil/sediment samples based on a known weight of blank sample. However, frequently aqueous equipment blanks and bottle blanks are collected to evaluate soil/sediment contamination associated with sampling. **Aqueous equipment (rinsate) blank results and bottle blank results will not be used to determine blank action levels for non-aqueous samples.** Analytes that are present in both the non-aqueous sample and the associated aqueous equipment blank or bottle blank will be flagged EB (Equipment Blank) or BB (Bottle Blank), respectively. The degree of "sampling error" that this flagged sample result represents will be left to the determination of the end user.

If a contaminant is found in a blank but not in the aqueous sample, no action is taken. If a

contaminant is found in both a blank and an aqueous sample, then the validator should note this problem in the Data Validation Memorandum and qualify the data according to the following guidance:

> If the blank action level for an analyte is determined using the value from a bottle blank or equipment blank, then the positive values in the bottle or equipment blank should be reported unqualified on the Data Summary Tables. However, if the blank action is determined using the value from the laboratory blank (e.g., method, cleanup, or instrument), then the positive values in the bottle or equipment blank should be qualified. (See example # 6)

If analytes are present in both the non-aqueous sample and the associated aqueous equipment blank or bottle blank, then the results for these analytes in the non-aqueous sample will be flagged EB (Equipment Blank) or BB (Bottle Blank), respectively. The degree of sampling error that this flagged sample result represents will be left to the determination of the end user. However, the data validator should note this problem in the Data Validation Memorandum.

Use of professional judgment is suggested when equipment and bottle blanks are associated with highly contaminated samples and are not likely to have contributed to sample contamination.

For aqueous and non-aqueous samples, contamination found in the equipment or bottle blank must be reported to the sampler and the EPA Regional Project Manager.

2.   Method Blanks:

a.   An acceptable pesticide/PCB method blank must be extracted with each sample delivery group or each 20 samples of similar matrix in each sample delivery group or whenever a sample extract procedure is performed. The method blank must undergo all cleanup procedures including Gel Permeation Chromatography (GPC) and Florisil. The method blank must be analyzed on each gas chromatography (GC) system used to analyze samples.

b.   A sulfur cleanup blank must be analyzed whenever part of a set of samples extracted together requires sulfur cleanup. If the entire set of samples associated with a method blank requires sulfur cleanup, then the method blank must be carried through the sulfur cleanup procedures. In that case, the method blank can also be considered a sulfur cleanup blank and no separate sulfur cleanup blank is required.

3.   GC Instrument Blanks:

a.   An acceptable GC instrument blank must be analyzed at least once every 12 hours and immediately prior to the analysis of either the continuing calibration standards (INDA and INDB) or the Performance Evaluation Mixture (PEM).

b.   A GC instrument blank should be analyzed after any sample with peaks that exceed the calibration range to demonstrate that the system is not contaminated.

4.   GPC Instrument Blanks:

   a.   A GPC blank must be analyzed after each GPC calibration. The GPC blank consists of 5 mLs of methylene chloride and is not spiked with surrogates.

5.   All blanks (except GPC blanks) must be spiked with surrogate analytes according to the method.

   a.   The retention times of the surrogates in each blank must be within the retention time windows calculated from the initial calibration.

   b.   Blank surrogate analytes must meet method surrogate analyte QC acceptance criteria for recovery. The default criteria are listed in Appendix F.

6.   No contaminants should be present in the blanks. The concentrations of any contaminants found in the blanks should be less than the QC acceptance criteria specified in the QAPP/SAP.

C.   EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from blank anomalies should be noted in the Data Validation Memorandum. The validator should also document and justify all technical decisions made based on professional judgment in the Data Validation Memorandum. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. **Qualification should be based upon a comparison of the sample concentration(s) with the highest blank concentration associated with the sample delivery group.** However, in cases of specific instrument and/or method blank contamination, the validator should use professional judgment to qualify only those samples associated with that isolated blank contamination. Likewise, the validator may need to apply blank qualifications to a sample delivery group based on associated equipment, trip, or bottle blank data that exists in another sample group data package. **Sample results must not be corrected by subtracting any blank values.**

C. EVALUATION	D. ACTION
1. a. Verify that the correct number and type of blanks have been collected and analyzed in accordance with the EPA approved QAPP or SAP. b. Ascertain if aqueous equipment (rinsate) blanks or aqueous bottle blanks have been collected with non-aqueous samples to identify sources of field contamination.	1. a. If the correct number and type of blanks have not been collected and analyzed, then the validator should note this deviation from the EPA approved QAPP or SAP in the Data Validation Memorandum. The validator should use professional judgment to qualify sample data when blank data are absent. When required equipment (rinsate) or bottle blanks are not identified on the chain of custody, then the validator must contact the sampler or site project manager to obtain this information and note this contact on the Blank Analysis validation worksheet. b. If positive results are detected in the aqueous equipment (rinsate) blanks and/or bottle blanks <u>and</u> the associated <u>non-aqueous</u> samples, then the validator should flag (EB or BB) those detected analytes in the associated non-aqueous samples to indicate to the end user that an indeterminate amount of sampling error has potentially affected the sample results.
2. a. Verify that a method blank analysis has been reported per matrix, per concentration level, for each 12-hour time period on each GC system used to analyze each extraction batch of pesticide/PCB samples. The validator should review Form IV PEST (the pesticide Method Blank Summary) to identify the samples associated with each method blank. b. Verify that sulfur cleanup blanks were analyzed at the required frequency. Verify that a Form IV PEST was completed listing all the samples associated with the method blank, and that a <u>second</u> Form IV PEST was completed listing only those samples associated with the sulfur cleanup blank.	2. a. If method blanks were not analyzed at the required frequency and for each matrix and concentration level, extraction technique and batch and on each GC system used to analyze sample extracts, then the validator should use professional judgment to determine whether or not the associated sample data should be qualified. b. If a required sulfur blank was not analyzed, then the validator should use professional judgment to determine the effect on the data and qualify the sample results accordingly.

C. EVALUATION	D. ACTION
*2. c. Verify from the raw data that the extraction and/or analysis dates and times, sample IDs, file IDs, instrument IDs, etc. are accurately reported on the tabulated result forms.	2. c. If review of the raw data reveals discrepancies and/or transcription errors, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
3. a. Verify from Form VIII PEST that an instrument blank was analyzed every 12 hours as part of the required analytical sequence.	3. a. If instrument blanks were not analyzed at the required frequency on each GC system used to analyze sample extracts, then the validator should use professional judgment to determine whether the associated sample data should be qualified.
* b. Verify from the raw data that a GC instrument blank was analyzed after each sample with peaks that exceeded the calibration range.	b. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), then sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgment should be used to determine if instrument contamination has affected any positive analyte identification and/or quantitation, and to determine whether or not the affected sample data should be qualified or rejected. If contamination is suggested, then this should be noted in the Data Validation Memorandum.
*4. Verify from the raw GPC data that a GPC instrument blank was analyzed after the GPC calibration and prior to sample analysis.	4. If a GPC instrument blank was not analyzed at the method-required frequency, then the validator should evaluate the method blank data and use professional judgment to qualify sample data associated with that GPC cleanup procedure.

C. EVALUATION	D. ACTION
5. a. Verify from Form VIII PEST that the surrogate retention times for all blanks analyzed are within the established retention time windows.	5. a. If blank surrogate retention times have shifted, then the validator should use professional judgment in applying blank actions. The possibility of false positives or false negatives being incorrectly reported for the blank should be evaluated.
b. Verify from Form VI PEST-1 that the surrogate retention time windows have been correctly calculated.	b. If the retention time windows have not been calculated correctly, then the validator should have the laboratory recalculate and resubmit Form VI PEST-1.
* c. Review the raw data for each blank to confirm that retention time data have been correctly transcribed to the tabulated forms. Review the blank chromatograms and quantitation reports to ensure that contamination has been accurately reported. For additional guidance refer to Section XII, Target Analyte Identification, in Part III.	c. If the laboratory has reported a false positive or a false negative and/or has incorrectly transcribed data, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
d. Verify from Form II PEST-1 and PEST-2 that blank surrogate recoveries meet method QC criteria.	d. If blank surrogate recoveries do not meet method criteria, then the validator should refer to Section VI, C.2.d for guidance.
* e. Check 10% of the raw blank data to confirm that surrogate recovery data has been accurately calculated and transcribed to the tabulated result forms.	e. If the laboratory has incorrectly calculated and/or transcribed blank surrogate recovery data, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
6. Review the tabulated reported results of all the blanks associated with the SDG.	6. If a contaminant is found in a blank but <u>not</u> in the aqueous sample, no action is taken. If a contaminant is found in both a blank and an aqueous sample, then the validator should note this problem in the Data Validation Memorandum and qualify the data according to the following guidance: **Note: If the blank action level for an analyte is determined using the value from a bottle blank or equipment blank, then the positive values in the bottle or equipment blank should be reported unqualified on the Data Summary Tables. However, if the blank action is determined using the value from the laboratory blank (e.g., method, cleanup, or instrument), then the positive values in the bottle or equipment blank should be qualified. (See example # 6)** If analytes are present in both the non-aqueous sample and the associated aqueous equipment blank or bottle blank, then the results for these analytes in the non-aqueous sample will be flagged EB (Equipment Blank) or BB (Bottle Blank), respectively. The degree of sampling error that this flagged sample result represents will be left to the determination of the end user. However, the data validator should note this problem in the Data Validation Memorandum. For aqueous and non-aqueous samples, contamination found in the equipment or bottle blank must be reported to the sampler and the EPA Regional Project Manager. Use of professional judgment is suggested when equipment and bottle blanks are associated with highly contaminated samples and are not likely to have contributed to sample contamination. If an analyte must be estimated (J) due to other validation criteria and an EB or BB is also applied, then use JEB or JBB in the Data Summary Table.

C. EVALUATION	D. ACTION
6. a. Determine whether or not any target analytes are present at or above the quantitation limit/CRQL in any of the blanks.	6. a. **Target Analyte Contaminants at or Above the Quantitation Limit/CRQL:** i. If the sample result for an analyte is greater than 5 times the highest concentration in any blank, then the analyte's concentration should be reported as unqualified. (See example #3 - 5x rule). ii. If the sample result for an analyte is less than or equal to 5 times the highest concentration of the analyte in any blank but greater than the quantitation limit, then the quantitation limit for that analyte should be elevated to the concentration found in the sample and reported as not detected (U). The validator should use professional judgment to determine if further elevation of the quantitation limit is required. (See example #1 - 5x rule). Note: The validator should note that blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be taken into consideration when applying the "5x" criteria, such that a comparison of the total amount of contamination is actually made. (See example #5). Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample data is deemed necessary. If the validator determines that the contamination originates from a source other than the sample, the sample data should be qualified. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurrence can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. In this case, the "5x" rule may not apply; the target analyte should be reported as not detected (U), and an explanation of the data qualification rationale should be provided in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
6. b. Determine if low level contamination below the quantitation limit exists in any of the blanks.	6. b. **Target Analytes Below the Quantitation Limit/CRQL:** i. If a positive sample result is reported at less than the quantitation limit and is also less than the blank action level, then the sample quantitation limit should be reported as non-detected (U) on the Data Summary Tables. (See example #2 - 5x rule). ii. If one or several target analytes are found at low levels, below the quantitation limit, in the laboratory blank(s), it may indicate a systemic problem in the laboratory and should be noted in the Data Validation Memorandum. iii. If contamination exists solely in the bottle or equipment (rinsate) blanks, then the validator should notify the sampler. The call should be documented in a telephone log that is included in the Data Validation Memorandum and the date of contact should be noted on the Blank Analysis Worksheet.
c. Determine if gross contamination greater than 10x CRQL for any analyte exists in any of the blanks.	c. **Gross Contamination** i. If gross contamination, greater than 10x CRQL for any analyte, exists in any blank, then the validator should reject (R) all positive hits for the affected analytes and accept the non-detects in samples associated with that blank due to interference. This serious problem should be discussed in the Data Validation Memorandum. ii. If gross contamination exists solely in the bottle or equipment (rinsate) blanks, then the validator should notify the sampler and the EPA Regional Project Manager. The call should be documented in a telephone log that is included in the Data Validation Memorandum and the date of contact should be noted on the Blank Analysis Worksheet.

C. EVALUATION	D. ACTION
*6. d. Determine if instrument contamination is isolated to specific sample sequences or isolated to one column.	6. d. If contamination is limited to a few samples due to instrument contamination or limited to one column, then the validator may use professional judgment to accept or qualify sample data in samples associated with the instrument blank contamination.
e. Review the raw data (chromatograms, mass spectra confirmatory data and quantitation reports) to confirm the presence of target analytes in the blanks and to evaluate the presence of additional contaminants.	e. If review of raw data suggests that additional contaminants are present or, conversely, the review indicates false positives have been reported, then the validator should contact the laboratory to obtain additional information and/or have the laboratory requantitate and resubmit all corrected raw data and forms. If a discrepancy remains unresolved, the validator must use professional judgment to decide which value is more accurate. Under these circumstances, the validator may determine that the sample data should be qualified or rejected. A discussion of the rationale for data qualification and the qualifiers used should be documented in the Data Validation Memorandum.
7. Evaluate the overall contamination in each type of blank to ascertain the probable source(s) of contamination. For example, a contaminated equipment blank might indicate decontamination problems, if the method, instrument, and bottle blanks were all clean.	7. If a review of the various types of blanks identifies a potential source of blank contamination, then the validator should discuss this problem in the Data Validation Memorandum. The validator should identify whether the measurement error is a result of either sampling or analytical error or both (see Data Validation Manual p.1).

*   Note: The following subsections are applicable only to a Tier III data validation:

C.2.c, C.3.b, C.4, C.5.b, C.5.d, C.6.e

E. EXAMPLES

Example #1: (Bottle blank target analyte contaminant ≥ CRQL, < 5x blank action level)

4,4'-DDT is detected in a water sample at greater than the CRQL, but less than 5x the bottle blank concentration.

<div align="center">

5x Rule

	ug/L
Bottle Blank Result	1.0
CRQL	0.5
4,4'-DDT Sample Result	4.0
Action Level	5.0
"Qualified" Sample Result	4.0U

</div>

In this case, all sample results where 4,4'-DDT is less than 5.0 ug/L (5 x 1.0) are reported as non-detected at an elevated quantitation limit on the Data Summary Table. The validator notes in the Data Validation Memorandum that the bottle blank was contaminated with 4,4'-DDT and documents the lot number of the sample bottle, and alerts the site project manager regarding a contaminated lot of bottles.

Example #2: (Instrument blank target analyte contaminant < CRQL, < 5x blank action level)

Endrin is detected in a water sample at less than the CRQL, and also less than 5x the instrument blank concentration. The instrument blank contained the highest concentration of endrin of all blanks analyzed. In addition, all field samples analyzed were associated with the same contaminated instrument blank.

<div align="center">

5x Rule

	ug/L
Instrument Blank Result	1.0
CRQL	0.5
Endrin Sample Result	0.4
Action Level	5.0
"Qualified" Sample Result	0.5U

</div>

In this case, the endrin sample result is less than 5.0 ug/L (1 x 5) and is reported non-detected at the CRQL on the Data Summary Table. The validator also notes the sample qualifications in the Data Validation Memorandum.

E. EXAMPLES

Example #3:   (Blank target analyte contaminant > 5x blank action level)

Gamma-BHC is detected in a water sample at greater than 5x the instrument blank concentration.

<div align="center">

5x Rule

	ug/L
Blank Result	1.0
CRQL	0.5
gamma-BHC Sample Result	10.0
Action Level	5.0
"Qualified" Sample Result	10

</div>

In this case the gamma-BHC sample result exceeded the blank action level of 5 ug/L (5 x 1.0) and the gamma-BHC sample result is unqualified on the Data Summary Table.

Example #4:   (Blank target analyte contamination in aqueous equipment blank collected with soil samples)

An aqueous equipment blank (rinsate) was included in a sample delivery group of soil samples. The validator examines the data and finds that the equipment contains 0.08 ug/L of dieldrin. The validator then reviews all other blank data and finds no further dieldrin contamination. One soil sample contains 7.0 ug/kg of dieldrin. The validator reports the soil sample result on the Data Summary Table as 7.0 (EB) to indicate to the end user that sampling error has potentially affected the sample results and notes this information in the Data Validation Memorandum.

Example #5:   (Application of sample weights and volumes with the 5x Rule)

Soil sample TAA35 was analyzed as a routine pesticide/PCB soil sample under CLP SOW OLM04.3 and contained 70% solids. The method blank was found to be contaminated with aldrin (2.2 ug/kg) and dieldrin (1.5 ug/kg). These blank results were reported by the laboratory on a dry weight basis and were the maximum levels of contamination found for these analytes in this sample delivery group. The validator determines the blank action level by applying the 5x rule. For the method blank the action level for aldrin was calculated to be 11.0 ug/kg (2.2 x 5), and the action level for dieldrin was calculated to be 7.5 ug/kg (1.5 x 5). The validator reviewed the sample results and found dieldrin (6.0 ug/kg) and aldrin (0.5 ug/kg) in TAA35.

The validator calculates the Quantitation Limits for dieldrin and aldrin:

$$\text{dieldrin QL} = \frac{\text{CRQL}}{\%\ \text{solids}} = \frac{3.3\ \text{ug/kg}}{0.7} = 4.7\ \text{ug/kg}$$

$$\text{aldrin QL} = \frac{\text{CRQL}}{\%\ \text{solids}} = \frac{1.7\text{ug/kg}}{0.7} = 2.4\ \text{ug/kg}$$

E.   EXAMPLES

Example #5: (Continued)

The validator applies the following action to the dieldrin and aldrin results of sample TAA35:

Dieldrin			Aldrin	
5x Rule			5x Rule	
	ug/kg			ug/kg
Blank Result	1.5	Blank Result	2.2	
CRQL	4.7	CRQL	2.4	
Sample Result	6.0	Sample Result	0.5	
Action Level	7.5	Action Level	11.0	
"Qualified" Sample Result	6.0 U	"Qualified" Sample Result	2.4 U	

- The dieldrin quantitation limit is <u>elevated</u> to the sample concentration result on the Data Summary Table as 6.0U, since the result is between the quantitation limit and the blank action level.

- The aldrin sample result on the Data Summary Table is <u>replaced</u> with the sample quantitation limit and is reported on the Data Summary Table as 2.4U, since the positive sample detect of 0.5, is below the quantitation limit and the blank action level.

The validator notes all actions taken in the Data Validation Memorandum.

Example #6:   (Application of laboratory blank action levels to equipment blanks)

The method blank for an aqueous batch of samples was contaminated with 0.5 ug/L of endrin. The equipment blank for this batch of samples was contaminated with 0.35 ug/L of endrin and 0.6 ug/L of dieldrin. Since endrin was detected in both the method blank and the equipment blank, the highest detected concentration is used to determine the blank action level. The method blank is therefore used to determine the blank action level of endrin.

Endrin		Dieldrin	
	ug/L		ug/L
Method Blank Result	0.5	Method Blank Result ND	
Equipment Blank Result	0.35	Equipment Blank Result	0.6
CRQL	0.5	CRQL 0.5	
Blank Action Level	2.5(5x0.5)	Blank Action Level	3.0 (5x0.6)

The endrin positive detect is qualified in the equipment blank and reported as 0.35U ug/L on the Data Summary Table. The blank action level for dieldrin is determined using the value from the equipment blank and as a result the dieldrin positive detect in the equipment blank is reported unqualified as 0.6 ug/L on the Data Summary Table. If positive hits for dieldrin are found in the samples, then the blank action level is applied at 3.0 ug/L (5 x 0.6 ug/L).