VII. INTERNAL STANDARDS

A. OBJECTIVE

Instrument performance and stability and laboratory precision throughout an analytical sequence are monitored by the addition of internal standard compounds. Internal standards (ISs) are added to every field sample, QC sample, standard and blank just prior to analysis. Evaluation of the behavior of internal standards is not necessarily straightforward. Interfering sample matrix effects, including high concentrations of target and non-target analytes, are frequently outside of the laboratory's control and may adversely affect the analysis of internal standards.

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-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile 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 QAPjP/SAP or amendment to the QAPjP/SAP.

1. The internal standard compounds specified in the method must be added to all samples, QC samples, standards and blanks at the required concentrations.

2. Internal standard area counts must be within the method QC acceptance criteria.

3. The retention time of the internal standard must be within the method QC acceptance criteria.

4. Samples must be reanalyzed and/or reextracted in accordance with method requirements if internal standard method QC acceptance criteria are not met.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from internal standard 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. Verify that the correct compounds were added to all samples, QC samples, standards and blanks at the method-specified concentrations.	1. If the laboratory did not add the required internal standard compounds to all samples, QC samples, standards and blanks at the correct concentration, then the validator must use professional judgment to determine how the associated sample data should be qualified or rejected.
2. Verify that all IS area counts are within the method QC acceptance criteria.	2. If an IS area count for a sample, QC sample, or blank is outside the method QC acceptance criteria, then the validator should: a. Estimate (J) positive detects for compounds quantitated using an IS area count greater than the upper limit of the method QC acceptance criteria. b. Accept (A) non-detects for compounds quantitated using an IS area count greater than the upper limit of the method QC acceptance criteria. c. Estimate (J) positive detects for compounds quantitated using an IS area count less than the lower limit of the method QC acceptance criteria. d. Estimate (UJ) non-detects for compounds quantitated using an IS area count less than the lower limit of the method QC acceptance criteria but greater than or equal to 20% of the associated daily continuing calibration standard area. e. Reject (R) non-detects for compounds quantitated using an IS area count less than 20% of the associated daily continuing calibration standard area or if internal standard performance exhibits a major abrupt drop-off, indicating a severe loss of sensitivity. Alternatively, professional judgment may be used to assess signal to noise ratios to qualify or reject sample data.

C. EVALUATION	D. ACTION
3. Verify that all IS retention times are within method QC acceptance criteria.	3. If an IS retention time for a sample, QC sample, or blank is outside the method QC acceptance criteria, then the validator should examine the chromatographic profile for that sample to determine if any false positives or negatives exist. For shifts of a large magnitude, the validator may consider partial or total rejection of the data for that sample fraction. The validator should use professional judgment to determine if positive detects can be reported based upon mass spectral identification criteria being met. The validator should consider, however, the possible presence of non-target compounds that are isomers of target compounds.
*4. Check raw data (e.g., chromatograms and quantitation reports) to verify that the internal standard retention times and areas are accurately reported on the tabulated forms.	4. 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.
5. a. Verify that if any internal standard compound area count or retention time is outside the method QC acceptance criteria, that the required reanalysis was performed to confirm that the non-compliance was due to sample matrix effects rather than poor laboratory performance.	5. a. If a laboratory fails to reanalyze a sample with an internal standard compound that is outside the method QC acceptance criteria, then the sample data should be qualified or rejected according to the guidelines above. The validator should note this problem in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
5. b. If there are two analyses for a particular fraction, then the validator must determine which are the best data to report. Considerations should include but are not limited to: - Magnitude and direction of the IS area shift; - Magnitude and direction of the IS retention time shift; - Technical holding times; - Comparison of the values of the target compounds reported in each analysis; - Other relevant QC.	5. b. If a sample has been analyzed and reported more than once, then the validator should use professional judgment when considering which analysis or portion of an analysis to report. The validator must consider all relevant QC information in making a decision.

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

C.4

Table VOA/SV-VII-1:

QUALIFICATION OF VOA/SV ANALYTES BASED ON INTERNAL STANDARD AREA COUNTS

Internal Standard Area Counts				
Sample Results	**Area Counts < 20% of associated calibration std. area**	**20% ≤ Area Counts < LL**	**LL ≤ Area Counts ≤ UL**	**Area Counts > UL**
Detects	J	J	A	J
Non-detects	R	UJ	A	A

LL - Lower Limit of method QC acceptance criteria based on associated calibration standard area
UL - Upper Limit of method QC acceptance criteria based on associated calibration standard area

E. EXAMPLES

Example #1: (Sequential instrument sensitivity loss for one volatile IS compound ending with sample IS area < LL of method QC acceptance criteria based on associated daily continuing calibration standard area)

IS = 1,4-difluorobenzene

12 Hour STD 27105
Upper Limit (+ 100%) 54210
Lower Limit (50%) 13553

	Sample AAA01	Sample AAA02	Sample AAA03	Sample AAA04
IS Area Count:	30000	22000	15000	10000
benzene concentration (ug/kg)	24	32	38	45

The validator reviews the IS area counts for samples analyzed by CLP SOW OLM03.2 and notes that the 1,4-difluorobenzene area counts decrease sequentially over time and the area counts for sample AAA04 are below the lower method QC acceptance limit but greater than 20% of the associated daily continuing calibration standard area. Upon review of the sample data, the validator ascertains that benzene was the only target compound detected in the samples. Therefore, the validator estimates (J) the benzene positive detects in sample AAA04 and estimates (UJ) quantitation limits for all other target analytes quantitated using 1,4-difluorobenzene in sample AAA04 on the Data Summary Table. The validator discusses the instrument's sensitivity loss and the sample qualifications in the Data Validation Memorandum.

Example #2: (One semivolatile IS compound with area counts < 20% of associated daily continuing calibration standard)

IS = 1,4-dichlorobenzene-d_4

12 Hour STD 76400
Upper Limit (+ 100%) 152800
Lower Limit (50%) 38200

	Sample AAA01	Sample AAA02	Sample AAA03	Sample AAA04
IS Area Count:	75000	73000	10000	76000
phenol concentration (ug/L)	35	10U	17	55

The validator reviews the IS area counts for samples analyzed by CLP SOW OLM03.2 and notes that the 1,4-dichlorobenzene-d_4 area count in sample AAA03 is less than 20% of the associated daily continuing calibration standard area (20% = 15280). Upon review of the sample data, the validator ascertains that phenol was the only target compound detected in the samples. Therefore, the validator estimates (J) the positive phenol detect in sample AAA03 and rejects (R) the quantitation limits for all other target analytes quantitated using 1,4-dichlorobenzene-d_4 in sample AAA03 on the Data Summary Table. The validator notes the sample qualifications in the Data Validation Memorandum.

E. EXAMPLES

Example #3: (One semivolatile IS compound with RT shift greater than method QC acceptance limit)

The validator reviews the IS data and determines that the retention time for chlorobenzene-d_5 has shifted by + 60 seconds which exceeds the ± 30 second QC acceptance limit allowable under CLP SOW OLM03.2. Upon inspection of the chromatographic profile, the validator determines that the mass spectral identification criteria have been met for positive detects associated with chlorobenzene-d_5. The validator accepts the positive detects associated with chlorobenzene-d_5 and rejects (R) the quantitation limits for all other target analytes quantitated using chlorobenzene-d_5 on the Data Summary Table. The validator discusses the possibility of false negatives in this sample in the Data Validation Memorandum.

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A. OBJECTIVE

Data for matrix spike/matrix spike duplicates (MS/MSDs) are generated to determine laboratory precision and method bias for specific sample matrices at the time of sample preparation and analysis. MS/MSD data can be used to determine long-term interlaboratory precision and bias of an analytical method for various matrices and are used in setting quality control acceptance criteria for spiking compounds. MS/MSD data should be used in conjunction with other QC data, such as field duplicate data and surrogate compound recoveries, to determine if a sample or an entire sample group should be qualified.

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-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile 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 QAPjP/SAP or amendment to the QAPjP/SAP.

1. In accordance with the SAP, QAPjP and/or method, a field sample of each matrix is spiked in duplicate with known concentrations of specific target compounds to generate an MS/MSD pair. Concurrently, the laboratory analyzes an unspiked aliquot and the MS/MSD pair of the field sample.

2. a. Field samples (not trip, equipment, or bottle blanks and not PE samples) must be spiked to assess matrix effects.

   b. Field samples chosen for MS/MSD analysis should not contain high levels of MS/MSD spiking compounds prior to spiking. Preferably, field samples chosen for MS/MSD analysis should contain low levels of the spiking compounds.

3. Spike recoveries must be within the QC acceptance criteria specified in the method, SAP or QAPjP.

4. Relative percent differences (RPDs) between MS and MSD recoveries must be within the QC acceptance criteria specified in the method.

5. The percent relative standard deviation (%RSD) between positively detected non-spike compounds in the unspiked sample, MS, and MSD must be less than or equal to 50%.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from matrix spike/matrix spike duplicate 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. Verify that the correct compounds were added at the required concentrations; that MS/MSD samples were analyzed at the proper frequency; and that MS/MSD results are provided for each sample matrix.	1. If the laboratory did not use the required compounds at the concentration and frequency specified in the method for each sample matrix, then the validator must use professional judgment to determine whether the associated sample data should be qualified.
2. a. Verify that a field sample was chosen for the MS/MSD.	2. a. If a trip, equipment or bottle blank or a PE sample was used for the MS/MSD, then the validator should note this information in the Data Validation Memorandum and discuss the impact on assessing laboratory precision, method bias, sample matrix effects and ultimately data usability.
b. Determine if an inappropriate sample containing high levels of the spiking compounds was chosen for the MS/MSD pair.	b. If the MS/MSD compounds were present in the field sample at high concentrations (e.g., 4x spike concentration) before spiking, then the validator must use professional judgment in assessing matrix spike recoveries and RPDs.
c. Ascertain if the MS/MSD analyses required dilutions.	c. If no MS/MSD data can be reported because of sample dilution, then the validator should note this problem in the Data Validation Memorandum and discuss the impact on assessing data usability in the case where laboratory precision and method bias information are absent.

C. EVALUATION	D. ACTION
3. Verify that all spike recoveries are within the QC acceptance criteria specified in the method.	3. a. If any spike recovery result is greater than the upper limit of the method QC acceptance criteria, then the validator should: i. Estimate (J) the positive detect for that affected compound in the unspiked sample. ii. Accept the non-detect for that affected compound in the unspiked sample. b. If any recovery result is greater than or equal to 10%, but less than the lower limit of the method QC acceptance criteria, then the validator should: i. Estimate (J) the positive detect for that affected compound in the unspiked sample. ii. Estimate (UJ) the non-detect for that affected compound in the unspiked sample. c. If any recovery result is less than 10%, then the validator should: i. Estimate (J) the positive detect for that affected compound in the unspiked sample. ii. Reject (R) the non-detect for that affected compound in the unspiked sample. d. If the majority of spike compound recoveries are outside the method QC acceptance criteria, then the validator may use professional judgment to estimate (J) or reject (R) <u>all</u> positive detects and estimate (UJ) or reject (R) <u>all</u> non-detects in the unspiked sample.

C. EVALUATION	D. ACTION
4. Verify that all the RPDs between the MS and MSD are within the QC acceptance criteria specified in the method.	4. If any RPD result is outside the method QC acceptance criteria, then the validator should: a. Estimate (J) the positive detect for that affected compound in the unspiked sample. b. Estimate (UJ) the non-detect for that affected compound in the unspiked sample. c. If the majority of the matrix spike RPDs are outside method QC acceptance criteria, then the validator should use professional judgment to estimate (J) all positive detects and estimate (UJ) or reject (R) all non-detects in the unspiked sample. Refer to Section VIII C. 8 and 9 for additional guidance.

C. EVALUATION	D. ACTION
5. a. Calculate the % RSD for the non-spiked target positive detects in the unspiked sample, the MS and the MSD.	5. a. If a non-detected result or a detect less than the quantitation limit is reported for a non-spiked target compound in one of the samples in the MS, MSD or unspiked sample set, then the validator should use the sample quantitation limit value for that compound to calculate the %RSD. If a non-detected result or a detect less than the quantitation limit is reported for a non-spiked target compound in two of the samples in the MS, MSD or unspiked sample set, then the validator should not calculate the %RSD but should use professional judgment to qualify sample data.
b. The unspiked sample, MS, and MSD may be considered a triplicate in determining the overall precision of the analytical method. Therefore, evaluate the %RSD data for positive detects in the triplicate set.	b. If any %RSD is greater than 50%, then the validator should: i. Estimate (J) the positive detect for that affected compound in the unspiked sample. ii. Use professional judgment to qualify or accept the non-detect for that affected compound in the unspiked sample. If overall laboratory precision for the unspiked field sample, MS, and MSD is poor, then the validator may use professional judgment to qualify <u>all</u> positive detects and non-detects in the unspiked sample. The Data Validation Memorandum should include a discussion of the potential impact of laboratory precision on representativeness and usability of the data in meeting the project DQOs.

C. EVALUATION	D. ACTION
*6. Check and recalculate the analytical concentrations and percent recovery for at least one spiked compound per MS/MSD fraction. Verify that the recalculated value agrees within ± 10% of the reported value.	6. 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.
*7. Check and recalculate the RPD for at least one spiked compound per MS/MSD fraction. Verify that the recalculated value agrees within ± 10% of the reported value.	7. 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.
8. Evaluate the appropriateness of qualifying the entire data set based on MS/MSD laboratory precision and method/matrix bias results.	8. Generally, no action is taken based on the MS/MSD data alone to qualify an entire case. The qualification is limited to the unspiked sample associated with the MS/MSD. However, professional judgment may be used to qualify sample results across a particular aqueous matrix (i.e., all associated groundwater samples) or a homogeneous soil matrix.

C. EVALUATION	D. ACTION
9. Evaluate MS/MSD precision data to confirm the laboratory's ability to generate precise data and field duplicate precision data to assess overall precision. Surrogate recovery data can also be evaluated to identify laboratory precision issues and overall matrix precision issues.	9. If precision data for the laboratory MS/MSD pair, surrogate compound recoveries and field duplicate pair indicate a heterogenous matrix at the site or potential sampling error, then the validator may use professional judgment to qualify <u>all</u> affected compounds and/or <u>all</u> field sample results. This problem should be noted in the Data Validation Memorandum and the potential impact on the representativeness and usability of the data in meeting the project DQOs should be discussed. Refer to Section IX for additional guidance.

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

C.6, C.7

Table VOA/SV-VIII-1:

<u>QUALIFICATION OF ORGANIC ANALYTES IN THE UNSPIKED FIELD SAMPLE BASED ON MATRIX SPIKE RECOVERIES AND RPDs</u>

Sample Results	Recovery < 10%	10% ≤ Recovery < Lower QC Limit	Lower QC Limit ≤ Recovery ≤ Upper QC Limit	Recovery > Upper QC Limit	RPD > QC Limit
Detects	J	J	A	J	J
Non-detects	R	UJ	A	A	UJ

** Note that qualification and rejection generally are limited to the spiking compounds, however, the validator may use professional judgment to qualify or reject <u>all</u> positive detects or non-detects in the unspiked sample if the majority of spike compound recoveries and/or RPDs are outside the method QC acceptance criteria.

Table VOA/SV-VIII-2:

QUALIFICATION OF ORGANIC ANALYTES IN THE UNSPIKED FIELD SAMPLE BASED ON MS, MSD, AND UNSPIKED SAMPLE %RSD

Sample Results	%RSD ≤ 50%*	%RSD > 50%*	Two out of three sample results reported as non-detects
Detects	A	J	Professional Judgment
Non-detects	A	Professional Judgment	Professional Judgment

* If a non-detect is reported for a compound in only one of the samples in the MS, MSD or unspiked sample set, then the validator should use the sample quantitation limit value for that compound to calculate the %RSD.

E. EXAMPLES

Example #1: (High MS/MSD RPD for one compound)

Soil QC samples SAA99MS and SAA99MSD, analyzed as medium level soil samples under CLP SOW OLM03.2, have unacceptable RPD results for acenaphthene. Acenaphthene was detected in the unspiked sample, SAA99.

Sample No.	Compound	MS/MSD %Rec	MS/MSD %Rec Criteria	MS/MSD RPD	MS/MSD RPD Criteria
SAA99MS SAA99MSD	Acenaphthene	60/116	31-137	64	19

The validator evaluates the field duplicate pair and determines that the RPDs for all positive detects are less than 50%, indicating acceptable overall precision for this sampling event. The validator then concludes that the lack of laboratory precision in this sample is due to poor laboratory technique. The validator estimates (J) the positive detect for acenaphthene in the unspiked sample, SAA99, on the Data Summary Table. The validator discusses the lack of laboratory precision for one compound, acenaphthene, in the Data Validation Memorandum and notes that laboratory precision for the other semivolatile matrix spike compounds was acceptable.

E. EXAMPLES

Example #2: (Low MS/MSD recoveries for one compound)

Aqueous QC samples SAA22MS and SAA22MSD, analyzed under CLP SOW OLM03.2, have low toluene recovery results but acceptable RPD results. Toluene was detected in the unspiked sample, SAA22. Surrogate compound recoveries were acceptable for SAA22MS, SAA22MSD and the unspiked sample, SAA22.

Sample No.	Compound	MS/MSD %Rec	MS/MSD %Rec Criteria	MS/MSD RPD	MS/MSD RPD Criteria
SAA22MS SAA22MSD	Toluene	50/46	76-125	8	13

The validator evaluates the field duplicate pair and determines that the RPDs for all positive detects are less than 30%, indicating acceptable overall precision for this sampling event. The validator concludes that the sample matrix causes a reproducible negative bias for toluene in aqueous samples SAA22MS and SAA22MSD. The validator estimates (J) the positive detect for toluene in the unspiked sample, SAA22, on the Data Summary Table. The validator discusses the low matrix spike recoveries in the Data Validation Memorandum and notes that recoveries for the other volatile matrix spike compounds were acceptable.

Example #3: (High %RSD; High RPD, poor laboratory precision)

Soil samples SAA55, SAA55MS and SAA55MSD analyzed under CLP SOW OLM03.2, had high RPDs for two of the acid semivolatile matrix spike compounds in the MS/MSD, 2-chlorophenol (53%) and 4-nitrophenol (92%) and two base/neutral semivolatile spike compounds, 1,2,4-trichlorobenzene (65%) and acenaphthene (76%). 2-chlorophenol, 4-nitrophenol, 1,2,4-trichlorobenzene, and acenaphthene were not detected in the unspiked sample. The other remaining matrix spike compound RPDs were acceptable. The following non-spike target compound results were obtained for SAA55MS/MSD and the unspiked sample SAA55.

Sample No.	Compound	MS Conc. Dry Weight (ug/kg)	MSD Conc. Dry Weight (ug/kg)	Unspiked Sample Conc. Dry Weight (ug/kg)	% RSD
SAA55	2,4-Dimethylphenol	1200	350	600	61
SAA55	2,4,6-Trichlorophenol	380	1030	330U	67
SAA55	Hexachlorobenzene	920	330U	400	59

The validator evaluates the field duplicate pair and determines that the RPDs for all positive detects are less than 50%, indicating acceptable overall precision for this sampling event. The validator then concludes that the lack of precision is due to poor laboratory technique. The validator uses professional judgment to estimate (J) the positive detects for 2,4-dimethylphenol and hexachlorobenzene in SAA55 and estimate (UJ) all non-detects in sample SAA55 on the Data Summary Table. The validator discusses the poor laboratory precision and notes the sample qualifications in the Data Validation Memorandum.

E. EXAMPLES

Example #4: (Low MS/MSD recoveries for entire compound class)

Soil QC samples SAA01MS and SAA01MSD, analyzed under CLP SOW OLM03.2, have low spike recoveries for four of the five acid compounds in the matrix spike and the matrix spike duplicate (less than the specified QC acceptance criteria but greater than 10%); while base neutral matrix spike compounds meet QC acceptance criteria. The phenol-d_5 and 2-fluorophenol acid surrogate recoveries are at the low end of the QC acceptance criteria in SAA01MS and SAA01MSD.

Sample No.	Compound	MS % Recovery	MSD % Recovery	RPD	QC Acceptance Criteria	
					% Rec	RPD
SAA01MS/MSD	Phenol	21	21	0	26-90	35
	2-Chlorophenol	15	18	18	25-102	50
	4-Chloro-3-methylphenol	21	20	5	26-103	33
	Pentachlorophenol	14	14	0	17-109	47
	Phenol-d5 (surrogate)	26	28	NA	24-113	NA
	2-Fluorophenol (surrogate)	27	25	NA	25-121	NA

Upon review of the MS/MSD results and surrogate recoveries, the validator notes that the sample matrix causes a reproducible negative bias for acid compounds in soil QC samples SAA01MS and SAA01MSD. The validator reviews the surrogate recoveries for the unspiked sample and notes that the acid surrogate recoveries are within the QC acceptance criteria (at the low end of the QC acceptance range). The validator then reviews the surrogate recoveries for all samples associated with the sample delivery group to ascertain if acid surrogate recoveries are also low in the remaining samples.

Several samples, including the field duplicates, show low acid surrogate recoveries that were greater than 10%. The validator estimates (J) all positive acid detects in the unspiked MS/MSD sample and estimates (UJ) all acid non-detects in the unspiked MS/MSD sample. The validator uses professional judgment to estimate (J) the positive acid detects and estimate (UJ) the acid non-detects in all other samples associated with this sample delivery group in which acid surrogates recovered low. The validator reports qualified data on the Data Summary Table and discusses the low bias in the Data Validation Memorandum.

E. EXAMPLES

Example #5: (High MS/MSD RPDs for multiple compounds)

Aqueous QC samples SAA08MS and SAA08MSD, analyzed under CLP SOW OLM03.2, have high RPDs for 2 acid and 3 base neutral compounds in the matrix spike/matrix spike duplicate pair. The matrix spike recoveries in the MS and MSD were all within QC acceptance criteria. All surrogate recoveries for SAA08MSD were acceptable except for the advisory surrogate, 2-chlorophenol-d_4. All surrogate recoveries for SAA08MS were acceptable except for nitrobenzene-d_5 and terphenyl-d_{14}. Hexachlorobenzene and dibenzofuran were the only positive detects in the unspiked sample, SAA08. The validator calculates the %RSD for hexachlorobenzene (59%) and dibenzofuran (70%).

Sample No.	Compound	MS % Recovery	MSD % Recovery	RPD	QC Acceptance Criteria	
					% Rec	RPD
SAA08MS/MSD	N-Nitroso-di-n-propylamine	43	80	60	41-116	38
	1,2,4-Trichlorobenzene	93	48	64	39-98	28
	2,4-Dinitrotoluene	87	33	90	24-96	38
	Pentachlorophenol	15	78	135	9-103	50
	2-Chlorophenol	96	40	82	27-123	40
	Nitrobenzene-d_5 (surrogate)	25	65	NA	35-114	NA
	2-Chlorophenol-d_4 (surrogate)	70	30	NA	33-110	NA
	Terphenyl-d_{14} (surrogate)	30	83	NA	33-141	NA

Sample No.	Compound	MS Conc. (ug/L)	MSD Conc. (ug/L)	Unspiked Sample Conc. (ug/L)	% RSD
SAA08	Hexachlorobenzene	20	80	85	59
	Dibenzofuran	57	22	110	70

Upon review of the MS/MSD results, surrogate recoveries, and the % RSDs, the validator notes the laboratory imprecision and suspects that problems occurred during extraction and/or analysis of the MS/MSD and/or unspiked sample. The validator then reviews the field duplicate data and surrogate recoveries for the remaining samples in the sample delivery group to assess other precision and bias data.

Surrogate recoveries in all other samples were acceptable. The field duplicate RPD data was also acceptable. Therefore, the validator determines that poor precision was limited to the MS/MSD pair. The validator uses professional judgment to estimate (J) all positive detects and estimate (UJ) all non-detects in the unspiked sample SAA08 on the Data Summary Table. The validator notes this problem in the Data Validation Memorandum.

IX. FIELD DUPLICATES

A. OBJECTIVE

Field duplicates measure the cumulative effects of both field and laboratory precision and hence provide an indication of overall precision. Therefore, field duplicates may have greater variability than laboratory duplicates which measure only laboratory precision. It is also expected that non-aqueous matrices will have a greater variance than aqueous matrices due to the heterogeneity of most non-aqueous samples (such as soil/sediment samples).

B. CRITERIA

1. The frequency of field duplicate analysis must support the site-specific Data Quality Objectives (DQOs) and be documented in the EPA approved QAPjP or SAP.

2. a. The RPD for all compounds detected at concentrations greater than the sample quantitation limit in aqueous matrices must be less than or equal to 30 percent.

   b. The RPD for all compounds detected at concentrations greater than the sample quantitation limit in non-aqueous matrices must be less than or equal to 50 percent.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from field duplicate 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. Identify which samples are field duplicates from the Chain-of-Custody form and/or the Traffic Report.	1. a. If field duplicates are not listed on the Chain-of-Custody form or the Traffic Report, then the validator should contact the sampler to ascertain if field duplicates were collected. If the forms were completed incorrectly or if field duplicates were not collected, then the validator should document this on the Data Validation Worksheet and in the Data Validation Memorandum.
b. Verify that the appropriate number of field duplicates per matrix sampled were collected and analyzed to support project DQOs.	b. If field duplicates were not collected at the required frequency to support project DQOs, then the validator should note the absence of field precision data in the Data Validation Memorandum and discuss how the lack of field precision data might potentially increase uncertainty surrounding site decisions.

C. EVALUATION	D. ACTION
2. Calculate the RPD for all compounds detected at concentrations greater than or equal to the sample quantitation limit in the field duplicate sets.	2. a. If any compound is detected at concentrations greater than or equal to twice the sample quantitation limit in both aqueous field duplicate samples and has an RPD greater than 30%, then the validator should estimate (J) the positive detects for that compound in both samples. If any compound is detected at concentrations greater than or equal to the sample quantitation limit but less than twice the sample quantitation limit in both aqueous field duplicate samples and has an RPD greater than 30%, then the validator should use professional judgment to accept, qualify, or reject the positive detects for that compound in the field duplicate samples taking into consideration the increased variability of data near the sample quantitation limit and the site-specific DQOs. b. If any compound is detected at concentrations greater than or equal to twice the sample quantitation limit in both non-aqueous field duplicate samples and has an RPD greater than 50%, then the validator should estimate (J) the positive detects for that compound in both samples. If any compound is detected at concentrations greater than or equal to the sample quantitation limit but less than twice the sample quantitation limit in both non-aqueous field duplicate samples and has an RPD greater than 50%, then the validator should use professional judgment to accept, qualify, or reject the positive detects for that compound in the field duplicate samples taking into consideration the increased variability of data near the sample quantitation limit and the site-specific DQOs.

C. EVALUATION	D. ACTION
2. Continued from above.	2. c. If any compound in a field duplicate pair has one positive detect that is greater than or equal to twice the sample quantitation limit and a duplicate positive detect that is less than twice the sample quantitation limit, and the RPD exceeds field duplicate precision criteria for that matrix, then the validator should use professional judgment to qualify the positive detects for that compound in the field duplicate samples. d. If any compound in a field duplicate pair has one non-detect and a duplicate positive detect that is greater than or equal to twice the sample quantitation limit, then the validator should estimate (J) the positive detect and (UJ) the non-detect for that compound in the field duplicate samples. (RPDs should not be evaluated for those duplicate pairs.) e. If any compound in a field duplicate pair has one non-detect or a reported value below the sample quantitation limit and a duplicate positive detect that is less than twice the sample quantitation limit, then the validator should use professional judgment to qualify the positive detects and non-detects for that compound in the field duplicate samples taking into consideration the increased variability of data at the sample quantitation limit and the project DQOs. (RPDs should not be evaluated for those duplicate pairs.) f. If any compound in a field duplicate pair has one non-detect or a reported value below the sample quantitation limit and a duplicate positive detect that is less than the sample quantitation limit, then the validator should use professional judgment to qualify the positive detects and non-detects for that compound in the field duplicate sample pair taking into consideration the increased variability of data at the sample quantitation limit and the project DQOs (RPDs should not be evaluated for those duplicate pairs).

C. EVALUATION	D. ACTION
*3. Check and recalculate the analytical concentrations for at least one positive detect and one sample quantitation limit (for a diluted sample or soil sample) for each fraction, in every field duplicate sample, in accordance with Section VOA/SV-XIII, C.1 - C.3.	3. If calculation and/or transcription errors are detected, then the validator should follow the procedures outlined in Section VOA/SV XIII, D.1 - D.3.
4. Evaluate the appropriateness of qualifying the entire data set based on field duplicate results.	4. If field duplicate data indicate poor field precision and general sample heterogeneity and/or possible sampling error, then professional judgment may be used to qualify data for <u>all</u> samples of the same matrix.
5. Evaluate field duplicate precision data to assess overall precision and to verify the field sampler's ability to collect representative duplicate samples. MS/MSD precision data should be evaluated to verify the laboratory's ability to generate precise data. Surrogate recovery data can also be evaluated to identify laboratory precision issues and overall matrix precision issues.	5. If precision data for the field duplicate pair, surrogate compound recoveries and laboratory MS/MSD pair indicate a heterogeneous matrix at the site or potential sampling error, then the validator may use professional judgment to qualify <u>all</u> affected compounds and/or <u>all</u> affected field sample results. This problem should be noted in the Data Validation Memorandum and the potential impact on the representativeness and usability of the data in meeting project DQOs should be discussed. Refer to Section VIII for additional guidance.

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

C.3

Table VOA/SV-IX-1:

<u>QUALIFICATION OF ORGANIC ANALYTES IN FIELD DUPLICATES - SITUATION 1: POSITIVE DETECTS IN BOTH FIELD DUPLICATES</u>

Relative Percent Difference	**Aqueous > 30% Non-Aqueous > 50%**	**Aqueous > 30% Non-Aqueous > 50%**	**Aqueous > 30 Non-Aqueous > 50%**
Sample Results	**Both duplicate sample concs. ≥ 2 X QL**	**QL ≤ both duplicate samples concs. < 2 X QL**	**One sample conc. ≥ 2 X QL QL ≤ Other sample conc. < 2 X QL**
Detects	J	Professional Judgment	Professional Judgment
Non-detects	NA	NA	NA

* QL = Sample Quantitation Limit

Note: Qualification refers to field duplicate sample results only. Professional judgment may be utilized to apply field duplicate actions to all samples of the same matrix.

Table VOA/SV-IX-2:

QUALIFICATION OF ORGANIC ANALYTES IN FIELD DUPLICATES - SITUATION 2: POSITIVE DETECT IN ONLY ONE FIELD DUPLICATE**

Aqueous and Non-Aqueous		
Sample Results	**One Sample Conc. = ND (or value reported as less than the QL) QL ≤ Other Sample Conc. < 2 X QL**	**One sample conc. = ND (or value reported as less than the QL) Other sample conc. ≥ 2 X QL**
Detects	Professional Judgment	J
Non-detects	Professional Judgment	UJ

* QL = Sample Quantitation Limit

** RPD should not be evaluated for these duplicate pairs

Note: Qualification refers to field duplicate sample results only. Professional judgment may be utilized to apply field duplicate actions to all samples of the same matrix.

E. EXAMPLES

Example #1: (Both field duplicate sample concentrations ≥ 2X QL; RPD > 50%; Acceptable laboratory precision)

Soil samples SAA11 and SAA12 are field duplicates, analyzed under CLP SOW OLM03.2, and they contain 89% and 85% solids, respectively. Sample SAA11 has a detected concentration of benzene of 100 ug/kg. Sample SAA12 has a detected concentration of benzene of 250 ug/kg. The validator calculates the Relative Percent Difference (RPD) and determines that the RPD equals 86%. The validator notes that both results are greater than twice the sample Quantitation Limit (QL). The QL for benzene in sample SAA11 is 11 ug/kg and for sample SAA12 is 12 ug/kg. The validator reviews the MS/MSD data and determines that laboratory precision was acceptable. As a result, the validator estimates (J) the positive benzene detects in the field duplicate samples only, on the Data Summary Table, and notes the qualification and justification in the Data Validation Memorandum. The validator also notes that poor field precision may be due to a heterogenous matrix or a result of sampling error.

Compound	SAA11		SAA12		RPD
	Sample Conc. (ug/kg)	Sample QL (ug/kg)	Sample Conc. (ug/kg)	Sample QL (ug/kg)	
benzene	100	11	250	12	86

E. EXAMPLES

Example #2: (QL ≤ both field duplicate sample concentrations < 2X QL; RPD > 50%; Acceptable laboratory precision)

Soil samples SAA21 and SAA22 are field duplicates, analyzed under CLP SOW OLM03.2, and they contain 50% and 52% solids, respectively. Sample SAA21 has a detected concentration of trichlorophenol of 690 ug/kg. Sample SAA22 has a detected concentration of trichlorophenol of 1220 ug/kg. The validator determines that the RPD equals 56%. The sample QL for trichlorophenol in sample SAA21 is 660 ug/kg based on 50% solids and the sample QL for sample SAA22 is 630 ug/kg based on 52% solids. The validator reviews the MS/MSD results and determines that laboratory precision is acceptable. The validator notes that both field duplicate results are between the sample QL and twice the sample QL. As a result, the validator uses professional judgment to accept the trichlorophenol results in the field duplicate samples taking into consideration the increased variability of data near the quantitation limit. The validator notes in the Data Validation Memorandum that field duplicate precision was acceptable.

Compound	SAA21		SAA22		RPD
	Sample Conc. (ug/kg)	Sample QL (ug/kg)	Sample Conc. (ug/kg)	Sample QL (ug/kg)	
trichlorophenol	690	660	1220	630	56

Example #3: (One sample concentration = ND; One sample concentration ≥ 2X QL; Acceptable laboratory precision)

Aqueous samples SAA31 and SAA32 are field duplicates, analyzed under CLP SOW OLM03.2. Sample SAA31 has a detected concentration of trichloroethene of 25 ug/L. Trichloroethene was not detected in sample SAA32. The validator notes that the positive trichloroethene detect in sample SAA31 is greater than twice the sample QL (10 ug/L). The validator reviews the MS/MSD data and determines that laboratory precision was acceptable. The validator estimates (J) the positive trichloroethene detect in sample SAA31 and estimates (UJ) the quantitation limit of the trichloroethene non-detect in sample SAA32 on the Data Summary Table based on poor field precision. The validator notes the qualification in the Data Validation Memorandum and also suggests that poor field precision may be due to sampling error.

Compound	SAA31		SAA32		RPD
	Sample Conc. (ug/L)	Sample QL (ug/L)	Sample Conc. (ug/L)	Sample QL (ug/L)	
trichloroethene	25	10	ND	10	NA

E. EXAMPLES

Example #4: (One sample concentration = ND; One sample concentration < 2X QL; Acceptable laboratory precision)

Soil samples SAA41 and SAA42 are field duplicates, analyzed under CLP SOW OLM03.2, and they contained 90% and 85% solids, respectively. Sample SAA41 has a detected concentration of chlorobenzene of 19 ug/kg. Chlorobenzene was not detected in sample SAA42. The validator notes that the positive chlorobenzene detect is between the sample QL and twice the sample QL. The sample QL for chlorobenzene in sample SAA41 is 11 ug/kg and in sample SAA42 is 12 ug/kg. The validator reviews the MS/MSD results and determines that RPD criteria were met for chlorobenzene, indicating acceptable laboratory precision. As a result, the validator uses professional judgment to accept the positive chlorobenzene detect in sample SAA41 and to accept the chlorobenzene non-detect in sample SAA42, taking into consideration the increased variability of data near the quantitation limit. The validator reports the results on the Data Summary Table and notes this in the Data Validation Memorandum.

Compound	SAA41		SAA42		RPD
	Sample Conc. (ug/kg)	Sample QL (ug/kg)	Sample Conc. (ug/kg)	Sample QL (ug/kg)	
chlorobenzene	19	11	ND	12	NA

Example #5: (Both duplicate concentrations ≥ 2X QL; Poor field and laboratory precision)

Soil samples SAA34 and SAA35 are field duplicates, analyzed under CLP SOW OLM03.2, and they contain 90% and 95% solids, respectively. Sample SAA34 has a detected concentration of pyrene of 1400 ug/kg. Sample SAA35 has a detected concentration of pyrene of 3500 ug/kg. The validator calculates the Relative Percent Difference (RPD) and determines that the RPD equals 86%. The validator notes that both results are greater than twice the sample QL. The sample QL for pyrene in sample SAA34 is 370 ug/kg and the sample QL for pyrene in sample SAA35 is 350 ug/kg. The validator reviews the MS/MSD data for samples SAA34 MS/MSD and determines that the RPD for pyrene equals 61%. The validator is unable to determine the source of the imprecision since both the lab and field precision were poor; therefore, the validator uses professional judgment to estimate (J) the positive pyrene detects in all samples associated with the sample delivery group and estimates (UJ) the quantitation limits for pyrene non-detects in all samples associated with the sample delivery group. The validator reports the qualified data on the Data Summary Table and justifies the qualification in the Data Validation Memorandum. The validator notes that the source of the imprecision cannot be determined.

Compound	SAA34		SAA35		RPD
	Sample Conc. (ug/kg)	Sample QL (ug/kg)	Sample Conc. (ug/kg)	Sample QL (ug/kg)	
pyrene	1400	370	3500	350	86

X. SENSITIVITY CHECK

A. OBJECTIVE

Although most CLP SOWs do not incorporate the analysis of sensitivity checks, many EPA methods do require that a Method Detection Limit (MDL) study be performed prior to sample analysis and/or that a Laboratory Fortified Blank (LFB) be analyzed at the time of sample analysis. The MDL study generates statistically-based detection limits and can be used to assess method sensitivity, laboratory precision and method bias for specific compounds within an analytical method on a specific instrument and column. An LFB, a type of Laboratory Control Sample, is a reagent blank spiked with several or all of the target compounds at or below their quantitation limits. LFB data can be used to assess laboratory sensitivity and bias for specific compounds at the quantitation limit within an analytical method on a specific instrument and column at the time of sample preparation and analysis. To determine sample qualification, the MDL study is evaluated prior to the LFB data.

Region I routinely uses MDL studies as a pre-qualification check to verify the laboratory's ability to meet the technical specification/method requirements prior to contract award and field sample receipt. Region I also routinely includes LFB analyses to document the method sensitivity and bias associated with the day-to-day preparation and analysis of field 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-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile 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 QAPjP/SAP or amendment to the QAPjP/SAP.

1. Method Detection Limit (MDL) Study

a. The method detection limit (MDL) for each compound of interest must be established in accordance with the specified method and the Code of Federal Regulations (40 CFR Part 136, App. B). A minimum of seven replicates must be analyzed for each matrix of interest.

b. Surrogates and internal standards must be spiked into each MDL sample as specified in the method. Internal standard area counts and retention times must meet method QC acceptance criteria. Recoveries and %RSDs for surrogates and target compounds must meet the criteria specified in the method. If the method does not specify recovery and/or replicate %RSD criteria, then the %RSD for the seven replicates should be less than or equal to 25% and the mean recovery for target compounds and surrogates should be between 80-120%.

c. Samples must be analyzed on the same instrument under the same conditions (trap, column, temperature program, amount of sample purged, etc.) as was used for the MDL study.

1. d. The MDL study must be performed within one year prior to the start of the preparation and/or analysis of the samples.

e. The MDL for each compound must be less than or equal to that compound's method-required quantitation limit.

2. Laboratory Fortified Blank (LFB)

a. Verification of laboratory accuracy at the quantitation level requires the routine analysis of an LFB spiked with target compounds at the quantitation limit and, internal standard and surrogate compounds spiked at the concentrations specified in the method. The stock solution used for spiking the LFB must be prepared from a source other than the source used for preparing the initial and continuing calibration standards.

b. One LFB containing all the target compounds at the quantitation limit must be analyzed immediately

prior to sample analysis but after instrument tuning and calibration. Subsequently, an LFB must be analyzed every 12 hours. One LFB must be extracted with each sample delivery group of semivolatile samples, or whenever semivolatile samples are extracted, whichever is more frequent.

c. Method QC acceptance criteria must be met for surrogates, internal standards and target compounds. If the method does not specify recovery QC acceptance criteria for the LFB, then the recovery for target compounds should be between 60-140%. Surrogate compounds and internal standards for the LFB must meet validation criteria as per Sections VI and VII of this document.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
Qualification of data should be based on an combined evaluation of both the MDL study and LFB results. To determine appropriate sample qualification, the MDL study should be evaluated first and then the LFB results.	All potential impacts on the sample data resulting from LFB and/or MDL study 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. Method Detection Limit (MDL) Study	**1. Method Detection Limit (MDL) Study**
a. Verify that the MDL study was generated in accordance with the method and 40 CFR Part 136 App. B, and that a minimum of seven replicates for each matrix of interest were prepared and analyzed.	a. If the required MDL study was not performed at all or was not performed according to the CFR criteria, then the validator should evaluate the LFB data, if available, to determine the action to be taken. See Tables VOA/SV-X-1, VOA/SV-X-2, and VOA/SV-X-3. If no LFB data are available, then the validator should use professional judgment to assess the impact of analytical sensitivity on data quality.
b. Verify that internal standard area counts and retention times meet method QC acceptance criteria.	b. If internal standard area counts and/or retention times do not meet method QC acceptance criteria, then the validator should follow the guidance provided in Section VOA/SV-VII.

C. EVALUATION	D. ACTION
1. c. Compare all seven replicates of the MDL study to verify that the %RSD for each surrogate and target compound is less than or equal to 20%.	1. c. If the MDL target and surrogate compound %RSD criteria are exceeded, then the validator should evaluate initial calibration %RSDs to assess instrument precision and linearity. The validator should use professional judgment to assess the impact of laboratory precision on analytical sensitivity and data quality.
d. Compare all seven replicates of the MDL study to verify that the mean recovery for each target and surrogate compound is within 80-120%.	d. If the mean percent recovery for a target or surrogate compound is greater than 120%, then the validator should: - Use professional judgment to estimate (J) positive detects for that compound in all samples associated with that MDL study, taking into consideration the LFB results. - Accept the non-detects. If the mean percent recovery for a target or surrogate compound is less than 80% but greater than or equal to 10%, then the validator should: - Use professional judgment to estimate (J) positive detects for that compound in all samples associated with that MDL study, taking into consideration the LFB results. - Use professional judgment to estimate (UJ) the non-detects for that compound in all samples associated with that MDL study, taking into consideration the LFB results. If the mean percent recovery for a target or surrogate compound is less than 10%, then the validator should estimate (J) positive detects for that compound and reject (R) the non-detects for that compound in all samples associated with that MDL study.

C. EVALUATION	D. ACTION
*1. e. Check and recalculate the %RSDs and % recoveries for at least three compounds per MDL study. Verify that the recalculated values agree within ± 10% of the reported results.	1. e. 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, 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.
f. Verify that the samples were analyzed on the same instruments and under the same conditions (trap, column, temperature program, amount of sample purged, etc.) as was used for the MDL study.	f. If the samples were not analyzed on the same instruments or under the same conditions as the MDL study, then the validator should contact the laboratory to obtain the correct MDL study. If an acceptable MDL study is unavailable, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should use professional judgment to assess the impact of analytical sensitivity on data quality.
g. Compare the date of the MDL study to the dates of all associated sample analyses to verify that the MDL study was performed within one year of the start of the first sample prepared and/or analyzed in the sample delivery group.	g. If the MDL study was not submitted or was not performed within one year of the start of preparation and/or analysis of the first sample in the SDG, then the validator should contact the laboratory to obtain a current MDL study. If an acceptable MDL study is unavailable, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should evaluate the instrument's response to the lowest standard of the initial calibration and use professional judgment to assess the impact of analytical sensitivity on data quality.

C. EVALUATION	D. ACTION
1. h. Verify that all MDLs are less than or equal to the method-required quantitation limits. If the LFB criteria are not met, then laboratory performance related to method bias and method/instrument sensitivity is questionable.	1. h. If the MDL study reveals that a target compound has a detection limit greater than the method-required quantitation limit, then the validator should evaluate the LFB data. If no LFB data are available, then the validator should: i. Elevate the quantitation limit for that target compound in all samples associated with that MDL study to the lowest concentration calibration standard analyzed or to the laboratory-reported MDL, whichever is higher. ii. Estimate (J) positive detects which were below the elevated quantitation limit for that target compound in all samples associated with that MDL study.
2. Laboratory Fortified Blank (LFB)	**2. Laboratory Fortified Blank (LFB)**
* a. Check the standards preparation logs to verify that the stock standard used to prepare the LFB was from a source independent from the initial and continuing calibration standards.	a. If the LFB was not prepared from a source independent from the initial and continuing calibration standards, then the laboratory performance related to method bias and method/instrument sensitivity is questionable. The validator should review other calibration verification checks, i.e., PES analyses to ensure calibration accuracy. Professional judgment should be used to qualify sample quantitation limits.
b. Verify that an LFB was prepared and/or analyzed at the correct frequency and that it was spiked with the correct compounds at their quantitation limits.	b. If an LFB analysis was not performed or the LFB was not analyzed for the correct compounds at the proper frequency and concentration, then the validator should use professional judgment to assess the impact of analytical sensitivity on data quality.
c. Verify that the reported recoveries for all LFB spike compounds are within the method QC acceptance criteria.	c. Sample data should be qualified based on the number and type of compounds that recover outside the method QC acceptance criteria and based on the degree that compound recoveries exceed the criteria.

C. EVALUATION	D. ACTION
2. c. Continued from above.	2. c. i. If any of the LFB compound recoveries are outside the method QC acceptance criteria, then the LFB results should be used to qualify sample data for the specific compounds that are included in the LFB solution. The validator should use professional judgment to qualify sample data for non-LFB compounds, taking into account the compound's chemical class, compound recovery efficiency, and any analytical problems historically associated with the compound or that were encountered by the laboratory. ii. If an LFB compound recovery is greater than 140%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that LFB to indicate potential high bias. - Accept the quantitation limit of the affected compound in any sample associated with that LFB. iii. If more than half of the LFB compound recoveries are greater than 140%, then the validator should: - Estimate (J) all positive detects in all samples associated with that LFB to indicate potential high bias. - Accept all quantitation limits for non-detects in all samples associated with that LFB. iv. If an LFB compound recovery is less than 60% but greater than or equal to 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that LFB to indicate potential low bias. - Estimate (UJ) the quantitation limit of the affected compound in any sample associated with that LFB to indicate potential low bias.

C. EVALUATION	D. ACTION
2. c. Continued from above.	2. c. v. If more than half of the LFB compound recoveries are less than 60% but greater than or equal to 10%, then the validator should: - Estimate (J) all positive detects in all samples associated with that LFB to indicate potential low bias. - Estimate (UJ) all quantitation limits for non-detects in all samples associated with that LFB to indicate potential low bias. vi. If an LFB compound recovery is less than 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that LFB to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any samples associated with that LFB to indicate that the data are unusable due to the possibility of false negatives. vii. If more than half of the LFB compound recoveries are less than 10%, then the validator should: - Estimate (J) all positive detects in all samples associated with that LFB to indicate potential low bias. - Reject (R) the quantitation limits for all non-detects in all samples associated with that LFB to indicate that the data are unusable due to the possibility of false negatives.

C. EVALUATION	D. ACTION
2. c. Continued from above.	2. c. viii. If more than half of the LFB compound recoveries are outside the method QC acceptance limits in one LFB, where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular compound, class of compounds or the entire fraction for samples associated with that LFB. ix. Action on non-compliant surrogate recoveries should follow the guidance provided in Section VOA/SV-VI. Professional judgment should be used to evaluate the impact that a non-compliant LFB surrogate recovery has on the sample data. x. Action on non-compliant internal standard areas should follow the guidance provided in Section VII. Professional judgment should be used to evaluate the impact that non-compliant LFB internal standard areas have on the sample data.
* d. Check and recalculate the % recovery for at least one compound per LFB fraction. Verify that the recalculated value agrees within ± 10% of the reported result.	d. 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.

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

C.1.e, C.2.a, C.2.d

Table VOA/SV-X-1:

QUALIFICATION OF ORGANIC ANALYTES BASED ON MDL STUDY RESULTS

Sample Results	Mean % Recovery			
	%Rec < 10%	10% ≤ %Rec < 80%	80% ≤ %Rec ≤ 120%	%Rec > 120%
Detects	J	Professional Judgment*	A	Professional Judgment*
Non-Detects	R	Professional Judgment*	A	A
Sample Results	**% RSD**			
	> 25%		≤ 25%	
Detects	Professional Judgment**		A	
Non-detects	Professional Judgment**		A	

* Taking into consideration LFB results.
** Taking into consideration initial calibration %RSDs.

Table VOA/SV-X-2:

QUALIFICATION OF ORGANIC ANALYTES BASED ON LFB* RECOVERIES WHERE: ≤ ONE-HALF OF LFB COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS

Sample Results	%Recovery			
	%Rec < 10%	10% ≤ %Rec < 60%	60% ≤ %Rec ≤ 140%	%Rec > 140%
Detects	J	J	A	J
Non-detects	R	UJ	A	A

* LFB = Laboratory fortified blank spiked with several or all of the method target compounds at or below the quantitation limit.

Table VOA/SV-X-3:

QUALIFICATION OF ORGANIC ANALYTES BASED ON LFB* RECOVERIES WHERE: > ONE-HALF OF LFB COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS**

Sample Results	%Recovery			
	%Rec < 10%	10% ≤ %Rec < 60%	60% ≤ %Rec ≤ 140%	%Rec > 140%
All Detects	J	J	A	J
All Non-detects	R	UJ	A	A

* LFB = Laboratory fortified blank spiked with several or all of the method target compounds at or below the quantitation limit.

** Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

E. EXAMPLES

Example #1: (Low LFB recoveries for several compounds)

Low concentration water samples were analyzed under CLP SOW OLC02.1 and, therefore, no MDL study was required. LFB compounds, benzene, carbon tetrachloride, and trichloroethene recovered below QC acceptance criteria but greater than 10%, (22%, 40%, and 38%, respectively). The validator estimates (J) the positive benzene, carbon tetrachloride, and trichloroethene detects in all the field samples associated with the LFB to indicate potential low bias and estimates (UJ) the quantitation limits for the benzene, carbon tetrachloride, and trichloroethene non-detects in all the field samples associated with the LFB to indicate a decrease in sensitivity and the possibility of false negatives. The validator reports the qualified results on the Data Summary Table and notes this in the Data Validation Memorandum.

Example #2: (High LFB recoveries for two compounds; Low internal standard area counts)

Low concentration water samples were analyzed under CLP SOW OLC02.1 and, therefore, no MDL study was required. LFB compounds 1,2-dichloropropane and tetrachloroethene recovered outside the upper QC acceptance criteria (160% and 200%, respectively). The IS area for chlorobenzene-d5, in the LFB sample and in all field samples associated with the LFB, was reported below the QC acceptance criteria but greater than 20% of the continuing calibration IS response. Since all analytes associated with the IS chlorobenzene-d5 were estimated (J or UJ indicating a potential high bias) previously in all affected samples due to the low IS area counts, the validator notes the high LFB recoveries in the Data Validation Memorandum but takes no additional action on the Data Summary Table.

Example #3: (Low MDL recoveries for LFB compounds; Acceptable LFB results)

The analytical method used for sample analysis did not specify QC acceptance criteria for the MDL study. The validator uses the default criteria for mean % recoveries (80-120%) and %RSDs to evaluate the MDL data. The MDL study submitted by the laboratory did not meet the default MDL recovery criteria for styrene and vinyl chloride (55% and 32%, respectively). The validator examines the LFB data submitted with the field sample results and determines that all LFB method QC acceptance criteria were met including styrene and vinyl chloride. The validator accepts the field sample data based on the acceptable LFB results and notes the low MDL recoveries in the Data Validation Memorandum.

E. EXAMPLES

Example #4: (High LFB recoveries for two compounds; High MDL %RSDs for two compounds)

The analytical method used for sample analysis did not specify QC acceptance criteria for the MDL study. The validator uses the default criteria for mean % recoveries (80-120%) and % RSDs to evaluate the MDL data. The MDL study submitted by the laboratory did not meet default (25%) %RSD criteria for benzene and ethylbenzene (34% and 36%, respectively). The validator reviews the initial calibration %RSDs and determines that benzene and ethylbenzene met the initial calibration %RSD acceptance criteria. In addition, the analytical method used did not specify QC acceptance criteria for the LFB. The validator uses the default recovery criteria of 60-140% to evaluate LFB results. The validator examines the LFB submitted with the analytical results and determines that benzene and ethylbenzene also exceeded the LFB % recovery criteria of 140% (164% and 170%, respectively). Since the initial calibration %RSDs were acceptable, the high MDL %RSDs were not utilized to qualify sample data. Based upon the LFB recoveries, the validator uses professional judgment to estimate (J) the positive benzene and ethylbenzene detects to indicate potential high bias for these two compounds and accept the quantitation limits for benzene and ethylbenzene non-detects in all field samples associated with the LFB. The validator reports the qualified results on the Data Summary Table and notes the sample qualifications in the Data Validation Memorandum.

XI. PERFORMANCE EVALUATION SAMPLES/ACCURACY CHECK

A. OBJECTIVE

Data for Performance Evaluation Samples (PESs) are generated to provide information on the overall accuracy and bias of the analytical method and on laboratory performance. PESs are evaluated for false negatives, false positives, and inaccurate target compound quantitation. In general, the most serious problem a PES can expose is the failure of the laboratory to properly detect and identify a PES compound. This failure is known as a false negative. False negatives significantly increase the "uncertainty" surrounding any site decisions made concerning the "cleanliness" or contamination present at a site. A second problem revealed by PES analysis is the laboratory' s erroneous detection of target and non-target compounds that were not spiked into the PES, otherwise known as false positives. False positives should always be evaluated in conjunction with blank data to ascertain the probable source(s) of contamination.
Finally, the PES provides information on the magnitude and direction of quantitative bias for the entire laboratory method, including sample preparation (extraction and cleanup) and analysis (chromatography and calibration). Sample data that are biased high or low can potentially impact site decisions, especially when sample data have target compound concentrations at or near project action levels.

Ideally, a PES is comprised of the same matrix as the field samples being evaluated. However, for many matrices (i.e., soil) PESs are not available. In these situations, a PES of another matrix (i.e., water) may be analyzed with the field samples to assess laboratory performance on the "analysis" portion, even though laboratory performance on the "sample preparation" portion cannot be assessed. The validator should use professional judgment when evaluating samples of one matrix using PES data from another matrix.

B. CRITERIA

1. Zero Blind Performance Evaluation Samples

A Zero Blind PES is a quality control sample that is of a composition and concentration known to the laboratory.

A Laboratory Control Sample (LCS) is a Zero Blind PES which is often used by the laboratory as an internal quality control check of analytical accuracy and method bias.

An LCS containing several or all of the target compounds spiked at concentrations at or below their quantitation limits is called a Laboratory Fortified Blank (LFB). Refer to Section X for additional LFB guidance.

a. An LCS is required by some EPA methods and certain CLP SOWs. The frequency, concentration, acceptance criteria and corrective actions for LCS analysis should be stated in the method, Sampling and Analysis Plan (SAP) or the Quality Assurance Project Plan (QAPjP) and should support the DQOs of the project. The LCS should be prepared in the proper matrix for each parameter at the concentration level and frequency required in the EPA-approved project SAP, QAPjP, and/or method. The LCS must contain one or more target compounds. The LCS must be prepared and analyzed concurrently with field samples contained in the sample delivery group.

1. b. The percent recoveries for LCS compounds must be within the method QC acceptance criteria.

c. Surrogate compounds and internal standards for the LCS must meet validation criteria as per Sections VI and VII of this document.

2. Single Blind Performance Evaluation Samples

A Single Blind PES is a quality control sample that is of a composition and concentration not known to the laboratory, but the sample is identified to the laboratory as a PES.

A Single Blind PES may be submitted with a sample delivery group to assess method bias, laboratory performance and to evaluate data quality. A Single Blind PES may also be submitted for analysis prior to sample shipment to prequalify a laboratory for a specific matrix and/or parameter.

a. The latest revision of the EPA Region I Performance Evaluation Program Guidance, requires that a Single Blind or Double Blind PES be sent with each sample delivery group (20 samples or less) that is sent to a laboratory. A PES is required for each matrix, parameter, and concentration level unless an EPA or non-EPA PES does not currently exist for that particular matrix, parameter, or concentration level.

The PE Program applies to the Superfund program including EPA Fund-lead and PRP/Federal Facility Oversight Projects. In addition, the PE Program applies to Fund-lead projects performed by States under Cooperative Agreements and other Federal Agencies under Interagency Agreements. The PE Program also applies to Non-Fund-
lead Superfund projects undertaken by potentially responsible parties. The PE Program also applies to Non-Superfund Programs.

EPA-provided PE samples are available for certain categories of Superfund work as specified in the latest revision of the EPA Region I Performance Evaluation Program Guidance. The EPA Performance Evaluation Chemist provides the current list of EPA-provided PE samples upon request. For those categories of Superfund work that do not have access to EPA-provided PE samples and for all Non-Superfund program work scientifically defensible PE samples should be obtained from commercial vendors.

b. Acceptance criteria for EPA PESs are statistically-derived by the Analytical Operations Center under the QATS contract. Tabulated report forms for EPA PESs must be submitted to the Region I OEME-QA Unit for scoring at the time of data validation, in accordance with the latest revision of the EPA Region I Performance Evaluation Program Guidance.

c. True values and QC acceptance criteria for all non-EPA PESs should be provided by the manufacturer and these acceptance criteria must be fully documented and must be scientifically defensible.

d. Surrogate compounds and internal standards for EPA and non-EPA Single Blind PE samples must meet validation criteria as per Sections VI and VII of this document.

3. Double Blind Performance Evaluation Samples

A Double Blind PES is a quality control sample that is of a composition and concentration not known to the laboratory and the sample is **not** identifiable as a PES nor is it identified to the laboratory as a PES.

A Double Blind PES may be submitted with a sample delivery group, in lieu of a Single Blind PES, to assess method bias, laboratory performance and to evaluate data quality.

a. The use of Double Blind PESs is dictated by the project DQOs and should be documented in the EPA-approved SAP and/or QAPjP.

b. True values and acceptance criteria for Double Blind PESs must be fully documented and must be scientifically defensible.

c. Surrogate compounds and internal standards for EPA and non-EPA Double Blind PE samples must meet validation criteria as per Sections VI and VII of this document.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from performance evaluation sample 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. Zero Blind PES - LCS	**1. Zero Blind PES - LCS**
a. Verify that an appropriate LCS sample (correct parameter, concentration level, target compounds and matrix) was prepared and analyzed at the required frequency for each sample delivery group in accordance with the EPA approved project SAP, QAPjP and/or method.	a. If an appropriate LCS was not analyzed at the required frequency for the correct parameters, concentration levels, target compounds or matrices, then the validator should use professional judgment to determine if the sample data should be qualified or rejected.
b. Verify that the required LCS results are provided for each sample delivery group.	b. If the required LCS results were not submitted for each sample delivery group, then the validator should contact the laboratory to obtain raw data and tabulated results.

C. EVALUATION	D. ACTION
1. c. Verify that the reported recoveries for all LCS spike compounds are within the method QC acceptance criteria.	1. c. Sample data should be qualified based on the number and type of compounds that recover outside the method QC acceptance criteria and based on the degree that compound recoveries exceed the criteria. i. If any of the LCS compound recoveries are outside the method QC acceptance criteria, then the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution. Professional judgment should be used to qualify sample data for non-LCS compounds, taking into account the compound's chemical class, compound recovery efficiency, and any analytical problems historically associated with the compound or that were encountered by the laboratory. ii. If an LCS compound recovery is greater than the upper limit of the method QC acceptance criteria, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that LCS to indicate potential high bias. - Accept the quantitation limit of the affected compound in any sample associated with that LCS. iii. If more than half of the LCS compound recoveries are greater than the upper limit of the method QC acceptance criteria, then the validator should: - Estimate (J) <u>all</u> positive detects in all samples associated with that LCS to indicate potential high bias. - Accept <u>all</u> quantitation limits for non-detects in all samples associated with that LCS.

C. EVALUATION	D. ACTION
1. c. Continued from above.	1. c. iv. If an LCS compound recovery is less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that LCS to indicate potential low bias. - Estimate (UJ) the quantitation limit of the affected compound in any sample associated with that LCS to indicate potential low bias. v. If more than half of the LCS compound recoveries are less than the lower limit of the method QC acceptance criteria but greater than or equal to 10%, then the validator should: - Estimate (J) all positive detects in all samples associated with that LCS to indicate potential low bias. - Estimate (UJ) all quantitation limits for non-detects in all samples associated with that LCS to indicate potential low bias. vi. If an LCS compound recovery is less than 10%, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that LCS to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any sample associated with that LCS to indicate that the data are unusable due to the possibility of false negatives.

C. EVALUATION	D. ACTION
1. c. Continued from above.	1. c. vii. If more than half of the LCS compound recoveries are less than 10%, then the validator should: - Estimate (J) <u>all</u> positive detects in all samples associated with that LCS to indicate potential low bias. - Reject (R) the quantitation limits for <u>all</u> non-detects in all samples associated with that LCS to indicate that the data are unusable due to the possibility of false negatives.
	viii. If more than half of the LCS compound recoveries are outside the method QC acceptance limits in one LCS, where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular compound, class of compounds or the entire fraction for samples associated with that LCS.
	ix. Based upon the number and type of compounds misquantified and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.
d. Evaluate surrogate compounds and internal standards for the LCS.	d. Action on non-compliant surrogate recoveries and internal standard area counts should follow the guidance provided in Sections VI and VII, respectively. Professional judgment should be used to evaluate the impact that non-compliant LCS surrogate recoveries and/or internal standard area counts have on the sample data.

C. EVALUATION	D. ACTION
*1. e. Check and recalculate the percent recovery for at least one compound per LCS fraction. Verify that the recalculated value agrees within ± 10% of the reported result.	1. e. 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.
2. Single Blind and Double Blind PESs a. Verify that an appropriate Single Blind or Double Blind PES (correct parameter, concentration level, target compounds and matrix) was analyzed at the required frequency for each sample delivery group in accordance with Region I PE policy and/or the EPA approved SAP and/or QAPjP. b. Verify that Single Blind PES results are provided for each sample delivery group in accordance with Region I PE policy.	**2. Single Blind and Double Blind PESs** a. If a required Single Blind or Double Blind PES was not analyzed at the required frequency for the correct parameters, concentration levels, target compounds or matrices, then the validator should use professional judgment to determine if the sample data should be qualified or rejected. b. If the PES results were not submitted for each sample delivery group, then the validator should contact the laboratory to obtain raw data and/or tabulated results. If a PES was not submitted to the laboratory by the sampler, then the validator should contact the sampler to confirm the omission of a PES and document that fact on the worksheet and in the Data Validation Memorandum.

C. EVALUATION	D. ACTION
2. c. **EPA PESs:** If the PES was supplied and scored by Region I OEME-QA, then the Region I PES Score Report must be evaluated to determine how many of the analytes met or exceeded PES acceptance criteria.	2. c. **Region I EPA PESs** Note: PES results should not be qualified based on QC sample data and should not be reported on the Data Summary Table. Rather, PES results should be discussed in the Data Validation Memorandum or Tier I Validation Cover Letter and PES Score Reports should be attached as supporting documentation.
• Evaluate the "TCL MISSES" to assess the potential for low bias and false negative sample results.	• Sample data should be qualified based on the number and type of "TCL MISSES" identified on the Region I PES Score Report. i. If a PES compound is not identified in the PES, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that PES to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives. ii. Based upon the chemical class, the number of compounds that were not identified, and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.
• Evaluate the "TCL CONTAMINANTS" and "TIC CONTAMINANTS" in conjunction with blank data to assess the potential for high bias and false positive sample results.	• Sample data should not be qualified based on the number and type of "TCL CONTAMINANTS" and "TIC CONTAMINANTS" identified on the Region I PES Score Report alone. i. If a TCL or TIC contaminant is detected in the PES and is also found in a blank, then the validator should evaluate and qualify sample data based upon blank contamination in accordance with Section V. ii. If a TCL or TIC contaminant is detected in the PES but is not present in any blank, then that interference is specific to the PES and does not impact sample data.

C. EVALUATION	D. ACTION
2. c. Continued from above. • Evaluate the "TCL HITS" that were misquantified to assess the potential for high and/or low bias in sample data.	2. c. Continued from above. • Sample data should be qualified based on the number and type of misquantified compounds (Action High/Action Low "TCL HITS") identified on the Region I PES Score Report. **Sample data should not be qualified based on "Warning Low/Warning High" scores for "TCL HITS".** i. If any of the PES compounds do not meet PES acceptance criteria, then the PES results should be used to qualify sample data for the specific compounds that are included in the PES sample. Professional judgment should be used to qualify sample data for non-PES compounds taking into account the compound's chemical class, compound recovery efficiency, and analytical problems historically associated with the compound or that were encountered by the laboratory. ii. If a PES compound is scored in the "Action High" category, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that PES to indicate potential high bias. - Accept the quantitation limit of the affected compound in any sample associated with that PES. iii. If more than half of the PES compounds are scored in the "Action High" category, then the validator should: - Estimate (J) all positive detects in all samples associated with that PES to indicate potential high bias. - Accept all quantitation limits for non-detects in all samples associated with that PES.

C. EVALUATION	D. ACTION
2. c. Continued from above.	2. c. iv. If a PES compound is scored in the "Action Low" category, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that PES to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives. v. If more than half of the PES compounds are scored in the "Action Low" category, then the validator should: - Estimate (J) all positive detects in all samples associated with that PES to indicate potential low bias. - Reject (R) the quantitation limits for all non-detects in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives. vi. If more than half of the PES compounds are scored in the "Action" levels in one PES, where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular compound, class of compounds or the entire fraction for samples associated with that PES. vii. Based upon the number and type of compounds misquantified and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.

C. EVALUATION	D. ACTION
2. c. Continued from above.	2. c. Continued from above.
• Evaluate "TIC HITS" and "TIC MISSES".	• Sample data should be qualified based on the number and type of "TIC HITS" and "TIC MISSES" identified on the Region I PES Score Report. i. If TIC identifications are required by the method, then the validator should use professional judgment to qualify the sample data based upon entries in the "TIC HITS" and "TIC MISSES" categories.
• Evaluate surrogate compounds and internal standards for the EPA PES.	• Action on non-compliant surrogate recoveries and internal standard area counts should follow the guidance provided in Sections VI and VII, respectively. Professional judgment should be used to evaluate the impact that non-compliant EPA PES surrogate recoveries and/or internal standard area counts have on the sample data.
d. **Non-EPA PESs** If the PES was obtained from a source other than Region I OEME-QA, then the validator should use the vendor's criteria to evaluate the PES results. Confirm that PES acceptance criteria are fully documented and scientifically defensible.	d. **Non-EPA PESs** If the non-EPA PES acceptance criteria are not fully documented and/or scientifically defensible, then the validator should use professional judgment to qualify or reject the sample data.
• Evaluate the "PES COMPOUND MISSES" to assess the potential for low bias and false negative sample results.	• Sample data should be qualified based on the number and type of "PES COMPOUND MISSES" identified from the vendor's acceptance criteria. i. If a PES compound is not identified in the PES, then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that PES to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives.

C. EVALUATION	D. ACTION
2. d. Continued from above.	2. d. Continued from above. ii. Based upon the chemical class, the number of compounds that were not identified, and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.
• Evaluate the "PES COMPOUND CONTAMINANTS" in conjunction with blank data to assess the potential for high bias and false positive sample results.	• Sample data should not be qualified based on the number and type of "PES COMPOUND CONTAMINANTS" identified from the vendor's acceptance criteria alone. i. If a PES COMPOUND CONTAMINANT is detected in the PES and is also found in a blank, then the validator should evaluate and qualify sample data based upon blank contamination in accordance with Section V. ii. If a PES COMPOUND CONTAMINANT is detected in the PES but is not present in any blank, then that interference is specific to the PES and does not impact sample data.
• Evaluate the "PES COMPOUND HITS" that were misquantified to assess the potential for high and/or low bias in sample results.	• Sample data should be qualified based on the number and type of misquantified "PES COMPOUND HITS" identified from the vendor's acceptance criteria. i. If any of the PES compounds do not meet acceptance criteria, then the validator should use the PES results to qualify sample data for the specific compounds that are included in the PES sample. Professional judgment should be used to qualify sample data for non-PES compounds, taking into account the compound's chemical class, compound recovery efficiency, and analytical problems associated with the compound either historically or that were encountered by the laboratory.

C. EVALUATION	D. ACTION
2. d. Continued from above.	2. d. Continued from above. ii. If a PES compound recovery is outside the upper limit of the vendor's documented acceptance limits (Note: The validator should confirm that the vendor's acceptance limits are calculated as plus and minus three standard deviations from the mean, similar to EPA-PES "Action Limits".), then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that PES to indicate potential high bias. - Accept the quantitation limit of the affected compound in any sample associated with that PES. iii. If more than half of the PES compound recoveries are outside the upper limit of the vendor's documented acceptance limits (See note above, Section 2.d.ii), then the validator should: - Estimate (J) all positive detects in all samples associated with that PES to indicate potential high bias. - Accept all quantitation limits for non-detects in all samples associated with that PES. iv. If a PES compound recovery is outside the lower limit of the vendor's documented acceptance limits (See note above, Section 2.d.ii), then the validator should: - Estimate (J) the affected compound when detected in any sample associated with that PES to indicate potential low bias. - Reject (R) the quantitation limit of the affected compound in any sample associated with that PES to indicate that the data are unusable due to the possibility of false negatives.

C. EVALUATION	D. ACTION
2. d. Continued from above.	2. d. Continued from above. v. If more than half of the PES compound recoveries are outside the lower limit of the vendor's documented acceptance limits (See note above, Section 2.d.ii), then the validator should: - Estimate (J) all positive detects in all samples associated with that PES to indicate potential low bias. - Reject (R) the quantitation limits for all non-detects in all samples associated with that PES to indicate that the data are unusable due to the possibility of false negatives. vi. If more than half of the PES compound recoveries are outside the vendor's documented acceptance limits in one PES (See note above, Section 2.d.ii), where some recoveries are low and some recoveries are high, then the validator should use professional judgment to qualify or reject a particular compound, class of compounds or the entire fraction for samples associated with that PES. vii. Based upon the number and type of compounds misquantified and a review of the project DQOs, the validator should use professional judgment to determine if the data set for an entire fraction or parameter is unusable and, therefore, should be rejected. Rejected data should be returned to the laboratory and payment denied.
• Evaluate surrogate compounds and internal standards for the non-EPA PES.	• Action on non-compliant surrogate recoveries and internal standard area counts should follow the guidance provided in Sections VI and VII, respectively. Professional judgment should be used to evaluate the impact that non-compliant non-EPA PES surrogate recoveries and/or internal standard area counts have on the sample data.

C. EVALUATION	D. ACTION
*2. e. Determine what percentage of PES analytes were below or above PES acceptance criteria.	2. e. If more than half of the PES compounds are high or low, then the validator should check the raw data and/or contact the laboratory to verify that the PE sample was prepared according to the PE instructions (if applicable). Check also that the appropriate PE instructions (for that PE concentration level) were sent to the laboratory.
* f. Check and recalculate the analytical concentrations for at least one compound per PES fraction. Verify that the recalculated value agrees within ± 10% of the reported result.	f. 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. i. If corrected data reports affect the original results reported on the initial EPA PES score report, then the validator should resubmit the corrected PES results to Region I OEME-QA for a PES rescore. Sample data should be reevaluated and requalified based on the corrected PES data. ii. If corrected data reports affect the original results reported for the initial non-EPA PES, then the validator should reevaluate and requalify sample data based on the corrected PES data.

* **Note: The following subsections are applicable only to a Tier III data validation: C.1.e, C.2.e, C.2.f**

Table VOA/SV-XI-1:

QUALIFICATION OF INDIVIDUAL ORGANIC ANALYTES BASED ON LCS RECOVERIES WHERE: ≤ ONE-HALF OF LCS COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS

Sample Results	% Recovery			
	%Rec < 10%	10% ≤ %Rec < LL	LL ≤ %Rec ≤ UL	%Rec > UL
Detects	J	J	A	J
Non-detects	R	UJ	A	A

LL - Lower Limit of method QC acceptance criteria
UL - Upper Limit of method QC acceptance criteria

Table V/SV-XI-2:

QUALIFICATION OF ORGANIC ANALYTES BASED ON LCS RECOVERIES WHERE: > ONE-HALF OF LCS COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS*

Sample Results	% Recovery			
	%Rec < 10%	10% ≤ %Rec < LL	LL ≤ %Rec ≤ UL	%Rec > UL
All Detects	J	J	A	J
All Non-detects	R	UJ	A	A

* Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

LL - Lower Limit of method QC acceptance criteria
UL - Upper Limit of method QC acceptance criteria

Table VOA/SV-XI-3:

QUALIFICATION OF INDIVIDUAL ORGANIC ANALYTES BASED ON PES RESULTS WHERE: ≤ ONE-HALF OF PES COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS

Sample Results	•Single Blind •Double Blind PES < Lower Limit "Action Low"	•Single Blind •Double Blind PES "Within Warning Limits" "Warning High/Warning Low"	•Single Blind •Double Blind PES > Upper Limit "Action High"
Detects	J	A	J
Non-Detects	R	A	A

Table VOA/SV-XI-4:

QUALIFICATION OF ORGANIC ANALYTES BASED ON PES RESULTS WHERE: > ONE-HALF OF PES COMPOUNDS OUTSIDE UPPER OR LOWER ACCEPTANCE LIMITS *

Sample Results	•Single Blind •Double Blind PES < Lower Limit "Action Low"	•Single Blind •Double Blind PES "Within Warning Limits" "Warning High/Warning Low"	•Single Blind •Double Blind PES > Upper Limit "Action High"
All Detects	J	A	J
All Non-Detects	R	A	A

* Professional judgment should be used when a combination of low recoveries and high recoveries are obtained.

E. EXAMPLES

Example #1: (One LCS compound < lower limit; One LCS compound > upper PES acceptance limit)

A Laboratory Control Sample (LCS) containing 10 compounds spiked at three times the quantitation limit is found to have chlorobenzene with a % recovery of 150% and vinyl chloride with a % recovery of 50%. The method QC acceptance criteria for LCS compound recoveries are 60-140%. This amounts to less than one-half of the spike LCS compounds being outside the LCS acceptance criteria. The validator estimates (J) positive detects for chlorobenzene and vinyl chloride in all field samples associated with that LCS. The validator accepts the chlorobenzene non-detects and estimates (UJ) the vinyl chloride non-detects in all field samples associated with that LCS. The validator reports qualified data on the Data Summary Table and notes that the chlorobenzene positive detects are biased high, the vinyl chloride positive detects are biased low and the vinyl chloride non-detects contain possible false negatives in the Data Validation Memorandum.

Example #2: (One Single Blind PES compound < lower PES acceptance limit)

A Single Blind Performance Evaluation Sample (PES) is found to have a chloroethane positive result that scored below the lower PES acceptance limit. The validator determines that less than one-half of the spike PES compounds are outside the PES acceptance criteria. Therefore, the validator estimates (J) positive chloroethane detects and rejects (R) the quantitation limits for chloroethane non-detects in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and notes that the positive chloroethane detects are biased low and chloroethane non-detects are rejected due to the possibility of false negatives in the Data Validation Memorandum.

Example #3: (More than one-half of PES compounds greater than upper PES acceptance limits)

A Single Blind PES is found to have more than one-half of the spike volatile PES compounds with % recoveries above the upper PES acceptance limits. The validator estimates (J) all positive detects in all field samples associated with that PES and accepts (A) all quantitation limits for non-detects in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and notes the positive volatile results are biased high in the Data Validation Memorandum.

Example #4: (More than one-half of PES compounds "Action High" or "Action Low")

A Single Blind PES is found to have more than one-half of the spike semivolatile PES compounds with results that do not meet PES acceptance criteria. Some of the PES compounds are flagged "Action Low" and some flagged "Action High". The site DQOs are to determine whether cleanup levels were achieved. The validator determines that analytical error yields uncertainty in quantitative accuracy which may adversely affect site decisions. Therefore, the validator uses professional judgment to estimate (J) all positive detects in all field samples associated with that PES and reject (R) all quantitation limits in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and discusses the limited use of the data in the Data Validation Memorandum.

E. EXAMPLES

Example #5: (One "TCL MISS")

A Single Blind PES is found to have one "TCL MISS" for vinyl chloride which is a contaminant of concern at the site. The validator estimates (J) all positive vinyl chloride detects and rejects (R) all vinyl chloride quantitation limits in all field samples associated with that PES. The validator reports qualified data on the Data Summary Table and discusses this in the Data Validation Memorandum.

Example #6: (One "TCL Contaminant", also in blank)

A Single Blind PES is found to have one "TCL Contaminant", 1,2-dichloroethane, at 45 ppb. The method blank contained 6 ppb of 1,2-dichloroethane, resulting in a Blank Action Level of 30 ppb. The validator uses the 1,2-dichloroethane Blank Action Level to evaluate the sample data and reports qualified data on the Data Summary Table. The validator suspects that the 1,2-dichloroethane false positive PES compound is a result of laboratory contamination and discusses this in the Data Validation Memorandum. PES results are not reported on the Data Summary Table.

Example #7: (One "TCL Contaminant", not in blank)

A Single Blind PES is found to have one "TCL Contaminant", 2-chlorophenol, which is not detected in any of the blanks but is detected in two samples. The validator determines that the 2-chlorophenol is an interference specific to the PES because it was not detected in any of the method, instrument, or storage blanks. The validator uses professional judgment to accept the positive 2-chlorophenol detects in the field samples. The validator reports the data unqualified on the Data Summary Table and discusses this in the Data Validation Memorandum.

XII. TARGET COMPOUND IDENTIFICATION

A. OBJECTIVE

Qualitative criteria for compound identification have been established to minimize the number of erroneous compound identifications. An erroneous identification can be either a false positive (reporting a compound that is not present) or a false negative (not reporting a compound that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives (non-detects). More information is available for false positives due to the requirement for submittal of data supporting positive identifications. False negatives represent an absence of data and, therefore, are more difficult to assess. However, false negatives can be revealed when a compound is identified and reported to be a TIC when it should have been reported as a target compound.

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-Volatile/Semivolatile method QC acceptance criteria listed in Appendices A and B should be used as the default criteria when none exist for the Volatile/Semivolatile analytical method utilized and when similar QC parameters are required by the non-CLP method and acceptance criteria have not been met. 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 QAPjP/SAP or amendment to the QAPjP/SAP.

1. The relative retention time (RRT) for the sample compound must be within ± 0.06 RRT units of the daily standard RRT.

2. Mass spectra for the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated daily calibration standard) must match according to the following criteria:

   a. All ions present in the standard mass spectrum at a relative intensity greater than 10 percent must be present in the sample spectrum.

   b. The relative intensities of these ions must agree within ± 20 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectrum, the corresponding sample ion abundance must be between 30 percent and 70 percent.)

   c. Ions present at greater than 10 percent in the sample mass spectrum but not present in the standard spectrum must be considered and accounted for.

3. All major chromatographic peaks (i.e., peaks present in the sample chromatogram at greater than 10 percent of the nearest internal standard) must be identified as either target compounds, TICs, surrogate compounds, or internal standards.

C. EVALUATION/ D. ACTION

C. EVALUATION	D. ACTION
	All potential impacts on the sample data resulting from target compound identification 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. Check that the RRT of a reported compound is within $\pm$ 0.06 RRT units of the standard RRT.	1. a. If the RRT of a reported compound is outside of the retention time criteria, then the validator should use professional judgment to determine if mass spectral identification criteria have been met and if the compound has been correctly identified. b. If the reported compound does not meet mass spectral identification criteria and has been incorrectly reported, then the validator should report the compound as a non-detect and document the rationale for this decision in the Data Validation Memorandum. c. If instrument/analytical column malfunctions have severely affected retention times, making data suspect, then the validator should use professional judgment to reject (R) all associated sample data.

C. EVALUATION	D. ACTION
*2. Compare all sample compound spectra to the laboratory standard spectra and verify that the mass spectral identification criteria are met.	2. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is left to the validator's discretion to obtain additional information from the laboratory if it is deemed necessary. If it is determined that incorrect laboratory identifications were made, 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 identification 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. Check the sample chromatogram to verify that all major peaks of interest are identified as either target compounds, TICs, surrogate compounds, or internal standards.	3. If a chromatographic peak is unaccounted for and is greater than 10% of the nearest internal standard, then the validator should have the laboratory requantitate and resubmit all corrected raw data and forms.
*4. The validator should be aware of situations (e.g., high concentration samples preceding low concentration samples or when VOA samples are purged in a contaminated sparge unit) when sample carryover is a possibility, and should use professional judgment to determine if instrument cross-contamination has affected any compound identification. An instrument blank should be run immediately after samples which cause detector saturation.	4. If cross-contamination has occurred, then the validator should use professional judgment to determine whether or not a reported target compound is native to the sample or an interferent from a previously analyzed sample. Additionally, the validator should use professional judgment to determine whether or not sample carryover has resulted in false negatives due to mass spectral identification criteria (pertaining to ions present and abundances) which cannot be met due to interfering ions from cross contaminants.

Note: **This section is applicable only to a Tier III validation - If a validator suspects compound misidentification while performing a Tier II validation, then the Site Manager must be contacted to approve the necessary full or partial Tier III validation.**

E. EXAMPLES

Example #1: (False negative-all major chromatographic peaks not identified)

The laboratory originally reported phenol as a TIC in the volatile fraction of soil sample SAA12. Phenol was reported as a non-detect in the semivolatile fraction. Upon review of the semivolatile chromatogram for sample SAA12, the validator notes that the laboratory failed to identify a peak that eluted within the phenol retention time window. The laboratory was contacted and requested to requantitate the false negative semivolatile phenol result and report phenol as a positive detect in the semivolatile fraction and deletes it from the VOA TIC list. The laboratory complied and the validator reports phenol as a positive detect in the semivolatile fraction on the Data Summary Table.

Example #2: (False positive; False negative-mass spectral identification criteria not met)

In aqueous sample SAA04, the validator notes that naphthalene and 2-chlorophenol have the same retention time on the quantitation report. The sample mass spectrum contains the molecular ion 128 and the laboratory reported naphthalene as a positive detect. Review of the mass spectrum shows a chlorine isotope ion at m/z 130 and fragmentation ions consistent with 2-chlorophenol, therefore, the validator determines that 2-chlorophenol is a more accurate identification of this peak. The laboratory was contacted and requested to requantitate the false positive naphthalene and false negative 2-chlorophenol. The validator reports 2-chlorophenol as a positive detect and naphthalene as a non-detect on the Data Summary Table.

Example #3: (False positive-sample compound RRT not within ±0.06 RRT units of the standard compound RRT)

The laboratory originally identified a peak as acetone and reported acetone as a positive detect in sample SAA67. The mass spectrum contained low area counts for ion 58 and the validator suspects a false positive. Upon review of the retention time data, the validator discovers that the RRT for the reported acetone peak was not within the standard ± 0.06 retention time window. The validator uses professional judgment to determine that acetone was misidentified. This unknown compound is less than 10% of the area of the nearest IS and, therefore, it is not reported as a TIC. The validator reports acetone as a non-detect on the Data Summary Table and documents this problem in the Data Validation Memorandum.