USEPA REGION II DATA VALIDATION SOP FOR SW-846 METHOD 8290 POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/ HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

PREPARED BY: _____ Date: 12/29/10
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PEER REVIEWED BY: _____ Date: 12/29/10
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Michael Mercado, Acting Chief HWSS

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Annual Review

REVIEWED BY: _____ Date: _____
Name

REVIEWED BY: _____ Date: _____
Name

1.0 Introduction

1.1 The attached Standard Operating Procedure (SOP) is applicable to polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/PCDF) data obtained using SW-846 Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, November 1992. Its scope is to facilitate the data validation process of the data reported by the contracting laboratory and also to ensure that the data is being reviewed in a uniform manner.

1.2 This SOP is based upon the quality control and quality assurance requirements specified in SW-846 Method 8290, Revision 0, November 1992. This SOP is based also upon additional QA/QC requirements prescribed in the Special Analytical Service (SAS) requests provided to the laboratory.

2.0 Responsibilities

2.1 The reviewer must be knowledgeable of the analytical method and its QC Criteria.

2.2 The reviewer must complete and/or file the following:

2.2.1 Data Assessment Checklist - The data reviewer must read each item carefully and must check yes if there is compliance, no if there is non compliance and N/A if the question is not applicable to the data.

2.2.2 Data Assessment Narrative - The data reviewer must present professional judgement and must express concerns and comments on the validity of the overall data package. The reviewer must explain the reasons for rejecting and/or qualifying the data.

2.2.3 Rejection Summary Form - The reviewer must submit the completed form using a ratio format. The numerator indicates the number of dioxins/furans data rejected; the denominator indicates the number of dioxins/furans fractions containing rejected compounds.

2.2.4 Organic Regional Data Assessment Summary - The data reviewer is also required to submit the completed Organic Regional Data Assessment Form.

2.2.5 Telephone Record Log - All phone conversations must be initiated by the technical project officer through SMO. If a phone call has been made, the reviewer must transcribe the conversation. After the data review has been completed, the white copy of the telephone log is mailed to the laboratory and the pink copy to SMO. The yellow copy is filed in the appropriate folder. A photocopy of the Telephone Record Log is attached to the Data Assessment Narrative.

2.2.6 Forwarded Paperwork - Upon completion of the review the following are to be forwarded to the Regional Sample Control Center (RSCC):

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2.2.6 Forwarded Paperwork - Upon completion of the review the following are to be forwarded to the Regional Sample Control Center (RSCC):

a. data package
b. completed data assessment checklist and narrative (original)

The reviewer will forward one copy of the completed Data Assessment and one copy of the Organic Regional Data Assessment to the appropriate Regional TPO.

2.2.7 Filed Paperwork - The following are to be submitted to the Monitoring Management Branch (MMB) files:

a. a photocopy of the Data Assessment Narrative
b. a photocopy of the Regional Data Assessment Summary
c. Telephone record Log (copy)
d. Rejection Summary Form

2.3 Rejection of Data - All values determined to be unacceptable on the Organic Analysis Data Sheet (Form I) must be flagged with an "R". The qualifier R means that due to significant QA/QC problems the analysis is invalid and it provides no information as to whether the compound is present or not. Once the data are flagged with R any further review or consideration is unnecessary. The qualifier "J" is used to indicate that due to QA/QC problems the results are considered to be estimated.

- The qualifier "NJ" indicates that there is presumptive evidence for the presence of the compound at an estimated value.
- The data reviewer must explain in the data assessment narrative why the data was qualified. He or she must also indicate all items of contract non-compliance.
- When 2,3,7,8- substituted TCDD, TCDF, PnCDD and PnCDF data are rejected (flagged "R") or qualified "J" the project officer must be notified promptly. If holding times have not been exceeded reanalysis of the affected samples may be requested.
- All qualifications and corrections to reviewed data must be made in red pencil.

PACKAGE COMPLETENESS AND DELIVERABLES _____CASE NUMBER: _____
LAB:_____SITE:_____

		YES	NO	N/A
I.0	**Data Completeness and Deliverables**			
1.1	Are the Traffic Report Forms present for all samples?	[___]	___	___
1.2	Is the Narrative or Cover letter present?	[___]	___	___
1.3	Are the Case Number and/or SAS numbers contained in the case narrative?	[___]	___	___
1.4	Do the Traffic Reports or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical problems, or other comments affecting the quality of the data?	___	[___]	___

ACTION: Use professional judgement to evaluate the effect of the noted problems on the quality of the data.

2.0 Reporting Requirements and Deliverables

2.1 All deliverables must be clearly labeled with the SMO number and the associated sample/traffic number. Missing or illegible or incorrectly labeled items must be identified. The contractor must immediately be contacted and requested to submit the missing or incorrect items.

2.2 The following forms were taken from the CLP SOW, DFLM01.1 and are specified in the SAS Request. Are these forms present?

a. Sample Data Summary (Form I PCDD-1)	[___]	___	___
b. PCDD/PCDF Toxicity Equivalency Factor (Form I, PCDD-2)	[___]	___	___
c. Second Column Confirmation Summary (Form I, PCDD-3)	[___]	___	___
d. Total Homologue Concentration Summary (Form II PCDD)	[___]	___	___
e. PCDD/PCDF Spiked Sample Summary (Form III PCDD-1)	[___]	___	___
f. PCDD/PCDF Duplicate Sample Summary (Form III PCDD-2)	[___]	___	___
g. PCDD/PCDF Method Blank Summary (Form IV-PCDD)	[___]	___	___
h. PCDD/PCDF Window Defining Mix Summary (Form V-PCDD-1)	[___]	___	___
i. Chromatographic Resolution Summary (Form V PCDD-2)	[___]	___	___
j. PCDD/PCDF Analytical Sequence Summary (Form V PCDD-3)	[___]	___	___
k. Initial Calibration (Form VI, PCDD-1, PCDD-2)	[___]	___	___
l. Continuing Calibration (Form VII,PCDD-1, Form VII,PDD-2)	[___]	___	___

	YES	NO	N/A
2.3 GC/MS Displays			
Are the following GC/MS displays present?			
a. Standard and sample SIM chromatograms. SIM and TIC chromatograms must list date and time of analysis; the file name; sample number; and instrument I.D. number	[___]	___	___
b. Percent peak resolution valley	[___]	___	___
c. GC column performance check raw data	[___]	___	___
d. SIM mass chromatograms must display quantitation ion, confirmation ion, and polychlorinated diphenylether ion, where applicable.	[___]	___	___
e. Integrated area and peak height must be listed for all peaks 2.5 times above background	[___]	___	___
f. All peaks must show retention time at the maximum height	[___]	___	___
2.4 Are the following Chain of Custody Records and in-house Laboratory Control Documents present?			
a. EPA Chain of Custody Records	[___]	___	___
b. SMO Sample Shipment Records	[___]	___	___
c. Sample log-in sheets	[___]	___	___
d. GC/MS Standard and Sample Run Log in chronological order	[___]	___	___
e. Sample Extraction Log	[___]	___	___
2.5 Was the sample data package paginated?	[___]	___	___

ACTION: If deliverables are missing call the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the reviewers narrative.

3.0 Holding Times

3.1 Have any of the following holding times been exceeded?			
a. For aqueous samples, 30 days from sample collection to extraction	[___]	___	___
b. For soil/sediment samples, 30 days from sample collection to extraction	[___]	___	___
c. For all samples 45 days from time of extraction to time of analysis	[___]	___	___

ACTION: If holding times are exceeded, flag all data as estimated ("J"). Holding time criteria do not apply to PE samples.

Note: All samples except fish and adipose samples must be stored in dark at 4°C. Fish and adiposetissue must be stored at -20°C in the dark.

YES NO N/A

4.0 Instrument Performance

4.1 Mass Calibration - Mass calibration of the MS must be performed prior to analyzing calibration solutions,blanks, samples, and QC samples. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analysis is performed Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. Include in the narrative, minimum required resolving power of 10000 was obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm, i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

Resolving Power = m/ m = 380.9760/0.038 = 10025.

4.1.1 Was mass calibration performed at the frequency given above? [___] ___ ___

4.1.2 Was the resolving power of PFK ion 380.9760 above 10000, when it was transmitted at the accelerating voltage corresponding to m/z ion 304.9824? [___] ___ ___

4.2 GC Column Performance Check Solution

The GC Column Performance Check solution must contain the first and the last isomers of each homologue PCDD/PCDF, (the internal and recovery standards are optional).The solution also should contain a series of other TCDD isomers for the purpose of documenting the chromatographic resolution.

4.2.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of GC column performance check solution at the beginning of every 12 hour period. Was this performed accordingly? [___] ___ ___

ACTION: If the GC column performance check solution was not analyzed at the required frequency, use professional judgement to determine the effect on the quality of the data.

4.2.2 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)? [___] ___ ___

YES NO N/A

4.2.3 For DB-5 or equivalent, the peak separation between the unlabeled 2378-TCDD and the peaks representing any other TCDD isomer shall be resolved with a valley of ≤ 25 percent. Was this criteria met? [___] ___ ___

% Valley = (x/y) x (100)

Y = The peak height of 2,3,7,8-TCDD isomer

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

ACTION: If the percent valley criteria are not met qualify all positive data J. Do not qualify non-detects.

4.2.4 Is the last eluting tetra chlorinated congener (1,2,8,9-TCDD) and the first eluting penta chlorinated congener (1,3,4,6,8-PeCDF) separated properly, since they elute within 15 seconds of each other? [___] ___ ___

ACTION: If one of the congener is missing, report that in the case narrative.

5.0 **Initial 5-Point Calibration** - The initial calibration standard solutions (HRCC1-HRCC5) must be analyzed prior to any sample analysis. They do not have to be analyzed daily, provided the continuing calibration standard met all criteria. However, initial calibration should be analyzed at least once every week and/or whenever the continuing calibration standard does not meet all criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the GC column performance check solution.Was the initial calibration performed at the frequency specified above?

[___] ___ ___

5.1 The following MS/DS conditions must be used:

5.1.1 Is mass calibration performed as per Section 4.1? [___] ___ ___

5.1.2 Is the total cycle time ≤ 1 second? [___] ___ ___

Note: The total cycle time includes the sum of all the dwell times and voltage reset times.

5.1.3 Were SIM data acquired for each of the ions listed in Table 6, including interfering ions? (see analytical method) [___] ___ ___

5.2 Were the following GC criteria met?

5.2.1 The chromatographic resolution between the 2378-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent. [___] ___ ___

5.2.2 In the HRCC3 solution, the chromatographic peak separation between 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD shall be resolved with a valley of ≤ 50 percent. [___] ___ ___

YES NO N/A

5.2.3 For all calibration solutions the retention times of the isomers must fall within the retention time windows established by the GC column performance check solution. In addition, the absolute retention times of recovery standards, $^{13}C_{12}$1234-TCDD and $^{13}C_{12}$-123789HxCDD shall not change by more than 10 seconds between the HRCC3 analysis and the analysis of any other standard.

5.2.4 The two SIM ions for each homolog must maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions. [___] ___ ___

5.2.5 The relative ion abundance criteria for PCDDs/PCDFs listed in Table 8 (see analytical method) must be met. [___] ___ ___

5.2.6 The relative ion abundance criteria for the labeled internal and recovery standards listed in Table 8 must be met. [___] ___ ___

5.2.7 For all calibration solutions, including HRCC3, the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be $\geq$ 10. [___] ___ ___

5.2.8 The percent relative standard deviations (% RSD) for the the mean response factors (RRF) from the 17 unlabeled standards must not exceed $\pm$ 20%, and those for the nine labeled reference compounds must not exceed $\pm$ 30%. [___] ___ ___

ACTION: 1. If the 25% percent valley for TCDD and 50% valley for HxCDD requirement are not met, quality positive data J. Do not qualify non-detects.The tetra, pentas and hexas (dioxins and furans) are affected. Heptas and Octas are not affected.

2. If the %RSD for each unlabeled isomer exceeds 20%,or the %RSD for each labeled isomer exceeds 30%, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.

3. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte R (reject).

4. If the ion abundance ratio for an internal or recovery standard falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.

5. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.

YES NO N/A

6. If the selected monitoring ions specified in Table 6 were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.

7. If mass calibration criteria as specified in Section 4.1 is not met, specify that in case narrative.

8. Non compliance of all other criteria specifiedabove should be evaluated using professional judgement.

5.2.9 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and internal standards were used. In addition, verify that the appropriate internal standard was used for each isomer.

To recalculate the response factor, use the equation:

$$RRFn = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RRFis = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

Where:

A_n^1 and A_n^2 = integrated areas of the two quantitation ions of isomer of interest (Table 6).

A_{is}^1 and A_{is}^2 = integrated areas of the two quantitation ions of the appropriate internal standard (Table 6).

A_{rs}^1 and A_{rs}^2 = integrated areas of the two quantitation ions of the appropriate recovery standard (Table 6).

Q_n = quantity of the unlabeled PCDD/PCDF analyte injected (pg)

Q_{is} = quantity of the appropriate internal standard injected (pg)

Q_{rs} = quantity of the appropriate recovery standard injected (pg)

YES NO N/A

6.0 Continuing Calibration (HRCC3)

The continuing calibration must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A continuing calibration is also required at the end of a 12 hour shift. Was the continuing calibration run at the required frequency? [___] ___ ___

6.1 Were the following MS/DS conditions used?

6.1.1 The total cycle time was ≤ 1 second. [___] ___ ___

6.1.2 SIM data were acquired for each of the ions listed in Table 6 including diphenylether interfering ions (see analytical method). [___] ___ ___

6.2 Were the following criteria met?

6.2.1 For the continuing calibration solution the retention time of the isomers must fall within the retention time windows established by the GC column performance check solution. [___] ___ ___

6.2.2 The absolute retention time of the recovery standards $^{13}C_{12}$1234-TCDD and $^{13}C_{12}$123679 HxCDD shall not change by more than 10 seconds between the initial HRCC3 and ending HRCC3 standard analyses. [___] ___ ___

6.2.3 The two SIM ions for each homolog must maximize simultaneously (± 2 sec) and within 3 seconds of the corresponding ions of the labeled isomers. [___] ___ ___

6.2.4 For the HRCC3 standard solution, the signal to noise ratio (S/N) for the unlabeled PCDD/PCDF ion shall be greater than 2.5. [___] ___ ___

6.2.5 For the internal standards and the recovery standards,the signal to noise ratio (S/N) shall be greater than 10. [___] ___ ___

6.2.6 The relative ion abundance criteria (Table 8 - analytical method) for all PCDD/PCDF shall be met. [___] ___ ___

6.2.7 The relative ion abundance criteria for all internal and recovery standards (Table 8 – analytical method) must be met. [___] ___ ___

6.2.8 The %Difference of RRF of each unlabeled analyte must be within ±20 percent of the mean RRF established during the initial calibration. The measured RRFs for each of the labeled standards must be within ± 30 percent of the mean RRF established during the initial calibration.

[___] ___ ___

Spot check response factor calculations and ion ratios.
Verify that the appropriate quantitation ions for the unlabeled PCDD/PCDFs and internal standards were used.

YES NO N/A

6.2.9 Was the same internal standard used to calculate RRF for each PCDD/PCDF homolog in the initial calibration? [___] ___ ___

6.2.10 Was the chromatographic peak separation on DB-5 (or equivalent) column between unlabeled 2378-TCDD and the peaks representing any other unlabeled TCDD) isomers resolved with a valley of ≤ 25 percent? [___] ___ ___

6.2.11 Was the chromatographic peak separation between the 123478-HxCDD and the 123678-HxCDD in the HRCC3 solution resolved with a valley of ≤50 percent? [___] ___ ___

ACTION: 1. If any of the requirements listed in sections 6.1.1, 6.1.2, 6.2.1, 6.2.2, and 6.2.9 are not met, use professional judgement to determine the validity of the data.

2. If any requirements listed in sections 6.2.3, 6.2.4, 6.2.5, 6.2.6, and 6.2.7 are not met reject all data (flag R) directly affected by each specific problem.

3. When the %D of the RRF is in between 30% and 50%, all the data for the outlier congeners are flagged J. Data with %D above 50% are rejected (R).

4. If the continuing calibration standard was not analyzed at the required frequency, reject all the data. Contact TPO to initiate reanalysis.

5. If the 25 percent valley (6.2.10) and 50 percent valley (6.2.11) criteria are not met, qualify all positive data with J. Do not qualify non-detects. Note: The tetras, pentas and hexas (dioxins and furans) are affected. Heptas and octas are not affected. If the percent valley is >75 percent and 2378-TCDD is non-detect but 1234-TCDD or an adjacent TCDD isomer is present, the data is questionable. The sample must be reanalyzed. Contact TPO. If the valley criteria for HxCDD are not met, but the valley criteria for TCDD are met or vice-versa, use professional judgement to determine which data must be qualified.

6. If the HRCC3 standard performed at the end of the 12 hour shift did not meet criteria specified in Sections 6.2.1, 6.2.4, 6.2.5, 6.2.6, and 6.2.7, examine the samples which were analyzed prior to this standard and use professional judgement to determine if data qualification is necessary.
7. For all other criteria, use professional judgement.

YES NO N/A

6.2.12 To recalculate RRFs for the unlabeled target analytes, and the RRFs for the nine labeled internal standards, use the following equations:

$$RRFn = \frac{(An^1 + An^2) \times Qis}{(Ais^1 + Ais^2) \times Qn}$$

$$RRFis = \frac{(Ais^1 + Ais^2) \times Qrs}{(Ars^1 + Ars^2) \times Qis}$$

An^1, An^2, Ais^1, Ais^2, Ars^1, Ars^2, Qn, Qis and Qrs are defined in Section 5.2.9.

To calculate percent difference use the following equation:

$$\% \text{ Difference} = \frac{(RRFi - RRFc) \times 100}{RRFi}$$

Where:

RRFi = Relative response factor established during initial calibration
RRFc = Relative response factor established during continuing calibration

7.0 Sample Data

7.l Were the following MS/DS conditions used?

7.1.1 The total cycle time was $\leq$ 1 second. [___] ___ ___

7.1.2 SIM data were acquired for each of the ions listed in Table 6 (see analytical method) including diphenylether interfering ions. [___] ___ ___

7.2 Were the following identification criteria met?

7.2.1 For the 2378 substituted isomers found present and for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard. [___] ___ ___

7.2.2 For the 2378 substituted isomer reported present, and for which a labeled standard does not exist, the relative retention time (RRT) of the analyte must be within $\pm$.005 RRT units of the RRT established by the continuing calibration standard (HRCC3). [___] ___ ___

YES NO N/A

7.2.3 For non-2378 substituted compounds (tetra through octa) found present, the retention time must be within the window established by the GC column performance check solution, for the corresponding homologue. [___] ___ ___

7.2.4 All specified ions listed in Table 6 (analytical method) for each PCDD/PCDF isomer and the labeled standards must be present in the SICP. The two SIM ions for the analyte, the internal standards and recovery standards must maximize simultaneously ($\pm$2 seconds). [___] ___ ___

7.2.5 The integrated ion current for each characteristic ion of the analyte identified as positive, must be at least 2.5 times background noise and must not have saturated the detector. [___] ___ ___

7.2.6 The integrated ion current for the internal and recovery standard characteristic ions must be at least 10 times background noise. [___] ___ ___

7.2.7 The relative ion abundance criteria (Table 8 – analytical method) for all PCDDs/PCDFs found present must be met. [___] ___ ___

7.2.8 The relative ion abundance criteria for the internal and recovery standards must be met (Table 8 - analytical method). [___] ___ ___

7.2.9 The identification of a GC peak as a PCDF can only be made if no signal having a S/N $\geq$ 2.5 is detected at the same time in the corresponding polychlorinated diphenyl ether channel. Is the above condition met? [___] ___ ___

7.2.10 The analyte concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range. Was the above criteria met? [___] ___ ___

NOTE: The analytical method clearly states that samples containing analytes having concentrations higher than 10 times the upper MCLs should be analyzed using a less sensitive, high resolution GC/low resolution MS method.

ACTION:
1. Reject (flag R) all positive data for the analytes which do not meet criteria listed in Sections 7.2.1, 7.2.2, 7.2.3, and 7.2.4.
2. If the criteria listed in section 7.2.5 are not met but all other criteria are met, qualify all positive data of the specific analyte with J.
3. If the requirements listed in section 7.2.6 are not met but all other requirements are met qualify the positive data of the corresponding analytes with "J".
4. If the analytes reported positive do not meet ion abundance criteria, section 7.2.7, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

YES NO N/A

5. If the internal standards and recovery standards do not meet ion abundance criteria (Table 8 - analytical method) but they meet all other criteria flag all corresponding data with "J".
6. If PCDF is detected but an interfering PCDPE is also detected (see Section 7.2.9) reject the PCDF data (R). The reported value of PCDF is changed to EMPC.
7. If the lab did not monitor for PCDPEs, qualify all positive furan data J.

7.2.11 Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration and EMPC. Ensure that the proper PCDDs/PCDFs and internal standards were used.

To recalculate the concentration of individual PCDD/PCDF isomers in the sample use the following equation:

ALL MATRICES OTHER THAN WATER

$$Cn\ (pg/g) = \frac{Qis \times (An^1 + An^2)}{W \times (Ais^1 + Ais^2) \times RRFn}$$

WATER

$$Cn\ (ng/L) = \frac{Qis \times (An^1 + An^2)}{V \times (Ais^1 + Ais^2) \times RRFn}$$

Where:

An^1 and An^2 = integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest (Table 6).

Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard (Table 6).

W= Weight (g) of sample extracted
V= Volume (ml) of sample extracted
Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction
RRFn= Calculated relative response factor from continuing calibration (see Section 7.7 of the analytical method).

Note: See CLP/SOW DFLMO1.1, Section 15.3 for calculations when any internal standard in a diluted sample is less than 10% of the internal standard area in the continuing calibration standard.

YES NO N/A

7.3 Estimated Detection Limits (EDL)

7.3.1 Was an EDL calculated for each 2,3,7,8-substituted isomer that was not identified regardless of whether other non-2378 substituted isomers were present? [___] ___ ___

7.3.2 Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

$$EDL\ (pg/g) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{W \times (His^1 + His^2) \times RRFn}$$

WATER

$$EDL\ (ng/L) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{V \times (His^1 + His^2) \times RRFn}$$

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor (see Paragraph 10.4.3 of the SOW).

Qis, RRFn, W and V are defined in Section 7.2.11.

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation.If the area algorithm was used, the validator should contact the laboratory for recalculation.The TPO must be notified.

7.4 Estimated Maximum Possible Concentration (EMPC)

7.4.1 Was an EMPC calculated for 2378-substituted isomers that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria? [___] ___ ___

7.4.2 Use the equation below to check EMPC calculations:

ALL MATRICES OTHER THAN WATER

$$EMPC\ (ug/L) = \frac{(Ax^1 + Ax^2) \times Qis \times D}{(Ais^1 + Ais^2) \times RRFn \times W}$$

WATER

$$EMPC\ (ng/L) = \frac{(Ax^1 + Ax^2) \times Qis \times D}{(Ais^1 + Ais^2) \times RRFn \times V}$$

YES NO N/A

Where:

Ax^1 and Ax^2 = areas of both quantitation ions.

Ais^1, Ais^2, Qis, RRF, W, and V are defined in Section 7.2.11. D is dilution factor defined in Section 10.4.3 of the CLP/SOW.

Action: 1. If EDL or EMPC of an analyte which was not reported as present is missing, contact the laboratory for correction.
2. If the spot check calculations yielded EDLs or EMPCs different from those reported in Form I,contact the laboratory for an explanation.
3. If EDLs or EMPCs for the most toxic analytes (TEF$\geq$ 0.05) are above CRQLs contact TPO for sample reanalysis.

7.5 Method Blanks

7.5.1 Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?
[___] ___ ___

7.5.2 If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event?
[___] ___ ___

7.5.3 Acceptable method blanks must not contain any signal of 2378-TCDD, or 2378-TCDF, equivalent to a concentration of > 20 ppt for soils or 0.2 ppt for water samples.Is this criteria met? [___] ___ ___

7.5.4 For other 2378- substituted PCDD/PCDF isomers of each homologue, the allowable concentration in the method blank is less than 1/10 of the upper MCL specified in Table 1 of the method or the area must be less than 2% of the area of the nearest internal standard.Is this criteria met? [___] ___ ___

7.5.5 For the peak which does not meet identification criteria as PCDD/PCDF in the method blank, the area must be less than 5% of the area of the nearest Internal Standard.Was this condition met?
[___] ___ ___

ACTION: 1. If the proper number of method blanks were not analyzed, notify the contractor.If they are unavailable, reject all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

YES NO N/A

2. If the method blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD,12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL listed in Table 1 of the method, reject all contaminant compound positive data for the associated samples (flag R) and contact the technical project officer to initiate reanalysis if it is deemed necessary.

3. If the method blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

7.6 Rinsate Blank

7.6.1 One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent.Was rinsate blanks collected at the above frequency? [___] ___ ___

7.6.2 Do any rinsate blanks show the presence of 2378-TCDD,2378-TCDF, and 12378PeCDD at amounts > .5 ug/L or any other analyte at levels > 1μg/L? [___] ___ ___

ACTION
If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the technical project officer to discuss what proper action must be taken.

7.7 Field Blanks

7.7.1 The field blanks are PEM samples (blind blanks) supplied by EPA from EMSL-LV at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil.The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

Were the following conditions met?

7.7.2 Acceptable field blanks must not contain any signal of 2378-TCDD, 2378-TCDF, 12378-PeCDD and 12378-PeCDF equivalent to a concentration of > 20 ppt. [___] ___ ___

7.7.3 For other 2378 substituted PCDD/PCDF isomers of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method. [___] ___ ___

YES NO N/A

ACTION: When the field blank is found to be contaminated with target compounds, apply the same action as described for the method blank (section 7.5).

NOTE: Contact EPA EMSL/LV to verify that the PEM blank (field blank) did not contain any PCDD/PCDF isomers and ask their assistance in the evaluation of the PE field blank.

8.0 Internal Standard Recoveries (Form I)

8.1 Were the samples spiked with all the internal standards as specified in the method? [___] ___ ___

8.2 Were internal standard recoveries within the required (40 - 135%) limits? [___] ___ ___

8.3 If not, were samples reanalyzed? [___] ___ ___

ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (135 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data R (Reject). when highly toxic isomers (TEF$\geq$ 0.05) are affected, notify TPO to initiate reanalysis.

Recalculate the percent recovery for each internal standard in the sample extract, Ris, using the formula:

$$Ris = \frac{(Ais^1 + Ais^2 \times Qrs \times 100\%}{(Ars^1 + Ars^2 \times RRFis \times Qis}$$

Ais^1, Ais^2, Ars^1, Ars_2, Qis, Qrs and RRFis are defined, previously.

9.0 Recovery Standards

There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

9.1 Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration? Area upper limit= +100% of recovery standard area .Area lower limit= -50% of recovery standard area. [___] ___ ___

	YES	NO	N/A
9.2 Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?	[___]	___	___

ACTION: 1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported flag all associated non-detect data as unusable (R) and the positive data J.

3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the GC column performance check solution.

10.0 PEM Interference Fortified Blanks

10.1 One known blank usually an interference fortified soil/sediment sample, supplied by EPA, EMSL-LV, is designated by the sampling team for the laboratory for spiking.The frequency of this QC sample is one per group of 20 environmental samples or one per samples collected over one week period, whichever occurs first. The sample is spiked by the laboratory with the appropriate volume of the matrix spiking solution and then extracted and analyzed with other samples.

10.2 Was a fortified PEM blank analyzed at the frequency described above?	[___]	___	___
10.3 Was the percent recovery of 2378-TCDD and other 2378-substituted compounds within the 50 to 150 percent control limits?	[___]	___	___

ACTION: 1. If the recovery of a 2,3,7,8-substituted isomer falls outside the 50-150 percent control limit, flag all positive and non-detect data of the same and related isomers in the same homolog series with J. However, if the recovery is below 20%, qualify all associated non-detects R.Notify the TPO. Reanalysis may be initiated.

2. If no fortified PEM blank was analyzed, use professional judgement to assess data validity.

NOTE: This blank, as prescribed above in Section 10.1,however, is not given in the analytical method.

	YES	NO	N/A

11.0 Matrix Spike (Field Sample)

11.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix? [___] ___ ___

11.2 Was the percent recovery of 2378-TCDD and other 2378- substituted PCDDs/PCDFs within 50 to 150 percent? [___] ___ ___

ACTION: If problems such as interferences are observed,use professional judgement to assess the quality of the data. The 50-150% limits of the matrix spike data may be used to flag data of the spiked sample only. The matrix spike data of the PE blank sample are more important and must be used primarily in data validation.

12.0 Environmental Duplicate Samples

12.1 For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate.Were duplicate samples collected at the above frequency? [___] ___ ___

Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8 substituted isomers and 50% for the rest of the congeners? [___] ___ ___

ACTION: The duplicate results must be used in conjunction of other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.

13.0 Performance Evaluation Samples

13.1 Included among the samples are sets of performance evaluation samples containing known amounts of unlabeled 2378-TCDD or a mixture of 2378-TCDD and other PCDD/PCDF isomers. The PE samples are provided by the Region, and must be analyzed at the frequency of one set per batch of 20 samples, or one per samples collected over a period of one week, whichever occurs first.

13.2 Were the analytical results within the EPA 99% acceptance criteria? [___] ___ ___

ACTION: 1. The PE samples must be validated as if they were environmental samples. There is no holding time for PE samples.

2. PE samples containing only 2378-TCDD When 2378-TCDD was not qualitatively identified, or if the reported concentration is outside the 99% acceptance window all positive and negative (EMPC/EDL) data for all associated samples are rejected.

YES NO N/A

3. PE samples containing a mixture of PCDD/PCDF isomers
When the reported concentration of any analyte is outside the EPA 99% confidence interval, all positive and negative (EMPC/EDL) data of the 2378 substituted isomers within the same homologue for all associated samples are rejected.

4. When PCDD/PCDF data are rejected because of PE results, the EPA technical project officer must be notified. Reanalysis may be initiated.

5. For PE blind blanks see Section 7.7 (Field Blanks).

14.0 Second Column Confirmation

14.1 Was a second column confirmation performed? [___] ___ ___

14.2 Was the sample extract reanalyzed on a 30 m DB-225, fused silica capillary column, for 2,3,7,8 TCDF using the GC/MS conditions given in Section 7.9.7.1.2 of the analytical method?
[___] ___ ___

NOTE: The concentration of 2,3,7,8 TCDF obtained from the primary column (DB-5) should only be used for qualification, due to better QC data associated with the primary column. Also note that the confirmation and quantitation of 2,3,7,8-TCDD may be accomplished on a SP-2330 GC column.

ACTION: If confirmation is missing, use professional judgement, or contact TPO for assistance.

14.3 Did the second column meet the calibration and linearity specification in Sections 5.0 and 6.0 above? [___] ___ ___

14.4 Was the % D of the quantitation results of the two columns less than 50?
[___] ___ ___

15.0 Sample Reanalysis

15.1 The Region II TPO will evaluate the need for reanalyzing the samples with qualified data based on site-specific Regional Data Quality Objectives. The rerun may be billable or non billable as specified in the SOW. SMO should be notified of all reruns.

	YES	NO	N/A

15.2 Due to a variety of situations that may occur during sample analysis the laboratory is required to reanalyze or reextract and reanalyze certain samples. If a reanalysis was required but was not performed, contact TPO to initiate reanalysis. List below all reextractions and reanalyses and identify the PCDD/PCDF sample data summaries (Form I) which must be used by the data user (when more than one is submitted).

16.0 Isomer Specificity and Toxicity Equivalency Factor (TEF) -

When calculating the 2378-TCDD Toxicity Equivalency of a sample only those 2378 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve isomer specificity.

16.1 Did the lab include EMPC or EDL values in the toxicity equivalency calculations? [___] ___ ___

16.2 Were all samples, whose toxicity equivalency exceeded the required values were reanalyzed on a confirmation column to establish isomer specificity? [___] ___ ___

ACTION: 1. If the toxicity equivalency calculations were not performed properly notify TPO.

2. If the toxicity equivalency exceeded the required limits (0.7 ppb for soil/sediment, 7ppt for aqueous and 7ppb for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify TPO.

PCDFs/PCDDs Data Assessment

CASE NO._____ LABORATORY_____
Site_____ SAMPLE NO._____

DATA ASSESSMENT:

All data are valid and acceptable except those values which have been qualified R (rejected) or qualified "J" (estimated). Rejected data does not imply the analyte is not present. It means that due to significant QC problems the analysis is invalid and it provides no information as to whether the compound is present or not.

All action is detailed below and on the attached sheets.

Reviewer's Signature: _____ Date:____/____/20____

Verified By: _____ Date:__/__/20__

Case#_____

Site:_____

Lab:_____

Overall Assessment

Case#_____

Site:_____

Lab:_____

Contract Problems/Non-Compliance