UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION III

DIOXIN/FURAN DATA VALIDATION GUIDANCE

DRAFT

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1 PURPOSE/

The purpose of this guidance is to evaluate the quality and usability of dioxin data generated by a contract laboratory for utilization by Region 3. This procedure includes low and high resolution Mass Spectrometry (MS).

2 SCOPE

This document shall guide a qualified data reviewer through the validation process for a dioxin data package submitted to EPA Region 3. This document is only a guide. The data reviewer is often called upon to make decisions based upon his or her professional judgment. This guidance is based on DFLM01.2 for Low Resolution MS, Method 1613 Revision B for High Resolution MS, and Region 3 technical specifications.

Note: The foundation of this Guidance is based on DFLM01.2 and the Draft National Functional Guidelines for Dioxin/Furan Data Validation. The referenced Data Review Forms are based on DFLM01.2. When High Resolution MS methods are utilized for analysis, "equivalent forms" relative to those listed in this Guidance will be provided by the laboratory. In addition, a few criteria listed in this Guidance are specific only to the Low Resolution MS. The reviewer should use this Guidance in conjunction with the method utilized for analysis.

3 DEFINITIONS

3.1	CERCLA Act	Comprehensive Environmental Response, Compensation, and Liability
3.2	CC	Continuing Calibration
3.3	CLASS	Contract Laboratory Analytical Services Support
3.4	DSF	Data Summary Form
3.5	EDL	Estimated Detection Limit
3.6	EMPC	Estimated Maximum Possible Concentration
3.7	GC/MS	Gas Chromatography / Mass Spectroscopy
3.8	HRMS	High Resolution Mass Spectroscopy
3.9	IS	Internal Standard - compounds added to every sample, standard, duplicate, blank and matrix spike at a known concentration, prior to extraction. Internal standards are used as basis for quantitation of the dioxin congeners.
3.10	LRMS	Low Resolution Mass Spectroscopy
3.11	PCDD	Polychlorinated Dibenzo Dioxin

3.12	PCDF	Polychlorinated Dibenzo Furan
3.13	PCDPE	Polychlorinated Diphenyl Ether
3.14	PEM	Performance Evaluation Material
3.15	PE Sample	Performance Evaluation Sample
3.16	QA	Quality Assurance
3.17	RPO	Regional Project Officer
3.18	RRF	Relative Response Factor
3.19	RRT	Relative Retention Time
3.20	RS	Recovery Standard - compounds added to every sample, standard, duplicate, blank and matrix spike extract, at a known concentration, prior to instrument analysis. Recovery standards are used as the basis for quantitation of the Internal Standards.
3.21	RSD	Relative Standard Deviation
3.22	SDG	Sample Delivery Group
3.23	SICP	Selected Ion Current Profile
3.24	SIM	Selected Ion Monitoring
3.25	S/N	Signal to Noise ratio
3.26	SOW	Statement of Work
3.27	TEF	Toxicity Equivalency Factor
3.28	WAM	Work Assignment Manager

4 SAFETY

The reports prepared per this guidance may require manipulation of associated raw data which may weigh in excess of twenty pounds. Individuals with medical restrictions which would impede their performance under this guidance must seek assistance from their supervisor.

5 PRELIMINARY REVIEW OF DIOXIN PACKAGE

5.1 Evaluation

Examine data package to confirm presence of all the following documents:

5.1.1 case narrative, packing slips, chain of custody, airbills, copy of DAS request, etc.
5.1.2 PE sample results
5.1.3 Method Blank
5.1.4 window defining mix summary
5.1.5 chromatographic resolution summary
5.1.6 initial calibration
5.1.7 continuing calibration
5.1.8 instrument sensitivity check

5.1.9 toxicity equivalency calculation
5.1.10 initial and continuing calibration for the 2nd column if applicable
5.1.11 matrix spike
5.1.12 duplicate
5.1.13 analytical sequence summary

5.2 Action

If any of the above items are missing, the Region 3 RPO must be notified to request missing data/documentation from the laboratory.

6 DIOXIN DATA VALIDATION

6.1 Performance Evaluation Materials (PEM)

6.1.1 Review Items: 1DFA (Form I PCDD-1, or equivalent), PEM Score Information

6.1.2 Objective

The Region has the option to provide the laboratory with PEM(s) to be analyzed with each SDG. The laboratory must demonstrate its ability to achieve acceptable results through analysis of PEM(s) associated with each SDG. The following guidelines shall be followed in cases where the PEM(s) were submitted by the Region for analysis by the laboratory and results from such analyses were included in the data package.

6.1.3 Criteria

A two-tiered system is used for PEM(s). The first tier is applicable to data falling within a statistically established 95% confidence interval or warning limit. The second tier is applicable to statistical data that fall between the 95% and 99% confidence intervals or action limits.

6.1.4 Evaluation and Action

Evaluation	Action
• Verify identity and concentration of TCDD/TCDF isomers in the PEM submitted with the case. • Verify the blank PEM sample is free of contaminants and has no positive results detected.	• If results are outside of EPA's 99% confidence level or action level, notify Region 3 WAM. • Under certain circumstances it may be necessary to use data that are not within the 99% confidence interval before reanalysis. In this case, the reviewer should evaluate other QC associated with the sample analysis (calibration, surrogate, internal standards and recovery standards) and use professional judgment as to data usability. • If results are outside the 95% confidence interval (warning limit) but within the 99% confidence interval, data for the analyte are usable without qualification. • If the blank PEM contains positive results, evaluate the method blank for presence of the same contaminants. If the same analytes were detected in the method blank, qualify the PEM data per Section 6.8. If the blank PEM results were higher than those found in the method blank, notify the Region 3 WAM. Note: Region 3 has experienced blank PEM results with significant levels of PCDDs/PCDFs. The PEMs currently cited in CERCLA were "certified" using low resolution MS only and are not appropriate for use in high resolution MS analysis.

6.2 Holding Time

6.2.1 Review Items: Chain-of-Custody Records, Extraction Logs, Instrument Injection Logs

6.2.2 Objective

To determine validity of results based on the holding time of samples from day of collection to day of extraction and day of extraction to day of analysis.

6.2.3 Criteria

Under 40CFR Part 136, holding time and preservation requirements for PCDD/PCDF in water samples have been established. These regulations require that water samples be preserved by neutralizing any chlorine residual with 0.008% sodium thiosulfate, and cooling to 4°C, using a holding time of seven days from date of collection to date of sample extraction. In addition, the maximum holding time of extracts is 40 days from date of extraction to date of sample analysis.

Holding time and preservation requirements for PCDD/PCDF isomers in non-aqueous matrices have not been promulgated by EPA.

Method 1613, Revision B, October, 1994, criteria require that water samples which contain a chlorine residual be treated with 80 mg sodium thiosulfate per liter and stored at 0 - 4°C in the dark. Samples with pH greater than 9, should be adjusted to pH 7-9 with sulfuric acid. Aqueous samples maintained in the above conditions may be stored for up to one year.

Method 1613B requires solid, semi-solid, oily, mixed-phase and tissue samples to be stored in the dark at <-10°C. Non-aqueous samples maintained in this condition may be stored for up to one year.

Method 1613B allows sample extracts preserved in the dark at <-10°C to be stored for up to one year from date of extraction prior to analysis.

Method 8290, Revision 9/94, specifies that all samples, except fish and adipose tissue samples, must be stored at 4°C in the dark, extracted within 30 days, and completely analyzed within 45 days of extraction. Fish and adipose samples must be stored at -20°C in the dark, extracted within 30 days, and completely analyzed within 45 days of collection (see Section 6.4 of Method 8290).

6.2.4 Evaluation and Action

Evaluation	Action
• Examine the Chain-of-Custody Records for date of sample collection and preservative. Examine laboratory extraction and injection logs for dates of sample extraction and analysis.	• For the purpose of Region 3 data, holding time and preservation requirements cited in Method 1613B, October, 1994, are used as guidelines. If holding time and preservation requirements of method 1613B were not met, qualify positive results as estimated "J" and non-detects as "UJ". • When holding time requirements for the method under which the samples were analyzed were not met, make a note in the validation report narrative.

6.3 Window Defining Mix

6.3.1 Review Items: 5DFA (Form V PCDD-1, or equivalent), Chromatograms

6.3.2 Objective

The Window Defining Mix (WDM) contains the first and final eluting isomer in each homologue and is analyzed to establish switching times for SIM descriptors (Table 1) and to verify chromatographic resolution.

6.3.3 Criteria

A. The WDM shall be analyzed:

- Before initial and continuing calibrations and on each instrument and new GC column.
- Each time a new calibration is performed.
- Each time instrument conditions that impact established retention time (RT) are altered.
- Any time the RT of either recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD or $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) in any analysis varies by more than 10 seconds from its RT in the most recent continuing calibration.

B. The laboratory may use discretion in setting the switching times for the homologues that overlap between descriptors.

C. If the GC columns utilized are other than those specified in the method used for analysis, the first and last eluting isomers in each homologue

must be determined experimentally on the column used and the appropriate isomers must then be used for window definition and switching times.

D. Allowable tolerance on the daily verification of the WDM should be less than ten (<10) seconds for the absolute retention times of all the components of the mixture.

6.3.4 Evaluation and Action

Evaluation	Action
A. Verify that the WDM is analyzed at the required frequency.	A. If WDM was not analyzed at required frequency, check whether the calibration standards met all specifications. If initial and continuing calibrations meet criteria, the reviewer can assume descriptor switching times are properly set and data are usable without qualification. Neglecting to analyze the WDM is a contract issue and should be noted in the report narrative for EPA action.
B. Determine correct RT windows for the various GC/MS descriptors. Verify that the correct RT windows were used during analysis.	B. The laboratory should be requested through the RPO/WAM to submit any missing information. If SIM descriptor switching times were not adequately selected, calibration criteria will be impacted. Evaluate calibration criteria to determine impact of this non-compliance.
C. If the GC columns used are other than those specified in the method, the laboratory must ensure that the first and final isomers in each homologue are represented in the window defining mix used to evaluate that column.	C. The laboratory should be requested through the RPO/WAM to submit any missing information.
D. Verify retention time of all positive results of dioxin and furan are within 10 seconds before the first eluting or within 10 seconds after final eluting isomer for that corresponding homologue.	D. All positive results of dioxin and furan must have a retention time within 10 seconds of corresponding homologue. Estimate (J) all positive and (UJ) non-detects for all analytes with retention shifts greater than 10 seconds of corresponding homologue.

6.4 Chromatographic Resolution

6.4.1 Review Items: 5DFB (Form V PCDD-2, or equivalent), the corresponding Selected Ion Current Profile (SICP) of each isomer for each of the analyses reported on 5DFB.

6.4.2 Objective

The objective is to evaluate the ability of the gas chromatographic column to resolve closely-eluting dioxin and furan isomers. An evaluation must be made for each column used in the analysis of samples.

6.4.3 Criteria

A. For analysis on a DB-5 column, chromatographic resolution is evaluated by the analysis of the CC3 continuing standard during both initial and continuing calibration. The chromatographic peak separation between $^{13}C_{12}$-2,3,7,8-TCDD peak and $^{13}C_{12}$-1,2,3,4-TCDD shall be resolved in the SICP with a valley of ≤ 25%. The chromatographic peak separation between the $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD in the CC3 solution shall be resolved with a valley of ≤ 50%.

$$Valley,\% = \frac{X}{Y} \times 100$$

where:

X = Height from baseline to bottom of valley between $^{13}C_{12}$-1,2,3,4-TCDD (or $^{13}C_{12}$-1,2,3,4,7,8-HxCDD) peak and $^{13}C_{12}$-2,3,7,8-TCDD (or $^{13}C_{12}$-1,2,3,6,7,8-HxCDD) peak.

Y = Peak height of $^{13}C_{12}$-2,3,7,8-TCDD (or $^{13}C_{12}$-1,2,3,6,7,8-HxCDD).

B. For analysis on a SP-2331 column, the chromatographic resolution is evaluated before analysis of calibration standards by analysis of a commercially available column performance mixture beginning the 12 hour period. The mixture shall contain the TCDD isomers that elute most closely with 2,3,7,8-TCDD on this GC column (1,4,7,8-TCDD and 1,2,3,7/1,2,3,8-TCDD pair). The peak separation between these two isomers must be ≤25%.

$$Valley,\% = \frac{Height\ of\ valley\ separating\ peaks}{Height\ of\ 2,3,7,8-TCDD\ peak} \times 100 = \leq 25\%$$

6.4.4 Evaluation and Action

Evaluation	Action
A. For all columns, verify from the SICPs that the ≤ 25% valley criteria for the TCDD isomers are met.	A. If GC resolution criteria for TCDD does not meet required specifications, positive results for tetra, penta and hexa isomers shall be qualified as "J" (for both dioxin and furans). The hepta isomers are not believed to be affected. OCDD and OCDF are not affected as there is only one isomer in each group. No action is taken for non-detects.
B. For the DB-5 column, verify that the ≤ 50% valley criteria for the HxCDD isomers are met.	B. If resolution criteria for the HxCDD isomers is not met, positive results for HxCDD isomers should be qualified "J" (both dioxin and furan). No action is needed for non-detected analytes. • The criteria for chromatographic resolution must be met for all standards and the data reviewer should use his or her professional judgment to determine severity of the problem and effect on final results.

6.5 Initial Calibration

6.5.1 Review Items: 6DFA (Form VI PCDD-1, or equivalent), 6DFB (Form VI PCDD-2, or equivalent), Raw Data for all standards

6.5.2 Objective

A. Compliance requirements for satisfactory instrument calibration are established to ensure the instrument capable of producing acceptable qualitative and quantitative data for compounds in the Target Compound List.

B. The purpose of initial calibration is to establish a linear range for the instrumentation. The initial calibration is not to be used for routine quantitation of samples. All samples are quantitated using Relative Response Factors (RRFs) established from the CC3 standard, run either as part of initial calibration or as a continuing calibration every 12 hours.

6.5.3 Criteria

A. Five concentration calibration solutions shall be analyzed prior to any sample analysis.

B. The ± 15% control limit for ion abundance criteria for PCDDs/PCDFs listed in Table 3 must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards in all solutions. The ^{37}Cl-2,3,7,8-TCDD clean-up standard contains no ^{35}Cl; thus the ion abundance ratio criteria does not apply to this compound.

C. The absolute retention times of recovery standards shall not change by more than 15 seconds between initial CC3 and analysis of any other standard.

D. For all calibration solutions, including CC1 solution, the signal-to-noise ratio (S/N) must be greater than 10 for internal standard and recovery standard ions and greater than 2.5 for unlabeled PCDD/PCDF ions. The percent recovery of the internal standard should be within 25-150%.

E. The percent Relative Standard Deviation (%RSD) of the five Relative Response Factors (RRFs)(CC1-CC5) for each unlabeled PCDD/PCDF and labeled internal standards must not exceed 20 percent.

$$\%RSD = \frac{Standard\ Deviation}{Mean\ RRF} \times 100$$

Note: No mean RRF or % RSD calculations are possible for the 2,3,7,8-substituted isomers which are present only in the CC3 solution.

F. For all unlabeled PCDD/PCDF and labeled standards, the selected ion current profile (SICP) for the two quantitation ions (and the confirmation ion M-[COC1]$^+$ in LRMS) must maximize simultaneously (±2 seconds). This does not apply to the clean up standard since only one ion is monitored.

6.5.4 Evaluation and Action

Evaluation	Action
A. Verify an initial calibration (five concentration standards) has been performed prior to any sample analysis.	A. If an initial calibration was not performed prior to sample analysis, all data should be rejected and qualified "R".
B. Verify correct concentrations and ions are being used for response factor (RF) calculations. Recalculate ~10% relative response factors (RRF) from raw data. • Verify correct internal standards (Table 4) are being used for target compounds as stated in the method.	B. If incorrect concentrations and ions are being used for response factor (RF) calculations, professional judgment should be used to determine effect on data. • If incorrect internal standards (Table 4) are being used for target compounds, professional judgment should be used to determine effect on data.
C. Confirm ion abundance ratios for native analytes and internal standards are within their control limits (Table 3). Recalculate 10% of the ratios and verify that the correct ions are being used.	C. If the analyte failed ion abundance ratio criteria, the reviewer should determine the extent of ratio dislocation from the theoretical window. If ion ratio is between 16-20%, qualify all non-detects "UJ" for all samples associated with that initial calibration. If ion ratio is greater than ± 20%, qualify all non-detects as unusable "R". Frequent occurrences of ion abundance outliers in standards may indicate MS tuning problems which require laboratory corrective action. When there is a chronic problem meeting ion abundance ratios for standards, positive results should be qualified "N" as tentatively identified. At reviewer's discretion, a more in-depth review to minimize qualification of data can be accomplished by considering the following. • If the ion abundance ratio is outside the limits for an analyte in the CC1 solution, the low-end results for that analyte are flagged "R". • If the ion abundance ratio in a more concentrated standard failed, the higher concentration is flagged "R".

Evaluation		Action	
D.	Verify retention time for all calibration standards are within retention time window and retention times for recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD are within 15 seconds of initial CC3 analysis RT.	D.	If the recovery standards RT drift by more than ± 15 seconds from initial CC3 analysis, the GC system is unusable and all data (detects & non-detects) should be qualified "R". If the retention times for any standards are not within the retention time window, estimate (J) all positive values and (UJ) not-detects associated with the RT shifts in the initial calibration.
E.	Verify S/N ratio is >10 for all internal and recovery standards and >2.5 for all unlabeled PCDD/PCDF isomers in all calibration standards.	E.	If S/N ratio is < 2.5 for any unlabeled standards, the instrument sensitivity may be impacted. In this case, all non-detects in samples analyzed since the last acceptable calibration should be rejected and qualify "R". If S/N ratio for the labeled internal and recovery standards are < 10, sensitivity of the instrument may be impacted. This outlier may also indicate that the internal standards were not properly spiked into this standard. Examine the IS S/N ratio in the continuing calibration (CC3) standards for any trend regarding this non-compliance. Also, examine recovery of the ISs as described in Section 6.11. Qualify data using professional judgment.
F.	Inspect mean RRF and ensure percent relative standard deviation (RSD) is ≤ 20% for all target and internal standard compounds.	F.	If an RSD is ≤ 20%, no qualification of data is required. If RSD is > 20% but < 30%, all associated data must be qualified as estimated (J or UJ). If RSD is > 30%, examine the possibility of directing the RSD to within 30% by discarding either the CC1 or CC5 RRF values. If discarding either of those two points bring the RSD within 30%, then reject data associated with the offending portion of calibration (low or high), depending on which point was discarded. If non-linearity impacted a majority of data, the data should be rejected (R) and the Region 3 TPO notified.

6.6 Continuing Calibration

6.6.1 Review Items: 7DFA (Form VII PCDD-1, or equivalent), 7DFB (Form VII PCDD-2, or equivalent), Raw data from the CC3 standard.

6.6.2 Objective

Compliance requirements for satisfactory instrument calibration are established to ensure the instrument capable of producing acceptable qualitative and quantitative data. Continuing calibration establishes 12-hour relative response factors on which quantitations are based, and additionally confirms satisfactory performance of the instrument on a day-to-day basis.

6.6.3 Criteria

A continuing calibration standard is analyzed to demonstrate validity of initial calibration. For a valid continuing calibration, the following criteria must be met:

A. The CC3 solution should be analyzed at the beginning of each 12-hour period.

B. GC Column Resolution, Ion Abundance, Retention Time and S/N ratio criteria as described under initial calibration.

C. Response factors for each analyte and internal standard in the CC3 solution must be within 30% of the mean RRF established during initial calibration. Check ~ 10% of the RRFs from raw data.

$$\left| \%D = \frac{RRF_i - RRF_c}{RRF_i} \times 100 \right|$$

where:

%D = Percent difference
RRFi = Initial calibration relative response factor
RRFc = Continuing calibration relative response factor

6.6.4 Evaluation and Action

Evaluation		Action	
A.	Verify continuing calibration was analyzed at required frequency and was compared to the appropriate initial calibration.	A.	If continuing calibration was not performed at required frequency, evaluate all other QC requirements (ion ratio, S/N ratio, RT). If all other QC criteria are acceptable, make a note relative to absence of continuing calibration data in the report narrative. Retention time, ion ratio or S/N outliers for internal and/or recovery standards may indicate system instability. Notify Region 3 WAM of the situation.
B.	Verify from raw data that GC column resolution criteria are met.	B.	Refer to Section 6.4 (Chromatographic Resolution) for guidelines.
C.	Verify from raw data that relative ion abundance criteria are met for all analytes (see Table 3).	C.	Any analyte in samples associated with a continuing calibration not meeting the ± 25% ion abundance criteria listed in Table 3 is to be rejected "R". Positive results should be qualified "N" due to questionable instrument stability. A note should be included in the report narrative regarding this non-compliance.
D.	Verify S/N ratio are met (see Section 6.5)	D.	Refer to Section 6.7 (Instrument Sensitivity) for guidelines.
E.	Verify response factors for each analyte and internal standard in CC3 solution are within 30% of the mean RRF established during initial calibration. Check ~10% of the RRFs from raw data.	E.	Data associated with an analyte with a %D between 30% and 50% should be flagged "J" for positive values and "UJ" for non-detected values. All associated non-detects with % D above 50% are rejected and qualified "R".
F.	Verify that the absolute retention time for the two recovery standards do not shift more than ± 15 seconds between initial CC3 analysis and continuing calibration standard.	F.	The recovery standards RT shift indicate an unstable GC system. If shift was greater than 15 seconds, qualify all data (detects and non-detects) as unusable "R".
G.	Verify that the two quantitation ions (and the confirmation ion M-$[COCl]^+$ in LRMS analysis) for all unlabeled and labeled PCDD/PCDF standards maximize simultaneously (± 2 seconds).	G.	If this criterion was not met for the calibration labeled and unlabeled standards, the non-detected analytes should be qualified "R".

6.7 Instrument Sensitivity Check

6.7.1 Review Items: Raw data for CC1 standard at end of each 12-hour shift and the associated chromatogram.

6.7.2 Objective

In order to demonstrate that the GC/MS system has retained adequate sensitivity during the course of sample analysis, the lowest concentration calibration standards CC1 is analyzed at the end of each 12-hour period during which samples and standards are analyzed.

6.7.3 Criteria

A. The GC/MS sensitivity must be demonstrated every 12 hours by analysis of a CC1 standard which must pass the following criteria:

- The absolute RT for the recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD must be within 10 seconds of initial CC3 and ending CC1 analysis. For all labeled and unlabeled PCDD/PCDF standards, the SICP for the two quantitation ions (and confirmation ion M-[COCl]$^+$ for LRMS) must maximize simultaneously (± 2 seconds).

- For the CC1 solution, S/N ratio must be > 10 for labeled internal and recovery standards and > 2.5 for the unlabeled PCDD/PCDF standards. The percent recovery of internal standards should be between 25 - 150 percent.

- Ion abundance ratio criteria described in Section 6.5 must be met.

6.7.4 Evaluation and Action

Evaluation	Action
A. Verify that the absolute RT for recovery standards $^{13}C_{12}$-1,2,3,4,-TCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD is within 15 seconds of initial CC3 and ending CC1 analysis. Verify the two quantitation ions (and confirmation ion M-[COCl]$^+$ for LRMS) maximize simultaneously (± 2 seconds).	A. If the RT changes more than ± 15 seconds, then look for reanalysis of samples. If reanalysis was not performed, notify Region 3 WAM to request reanalysis. In cases where this criterion was not met but the data needs to be used before reanalysis, examine the RT of the recovery standards in each sample.

Evaluation		Action	
B.	Verify that the CC1 solution's S/N ratio is >10 for labeled internal and recovery standard compounds and >2.5 for unlabeled PCDD/PCDF standards.	B.	If the quantitation ions S/N ratio is acceptable and all other QC criteria (RT, ion ratio) are met, then data are usable. If the two quantitation ions S/N ratio is < 2.5, all non-detects in samples analyzed since last acceptable CC1 should be rejected and qualified "R". If the S/N ratio for the labeled internal and recovery standards are < 10, the sensitivity of the instrument may be adversely impacted. This outlier may also indicate internal standards were not properly spiked into this standard. Examine the internal standard (IS) S/N ratio in the continuing calibration (CC3) standards for any trend of this non-compliance. Also, examine the recovery of the ISs as described in Section 6.11 and qualify data using professional judgment.
C.	Verify ion abundance ratios listed in Table 3 are met within ± 15% theoretical ion abundance window.	C.	If ion abundances ratios are not within specified 15% theoretical window, then integrity of data is at jeopardy. All results obtained since the last acceptable CC3 should be rejected "R".

6.8 Method Blank

6.8.1 Review Items: 4DF(Form IV PCDD, or equivalent), Raw data

6.8.2 Objective

The purpose of laboratory, instrument and field blank analyses is to determine presence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with samples (i.e., method blanks, instrument blanks, trip blanks, and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to identify an inherent variability in the data, or determine that the problem is an isolated occurrence not affecting other data.

6.8.3 Criteria

A. A method or instrument blank must be analyzed on each GC/MS system

for each extraction batch and each matrix for each 12-hour period.

B. Any confirmed labelled PCDD/PCDF analytes found in a blank must not exceed 2% of the signal for the appropriate internal standard.

C. An acceptable blank must not contain any chemical interference or noise at m/z of the unlabeled PCDD/PCDF ion that is > 5% of that associated with the internal standard quantitation ion.

D. The internal standard recovery must be between 25 - 150 percent for all blanks.

E. To avoid instrument carry over, an instrument blank should be analyzed following a sample analysis which contained an analyte at high concentration.

6.8.4 Evaluation and Action

Evaluation	Action
A. Verify a method or instrument blank has been analyzed for each extraction batch and each matrix for each 12 hour period on each GC/MS system used for analysis.	A. If the method blank was not analyzed at required frequency, non-detected results should be accepted without qualifying data. Use professional judgment to qualify positive results in the associated samples. If contamination is suspected, positive results should be flagged "J". Make a note relative to this non-compliance in the validation report narrative. If method or instrument blanks are missing from the data package, notify Region 3 WAM.

Evaluation	Action
B. Determine if any positive PCDD/PCDF analytes are found in any of the blanks analyzed. Recalculate and verify the concentration.	B. If blanks (method or field) are contaminated, use the highest concentration of contaminant found for qualifying purposes. Any compound detected in the sample (other than OCDD and OCDF) that was also detected in any associated blank is qualified "B", if the sample concentration is less than five times (≤ 5X) the blank concentration. If the detected analyte in the blank is OCDD/OCDF, then all OCDD/OCDF data that are less than 10 times the blank concentration are to be qualified "B". Make certain sample dilution factor, weight/volume and percent solids are accounted for in applying the 5X/10X rule. If there is convincing evidence that contamination is restricted to a particular instrument, matrix, or concentration level, qualify only associated samples (as opposed to all samples in the case) using the 5X/10X rule. If contaminants found are interfering non-target analytes at significant concentration, then make a note regarding this issue in the validation report narrative. **NOTE**: If any 2,3,7,8-chlorine substituted isomer was qualified "B" due to blank contamination, include the value for that isomer on the Data Summary Form (DSF); however, **do not** calculate the Toxicity Equivalent (TEQ) for that isomer and **do not** add to the total TEQ value.
C. Verify an instrument blank was analyzed following a sample which contained an analyte(s) at high concentration(s).	C. If an instrument blank was not analyzed when required, use professional judgment to evaluate cross-contamination. Sample results which are possible artifacts of carry-over should be qualified "B".

6.9 Matrix Spike

6.9.1 Review Items: 3DFA (Form III PCDD-1, or equivalent), Raw Data

6.9.2 Objective

In order to provide data relative to the accuracy of the analytical method, the laboratory is required to prepare and analyze a spike sample for every 20 samples for each matrix analyzed. If the Region or samplers have identified a particular sample to be used for the spike, the laboratory must use an aliquot of that sample. If the Region or samplers have not identified a specific sample for spiking, then the laboratory may choose a sample from the SDG; however, the sample chosen must not be a sample identified by the Region as a field or trip blank.

6.9.3 Criteria

A. For each matrix (soil/sediment, fly ash, waste or water, etc.) in a SDG (20 maximum), a matrix spike must be analyzed.

B. The same weight/volume of sample is spiked with 1 mL of the spiking solution (Table 5), allowed to equilibrate for 1 hour, then extracted, cleaned-up and analyzed.

C. The percent recovery (%R) of each spiked analyte must be in the range of 50 - 150 percent.

$$\%R = \frac{Spiked\ Sample\ Result - Sample\ Result}{Spike\ Added\ concentration} \times 100$$

6.9.4 Evaluation and Action

Evaluation		Action	
A.	Verify that for each matrix (soil/sediment, fly ash, waste or water, etc.) in a SDG (20 maximum), a matrix spike was analyzed.	A.	Neglect in analyzing a matrix spike for (soil/sediment, fly ash, waste or water) each SDG (20 maximum) is a contract issue. A note regarding this non-compliance should be included in the report narrative.
B.	Verify concentration and recovery of each analyte and recovery of each spiked compound. Recalculate ~10% of recoveries from raw data.	B.	No data are qualified based on the matrix spike outliers. However; in conjunction with other QC outliers, the reviewer may use spike results to determine sample data usability.
C.	Inspect positive results for non-spiked compounds in both parent and MS samples.	C.	Construct a table showing original sample results for non-spiked isomers and matrix spike results for those isomers. Calculate Relative Percent Difference (RPD) between the two results.

6.10 Laboratory Duplicate Analysis

6.10.1 Review Items: 3DFB (Form III PCDD-2, or equivalent), Raw Data

6.10.2 Objective

In order to provide data regarding the precision of the analytical method, the laboratory is required to prepare and analyze a duplicate of one sample for every 20 samples for each matrix being analyzed. If the Region or samplers have identified a particular sample to be used for the duplicate, the laboratory must use an aliquot of that sample. If the Region or samplers have not identified a specific sample for duplicate analysis, then the laboratory may choose a sample from the SDG; however, the sample chosen must not be a sample identified by the Region as a field or trip blank.

6.10.3 Criteria

A. For each matrix (soil/sediment, fly ash, waste or water, etc.) in a SDG (20 maximum), a duplicate sample must be analyzed.

B. The Relative Percent Difference (RPD) of any detected analyte must be less than or equal to 50 percent using the following equation:

$$RPD = \frac{|Sample\ Result - Duplicate\ Result|}{(Sample\ Result + Duplicate\ Result) / 2} \times 100$$

6.10.4 Evaluation and Action

Evaluation		Action	
A.	Verify that a duplicate sample has been analyzed for each matrix in an SDG.	A.	Neglect in analyzing a duplicate for (soil/sediment, fly ash, waste or water, etc.) each SDG (20 maximum) is a contract issue. A note regarding this non-compliance should be included in the report narrative.
B.	The RPD of any analyte detected must be within the 50% range.	B.	If RPD is greater than 50%, qualify all positive results "J" for associated samples. No action is needed for non-detects.

6.11 Internal Standard and Clean-Up Standard Recoveries

6.11.1 Review Items: 1DFA (Form I PCDD-1, or equivalent), Raw Data

6.11.2 Objective

The recovery of the internal and clean-up standards is the principal measure of extraction and clean-up step effectiveness, respectively. The $^{37}Cl_4$-2,3,7,8-TCDD clean-up standard is added to the sample extracts after extraction and before any clean-up steps to monitor efficiency of clean-up steps.

6.11.3 Criteria

If the original sample, prior to any dilutions, has any internal or clean-up standard with a percent recovery of less than 25% or greater than 150%, reextraction and reanalysis of that sample is required.

6.11.4 Evaluation and Action

Evaluation	Action
A. Verify that the correct internal standard was used in calculation of PCDD/PCDF values (Table 4). • Verify original sample, prior to any dilutions, has internal or clean-up standard recoveries between 25% and 150%. If not, verify that the sample in question was reextracted and reanalyzed. • If recovery of an internal standard is <10% for both initial and reanalysis, verify that results are quantitated using recovery standards.	A. If any internal or clean-up standard recoveries were outside the 25% - 150% in the original extract prior to any dilutions and no re-extraction/reanalysis was performed, notify Region 3 WAM. • Recoveries outside 150% indicate errors in quantitation of labeled compounds or problems with spiking of sample extract. High recoveries may also indicate matrix effect. Qualify positive results associated with that internal standard as "J". • If recoveries are ≥10% and < 25% in the original and reanalysis of the sample, qualify positive results "J" and non-detects "UJ". • If recovery of an internal standard is <10% in both initial and reanalysis, quantitation is severely impacted and results quantitated using recovery standards may be biased low. Qualify positive results "J" and non-detects "R". Make a note in the report narrative that reported results may be biased low.

6.12 Sample Analysis and Identification

6.12.1 Review Items: 1DFA (Form I PCDD-1, or equivalent), 2DF (Form II PCDD, or equivalent), Raw Data

6.12.2 Objective

To minimize erroneous identification of analytes. For a peak to be identified as a PCDD/PCDF component, verify the following criteria have been met.

6.12.3 Criteria

A. All chromatograms must be labeled with RT at the apex of each peak or in the quantitation report.

B. For positive identification of 2,3,7,8-TCDD/TCDF for which an isotopically labeled standard (internal or recovery) is present in the extract,

the absolute RT must be within -1 to +3 seconds of the RT of the corresponding ^{13}C-labeled standard.

C. If a labeled standard is not present, the Relative Retention Time (RRT) of the 2,3,7,8 analyte must be within 0.005 RRT units of the RRT established during CC3 analysis for that analyte.

$$RRT = \frac{RT \text{ of Analyte}}{RT \text{ of Corresponding IS}}$$

D. For non-2,3,7,8-compounds, the RT must be within the retention window established by window defining mix for the corresponding homologue (± 10 seconds on either side).

E. The two quantitation ions (and confirmation ion M-$[COCl]^+$ in LRMS analysis) must maximize simultaneously (± 2 seconds) for target analytes, internal and recovery standards.

F. The S/N ratio for each quantitation ion peak must be at least 2.5 times background noise. The internal standard S/N ratio must be greater than 10 times the background noise. In LRMS analysis, if the (M-$[COCl]^+$) ion does not meet the S/N ratio of ≥ 2.5 requirement but meets the remaining criteria, the isomer may be reported as PCDD/PCDF positive and data flagged "S" on Form Is by the laboratory.

G. Polychlorinated Diphenyl Ether (PCDPE) interferences must be monitored to determine interferences with furan isomers. If the PCDPE isomers had a S/N ≥ 2.5 and was within the PCDF isomer RT (± 2 seconds), the concentration of the furan isomer is reported as Estimated Maximum Possible Concentration (EMPC) by the laboratory.

H. The recoveries of the internal standards must be within 25% - 150%.

6.12.4 Evaluation and Action

Evaluation		Action	
A.	Verify absolute RT is within -1 to +3 seconds of the RT of the corresponding ^{13}C-labeled standard for positive identification of 2,3,7,8-PCDD/PCDF.	A.	If a peak falls outside the -1 to +3 second window, results cannot be positively identified as a PCDD/PCDF and should not be reported.
B.	Verify that if a labeled standard is not present, the RRT of the 2,3,7,8 analyte is within 0.005 RRT units of the RRT established by CC3 analysis.	B.	If the RRT criteria are not satisfied, data are reported as non-2,3,7,8 PCDD/PCDF by Region 3.
C.	Verify that for non-2,3,7,8 substituted isomers, the RT is within the ± 10 seconds of the RT windows established by the window defining mix.	C.	If the required RT is outside the WDM window, data should be considered non-detect.
D.	Verify quantitation ions and M-$[COCl]^+$ maximize simultaneously (± 2 sec) for target compounds.	D.	If the required RT was not met, results are reported as non-detects.
E.	Verify S/N ratio for each ion peak is at least 2.5 times background noise and the S/N ratio for each internal standard is at least 10 times background noise.	E.	If S/N criteria are not satisfied for the quantitation ions, results are reported as non-detects and qualified as estimated "UJ". If S/N ratio criteria are met except for the confirmation ion M-$[COCl]^+$, report the positive result. Make a note of this outlier in the report narrative.
F.	Verify theoretical ion abundance criteria listed in Table 3 are met. If ion abundances are greater than ± 15%, verify they are within Region 3 expanded window of ± 25%.	F.	If ion abundance criterion for a detected analyte is outside ± 15% theoretical ion abundance ratio but within Region 3 expanded ± 25%, report positive result as true PCDD/PCDF isomer and qualify "J" on the DSF. If ion abundance ratio is outside the ± 25%, confirm the value is reported as EMPC by the laboratory. If internal standard ion abundance ratio is outside ± 15% ratio, notify Region 3 WAM for action. When the standards are not positively identified by a laboratory, then the stability of mass spectra is in question. Qualify reported results as "N" and reject (R) the non-detects.

Evaluation	Action
G. Examine chromatogram for presence of polychlorinated diphenyl ether (PCDPE) interferences in PCDPE channel. Determine S/N ratio and RT relative to the furan isomer (± 2 Seconds).	G. If PCDPE interferences exist (S/N >2.5, RT within ± 2 seconds), qualify positive furan results "I".

6.13 Sample Quantitation and Total Homologue

6.13.1 Review Items: 1DFA (Form I PCDD-1, or equivalent) 2DFA (Form II PCDD, or equivalent), Raw Data

6.13.2 Objective

To minimize erroneous quantitation of analytes, verify the following criteria were used for quantitation of PCDD/PCDF. Recalculate 10% of the positive results.

6.13.3 Criteria

A. For a homologue that contains only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCCD and TCDF), the RRF of the 2,3,7,8- substituted isomer from CC3 standard must be used to quantitate both the 2,3,7,8-substituted and non-2,3,7,8- substituted isomers.

B. For a homologue that contains more than one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF and HpCDF), the RRF of the relative isomer from the CC3 standard must be used for calculation of the 2,3,7,8-substituted isomers.

C. For a homologue that contains one or more non-2,3,7,8- isomers, the RRF used for calculation must be the lowest RRF determined for 2,3,7,8-substituted isomers in the CC3 standard. This will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

D. In addition to the concentration of specific isomers, the total homologue concentrations must be reported. The total must include the 2,3,7,8-substituted isomers and all the non-2,3,7,8-substituted isomers. The total number of GC peaks included in the total homologue concentration must be specified by the laboratory.

E. Results must be reported in µg/Kg (Low Res) and ng/Kg (High Res) for

soil/sediment, fly ash and chemical waste and in ng/L (Low Res) and pg/L (High Res) for water samples.

6.13.4 Evaluation and Action

Evaluation		Action	
A.	Verify that for a homologue that contains only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCCD and TCDF), the RRF of the 2,3,7,8-substituted isomer from CC3 standard was used to quantitate both the 2,3,7,8-substituted and non 2,3,7,8- substituted isomers.	A.	If there is a discrepancy of > 10% between reviewers calculation and value reported, the laboratory should be requested through RPO to provide additional information and/or clarification to resolve differences. If the discrepancy remains unresolved, use professional judgment to decide which is the more reliable value and whether qualification is warranted. Note this discrepancy in the validation report narrative.
B.	Verify that for a homologue that contains more than one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF and HpCDF), the RRF of the relative isomer from the CC3 standard was used for calculation of the 2,3,7,8-substituted isomers.	B.	If there is a discrepancy of > 10% between reviewers calculation and value reported, the laboratory should be requested through RPO to provide additional information and/or clarification to resolve the differences. If the discrepancy remains unresolved, use professional judgment to decide which is the more reliable value and whether qualification is warranted. Note this discrepancy in the validation report narrative.
C.	Verify that for a homologue that contains one or more non-2,3,7,8-isomers, the RRF used for calculation was the lowest RRF determined for 2,3,7,8-substituted isomers in the CC3 standard. This will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.	C.	Follow the Action comment under A.

Evaluation		Action	
D.	Verify that in addition to the concentration of specific isomers, the total homologue concentrations have been reported on Form 2DF (Form II PCDD). The total must include the 2,3,7,8- substituted isomers and all the non-2,3,7,8-substituted isomers. Verify that the total number of GC peaks included in the total homologue concentration is correctly reported by the laboratory.	D.	Examine chromatograms to verify no false negatives/positives are reported. Any peak that meets the identification criteria (ion ratio, RT, S/N ratio) noted under Section 6.12 must be accounted for and reported. Many laboratories report 2,3,7,8-chlorine substituted TCDDs and TCDFs and total dioxins/furans concentrations including the 2,3,7,8-substituted isomers. Region 3 separates 2,3,7,8-chlorinated isomers from total isomers for each congener group and reports results as 2,3,7,8-chlorine substituted and "Other" dioxin/furan isomers. Subtract 2,3,7,8 PCDD results from the total PCDD results to obtain the concentrations for "Other" PCDD/PCDF isomers.
E.	Results must be reported in µg/Kg (Low Res) and ng/Kg (High Res) on a dry weight basis for soil/sediment, fly ash and chemical waste and in ng/L (Low Res) and pg/L (High Res) for water samples.	E.	Some laboratories provide % solids data; however, report the concentrations on a wet weight basis. Make certain that all results for non-aqueous matrix samples are corrected for moisture content and that the concentrations are reported on a dry weight basis. Note any discrepancies (i.e., sample results due to % solids correction) in the validation report narrative.

6.14 Estimated Detection Limit (EDL) and Estimated Maximum Possible Concentration (EMPC)

6.14.1 Review Items: 1DFA (Form I PCDD-1, or equivalent), Raw Data

6.14.2 Objective

A. For each analyte not detected, an Estimated Detection Limit (EDL) is calculated. The sample specific EDL is an estimate made by the laboratory of the concentration of a given analyte that would have to be present to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc. Because of the toxicological significance of PCDDs and PCDFs, the EDL value is reported for non-detected analytes rather than reporting the Contract Required Quantitation Limit (CRQL).

B. The Estimated Maximum Possible Concentration (EMPC) is a value reported by the laboratory regarding an isomer for which the signal-to-noise ratio is at least 2.5 for both quantitation ions that do not meet all the identification criteria listed under Section 6.12.

6.14.3 Criteria

A. The EDL is calculated for each 2,3,7,8-substituted isomer that is not identified in the sample extract.

$$Aqueous\ EDL\ (ng/L) = \frac{2.5\ x\ Q_{IS}\ x(H_{x1} + H_{x2})\ x\ D}{V\ x\ (H_{IS1} + H_{IS2})\ x\ RRF_n}$$

$$Soil\ EDL\ (ng/g) = \frac{2.5\ x\ Q_{IS}\ x(H_{x1} + H_{x2})\ x\ D}{W\ x\ (H_{IS1} + H_{IS2})\ x\ RRF_n}$$

where:

Q_{IS} * = Quantity (ng) of appropriate internal standard added to sample prior to extraction.

H_{X1}, H_{X2} = Peak heights of the noise for both quantitation ions of the PCDD/PCDF.

H_{IS1}, H_{IS2} = Peak heights of the internal standard quantitation ions

D = Dilution factor

V = Volume of sample extracted in liters

W * = Weight of sample extracted in grams

RRF_n = Relative Response Factor for the isomer of interest from CC3 standard

* = Note: High Resolution Mass Spectrometry (HRMS) aqueous and soil sample results are reported in units of pg/L and pg/g, respectively. The internal standard quantity in these analyses will be in the unit of pg. In cases where HRMS soil results are reported in ng/Kg, amend equation (i.e., sample weight in Kg) to reflect the final reported units.

B. An EMPC is calculated for 2,3,7,8-substituted isomers that have S/N ratio > 2.5 for both the quantitation ions, but do not meet all the identification criteria.

$$Aqueous\ EMPC\ (ng/L) = \frac{Q_{IS}\ x\ (A_{x1} + A_{x2})\ x\ D}{V\ x\ (A_{IS1} + A_{IS2})\ x\ RRF_n}$$

$$Soil\ EMPC\ (ng/g) = \frac{Q_{IS}\ x\ (A_{x1} + A_{x2})\ x\ D}{W\ x\ (A_{IS1} + A_{IS2})\ x\ RRF_n}$$

where:

Q_{IS} * = Quantity (ng) of appropriate internal standard added to sample before extraction

A_{X1}, A_{X2} = Integrated areas of both quantitation ions

A_{IS1}, A_{IS2} = Integrated areas of both quantitation ions of the appropriate internal standard

D = Dilution Factor

V = Volume of sample extracted in liters

W * = Weight of sample extracted in grams

RRF_n = Relative Response Factor for the isomer of interest

* = Note: High Resolution Mass Spectrometry (HRMS) aqueous and soil sample results are reported in units of pg/L and pg/g, respectively. The internal standard quantity in these analyses will be in the unit of pg. In cases where HRMS soil results are reported in ng/Kg, amend equation (i.e., sample weight in Kg) to reflect the final reported units.

6.14.4 Evaluation and Action

Evaluation	Action
A. Verify EDLs are properly calculated. Recalculate 10 % of EDLs from raw data. • EDL must be reported for each undetected analyte. Except when increased due to dilution of the extract, EDL must be less than the CRQL.	A. If EDLs are not properly calculated or reported notify RPO/WAM to request clarification from the laboratory. • If EDL > CRQL after adjusting for dilution, notify RPO/WAM for action and note this non-compliance in the validation report summary. • If there is a discrepancy of > 10 % between reviewer's calculation and the value reported, request laboratory clarification through RPO/WAM. If the discrepancy remains unresolved, use professional judgment to decide which is the more reliable value and if qualification of data is warranted.

Evaluation	Action
B. Verify analytes reported as EMPCs meet all identification criteria except ion ratio criteria of ± 15%.	B. Note that when other criteria (RT, S/N ratio) except ion ratio of ± 15% are met, the result is reported as EMPC by the laboratory. However, Region 3 uses ± 25% window for ion ratio. EMPC results with ion ratios > ± 15% but < ± 25% need to be reported as positive results and qualified "J". EMPC results with ion ratios > 25% are verified but are not reported by Region 3. The presence of EMPC should be noted in the validation report narrative.

6.15 Toxicity Equivalency Factor (TEF), Isomer Specificity and Second Column Confirmation

6.15.1 Review Items: 1DFB (Form I PCDD-2, or equivalent), Raw Data

6.15.2 Objective

Dioxin is an abbreviated term for a family of 210 related chlorine compounds known collectively as chlorinated dibenzo-p-dioxin and chlorinated dibenzofurans. Seventeen of the possible 210 chlorine congeners of dioxin and furan are 2,3,7,8-substituted. The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). All detected dioxin and furans are converted to 2,3,7,8-TCDD equivalents utilizing Toxicity Equivalent Factors (TEFs). Assuming toxic effects are additive, the TEFs for all isomers detected in a sample are totaled to obtain a Toxicity Equivalent (TEQ). The toxicity equivalent is used to determine if a second column confirmation or re-extraction/reanalysis is required.

Note: High Resolution GC/MS analysis requires confirmation if TCDD/TCDF are detected regardless of concentration.

6.15.3 Criteria

A. For each positively identified 2,3,7,8-chlorine substituted isomer, the TEF listed on Table 6 [also listed on form 1DFB (Form I PCDD-2)] is multiplied by the concentration to determine the TEF-adjusted concentration.

B. If the calculated TEQ value is greater than 7 ng/L for aqueous samples, greater than 0.7 µg/Kg for soil samples or greater than 7 µg/Kg for chemical waste samples, better isomer specificity than those that can be

achieved on a DB-5 column is required. The following may be exercised by the laboratory:

- The sample extract may be reanalyzed on a 60m SP-2330 or SP-2331 GC column to achieve better GC resolution and, therefore, better identification and quantitation of the individual 2,3,7,8-substituted isomers.
- The sample extract may be analyzed on a single GC column capable of resolving all 2,3,7,8-substituted PCDD/PCDFs from other isomers.
- For any sample analyzed on a DB-5 or equivalent column in which 2,3,7,8-TCDD and/or 2,3,7,8-TCDF is reported as EMPC, a second column confirmation which provides better isomer specificity is required, regardless of TEQ adjusted concentration or matrix.
- Values reported as EMPC or EDLs are not to be included in the total TEQ determination.

6.15.4 Evaluation and Action

Evaluation	Action
A. Verify 2,3,7,8-TCDD Toxicity Equivalency of the PCDD/PCDF present in sample has been calculated by summing the products of the concentration times the assigned TEF for each of the compounds listed in Table 6.	A. If calculations were not performed properly, report this non-compliance in the validation report narrative for contract action.
B. Verify confirmational analysis was carried out on an SP-2330, SP-2331 or another GC column capable of resolving all seventeen (17) 2,3,7,8-substituted isomers if: • TEQ > 0.7 µg/Kg for soil, sediment and fly ash • TEQ > 7.0 µg/Kg for chemical waste • TEQ > 7.0 ng/L for water. • High Resolution GC/MS analysis was utilized.	B. If second column confirmation was not performed, possibility of biased high results for 2,3,7,8-TCDF exists. Qualify positive results for this isomer as "J". Calculate %Ds between the two columns for detected results. Report the lower of the two values if the calculated concentrations of detected compounds did not agree within ± 25% between the two columns. Qualify the reported result as estimated "J".

Evaluation	Action
C. Verify that although 2,3,7,8-TCDD and/or 2,3,7,8-TCDF are reported as EMPCs on a DB-5 or equivalent column, a second column confirmation which provides better isomer specificity has been performed.	C. Concentrations reported as EMPC for which ion ratios are > 25% are not reported by Region 3. However, the lack of second column confirmation analysis should be noted in the validation report narrative for EPA action.

6.16 Required Sample Reruns

6.16.1 Review Items: Raw Data

6.16.2 Objective

Due to a variety of situations that may occur during sample analysis, the laboratory is required to reextract and reanalyze certain samples or groups of samples. Except in the case of dilutions, the term "rerun" indicates sample reextraction, cleanup, and reanalysis. When dilutions are required, the original extract is diluted and reanalyzed.

6.16.3 Criteria

A. If the original sample has a percent recovery of any internal and/or cleanup standard outside the 25 - 150% limit, then re-extraction and reanalysis are required.

B. If the internal or recovery standards S/N ratio is less than 10, then re-extraction/reanalysis is required.

C. If the ion ratio for any internal standard is outside the ± 15% theoretical ion abundance ratio, then reanalysis of the affected sample on a second GC column with different elution characteristics as described in Section 6.15 is required.

D. If the absolute RT of either $^{13}C_{12}$-1,2,3,4-TCDD or $^{13}C_{12}$-1,2,3,7,8,9-HxCDD recovery standard in a sample shifted by greater than 10 seconds from the retention time of that standard in the CC3 standard, reanalysis of the sample extract after investigation and correction of the problem is required.

E. If calculated concentration of any PCDD/PCDF analyte exceeds the calibration range, then the sample extract must be diluted and reanalyzed.

F. All samples with detected results associated with a contaminated method blank and any samples that contain peaks which do not meet all the qualitative identification criteria associated with a contaminated blank, must be re-extracted and reanalyzed.

G. If the chromatographic peak resolution is not resolved with a valley ≤ 25% in a sample, the GC/MS conditions must be adjusted and the affected samples "rerun". If this criterion is not met for a calibration standard, then all associated samples must be "rerun".

H. If a false positive is reported for a PE sample submitted by the region, the entire SDG must be re-extracted/reanalyzed upon notification by Contract Laboratory Analytical Services Support (CLASS).

I. If a concurrent PCDD/PCDF is being processed, the matrix spike and duplicate from that SDG may be shared with the rerun samples as long as the number of samples does not exceed 20.

6.16.4 Evaluation and Action

If the required reanalysis was not performed for the conditions listed below, notify the Region 3 TPO for EPA action.

Evaluation		Action	
A.	Verify that the required re-extraction/reanalysis was performed if the original sample had a percent recovery of any internal and/or cleanup standard outside the 25 - 150% range.	A.	If the "rerun" was not performed, notify the RPO/WAM. See Section 6.11 for action.
B.	Verify that a reextaction/reanalysis was performed if any internal or recovery standard ion had a S/N ratio < 10.	B.	See Section 6.11.
C.	Verify that a reanalysis on a second GC column was performed if any of the internal standard ion ratios are beyond the specified limits in Table 3.	C.	If the required reanalysis was not performed, notify the Region 3 RPO/WAM. When ion ratios for internal standards are outside the 15% window, reject the non-detects and qualify positive results as "N" (tentatively identified).

Evaluation		Action	
D.	Verify that a reanalysis was performed if the RT of the recovery standard has shifted by > 10 seconds from RT of that standard in the CC3 standard.	D.	If RT of any recovery standard shifted by more than 10 seconds, reject (R) all data (positives and non-detects).
E.	Verify sample extract was diluted and reanalyzed if the calculated concentration of any PCDD/PCDF analyte exceeds the calibration range.	E.	If dilution was not performed, qualify the reported results as estimated "J".
F.	Verify that all positive samples associated with a contaminated method blank, and any samples that contain peaks which do not meet all the qualitative identification criteria associated with a contaminated blank, were reextracted and analyzed.	F.	If re-extraction was not performed, notify the Region 3 WAM for action. If positive results are associated with contaminated blanks, follow guidelines provided in Section 6.8 for data qualification.
G.	Verify that if the chromatographic resolution was not resolved with a valley ≤ 25% in the sample, then the GC/MS conditions were adjusted and the affected samples were "rerun". If this criterion was not met for a calibration standard, then all associated samples were "rerun".	G.	See Sections 6.4, 6.5, and 6.6 for guidelines.
H.	Verify PE sample results are at least within 99% confidence interval (action limit).	H.	If the PE sample results are outside the 99% confidence interval, notify the Region 3 RPO/WAM for action and further instruction. Also see Section 6.1.
I.	Verify that a matrix spike and duplicate were performed for each group of samples rerun. If a concurrent PCDD/PCDF is processed, the matrix spike and duplicate may be shared as long as the number of samples does not exceed 20.	I.	If any required matrix spike and duplicate analyses were not performed with the rerun samples, make a note in the validation report narrative for EPA action.

6.17 Dilutions

6.17.1 Review Items: Raw Data (Quantitation Reports and Chromatograms)

6.17.2 Objective

A calibration range is defined by the initial calibration. All sample results must be within the calibrated range to be acceptable.

6.17.3 Criteria

A. If the concentration of any PCDD/PCDF in the sample has exceeded the calibration range or the detector has been saturated, a dilution must be performed.

DFLM01.2: Dilutions are performed using an aliquot of the original extract. Sufficient volume of recovery standard is added to this aliquot to yield a concentration of 0.5 ng/L (1.0 ng/L for ^{13}C-OCDD).

Method 1613B & 8290: Dilutions are performed by re-extracting the sample utilizing a one tenth aliquot of the initial weight/volume used. The concentrations of internal and recovery standards will remain the same as the initial extraction.

B. Diluted samples in which the MS response of any internal standard is > 10% of the MS response for that internal standard in the most recent continuing calibration standard should be quantified by the laboratory using the internal standards (DFLM01.2).

C. Diluted samples in which the MS response of any internal standard is < 10% of the MS response of that internal standard in the most recent continuing calibration standard should be quantified by the laboratory using the recovery standards (DFLM01.2).

6.17.4 Evaluation and Action

Evaluation	Action
A. Verify that all reported sample values are within the calibration range; if not, verify that the sample was diluted.	A. If a sample value is outside the calibration range, and a dilution was not performed, qualify all results outside the calibration range as estimated "J". Inform the Region 3 WAM and make a note in the validation report.

Evaluation	Action
B. Verify that the diluted sample results in which the MS response of any internal standard is < 10% of the MS response of that internal standard in the most recent continuing calibration standard are quantified by the laboratory using the recovery standards.	B. When dilutions are performed and the recovery of the internal standard is < 10% in the diluted analysis, the SOW requires the laboratory to calculate the results utilizing the areas of recovery standards instead of the areas of the internal standards. In the above case, it is preferred by Region 3 to use the undiluted sample results (original results which exceeded the calibration range) and qualify these data as "J". If the only result provided by the laboratory is the diluted sample result quantitated using the recovery standards, then report these data and qualify "J". In this case, make a note in the validation report narrative that this result is biased low.

7 POLLUTION PREVENTION

Paper generated during the performance of this guidance which is deemed not further usable is to be placed in the recycling bin.

8 REFERENCES

8.1 USEPA Contract Laboratory Program, Statement of Work for Analysis of Polychlorinated Dibenzo-P-Dioxin (PCDD) and Polychlorinated Dibenzofurans (PCDF), Multi-Media Multi-Concentration DFLM01.1, September 1991.

8.2 DRAFT USEPA Contract Laboratory Program, National Functional Guidelines for Dioxin/Furan Data Validation, Multi-Media Multi-concentration, January 1996.

8.3 Procedure for Region 3 Dioxin/Furan Data Validation, March 27, 1995.

9 TABLES

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Table 1

PCDD/PCDF Isomers In The Window Defining Mix For a 60 M DB-5 Column

Homologue	First Eluted	Last Eluted	Approximate Concentration (ng/µL)
TCDD	1,3,6,8-	1,2,8,9-	0.5
TCDF	1,3,6,8-	1,2,8,9-	0.5
PeCDD	1,2,4,7,9-	1,2,3,8,9-	0.5
PeCDF	1,2,3,6,8-	1,2,3,8,9-	0.5
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-	1.25
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-	1.25
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-	1.25
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-	1.25

Table 2

Ions Specified For Selected Ion Monitoring For PCDD/PCDF Isomers

Analyte	Quantitation Ions	Confirmation Ion ($M-[COCl]^+$) (1)
TCDD	320/322	259
PeCDD	356/358	293
HxCDD	390/392	327
HpCDD	424/426	361
OCDD	458/460	395
TCDF	304/306	243
PeCDF	340/342	277
HxCDF	374/376	311
HpCDF	408/410	345
OCDF	442/444	379
Internal Standards		
$^{13}C_{12}$-2,3,7,8-TCDD	332/334	---
$^{13}C_{12}$-1,2,3,7,8-PeCDD	368/370	---
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	402/404	---
$^{13}C_{12}$-2,3,6,7,8-HxCDD	402/404	---
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	424/426	---
$^{13}C_{12}$-OCDD	470/472	---
$^{13}C_{12}$-2,3,7,8-TCDF	316/318	---
$^{13}C_{12}$-1,2,3,7,8-PeCDF	352/354	---
$^{13}C_{12}$-2,3,4,7,8-PeCDF	352/354	---
$^{13}C_{12}$-1,2,3,47,8-HxCDF	384/386	---
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	384/386	---
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	384/386	---
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	384/386	---
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	418/420	---
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	418/420	---
Recovery Standards		
$^{13}C_{12}$-1,2,3,4-TCDD	332/334	---
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402/404	---
Clean-up Standard		
^{37}-Cl_4-2,3,7,8-TCDD	328 (2)	265
Polychlorinated diphenyl ether		
HxCDPE	376/---	---
HpCDPE	410/---	---
OCDPE	446/---	---
NCDPE	480/---	---
DCDPE	514/---	---

(1) - Confirmation ion is monitored only in Low Resolution analysis.
(2) - Only one quantitation ion is monitored for the cleanup standard.

Table 3
Criteria For Isotopic Ratio Measurement For PCDD/PCDF Isomers

Analyte	Selected Ions		Theoretical Ion Abundance	Control Limit ± 15%	± 25%
TCDD	320	322	0.77	0.65-0.89	0.58-0.96
PeCDD	356	358	1.55	1.32-1.78	1.16-1.94
HxCDD	390	392	1.24	1.05-1.43	0.93-1.55
HpCDD	424	426	1.04	0.88-1.20	0.78-1.30
OCDD	458	460	0.89	0.76-1.02	0.67-1.13
TCDF	304	306	0.77	0.65-0.89	0.58-0.96
PeCDF	340	342	1.55	1.32-1.78	1.16-1.94
HxCDF	374	376	1.24	1.05-1.43	0.93-1.55
HpCDF	408	410	1.04	0.88-1.20	0.78-1.30
OCDF	442	444	0.89	0.76-1.02	0.67-1.13
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	332	334	0.77	0.65-0.89	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	368	370	1.55	1.32-1.78	
$13C_{12}$-1,2,3,4,7,8-HxCDD	402	404	1.24	1.05-1.43	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	402	404	1.24	1.05-1.43	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	424	426	1.04	0.88-1.20	
$^{13}C_{12}$-OCDD	470	472	0.89	0.76-1.02	
$^{13}C_{12}$-2,3,7,8-TCDF	316	318	0.77	0.65-0.89	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	352	354	1.55	1.32-1.78	
$^{13}C_{12}$-2,3,4,7,8-PeCDF	352	354	1.55	1.32-1.78	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	384	386	0.51	0.43-0.59	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	384	386	0.51	0.43-0.59	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	384	386	0.51	0.43-0.59	
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	384	386	0.51	0.43-0.59	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	418	420	1.04	0.88-1.20	
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	418	420	1.04	0.88-1.20	
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	332	334	0.77	0.65-0.89	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402	404	1.24	1.05-1.55	

Table 4

Internal And Recovery Standards And The Associated PCDD/PCDF Analytes

~~Labeled Internal Standards & Associated Analytes (DFLM01.2)~~

Labeled Internal Standard	PCDD/PCDF
$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD, 1,2,3,7,8,-PeCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	OCDD, OCDF
$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF

Labeled Internal Standard & Associated Analytes (Method 1613B)

Labeled Internal Standard	PCDD/PCDF
$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
$^{13}C_{12}$-1,2,3,7,8-HxCDD	1,2,3,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD

Labeled Internal Standard & Associated Analytes (Method 1613B)

Labeled Internal Standard	PCDD/PCDF
$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,7,8-PeCDF	2,3,7,8-PeCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxCDF
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-1,2,3,4,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF

Recovery Standards & Associated Internal Standard

Labeled Recovery Standard	Labeled Internal Standard
$^{13}C_{12}$-1,2,3,4-TCDD	TCDD, TCDF, PeCDD, PeCDFs,
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	HxCDDs, HxCDFs, HpCDFs,

Table 5

Matrix Spike Solution Concentration

Analyte	Concentration (ng/L)
2,3,7,8-TCDD	2.5
2,3,7,8-TCDF	2.5
1,2,3,7,8-PeCDD	6.25
1,2,3,7,8-PeCDF	6.25
1,2,3,6,7,8-HxCDD	6.25
1,2,3,6,7,8-HxCDF	6.25
1,2,3,4,6,7,8-HpCDD	6.25
1,2,3,4,6,7,8-HpCDF	6.25
OCDD	12.5
OCDF	12.5

Table 6

**2,3,7,8-TCDD Toxicity Equivalency Factors (TEFs)
for PCDD/PCDF Isomers**

Analyte	TEF
2,3,7,8-TCDD	1.0
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	0.5
2,3,4,7,8-PeCDF	0.5
1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDD	0.001
OCDF	0.001