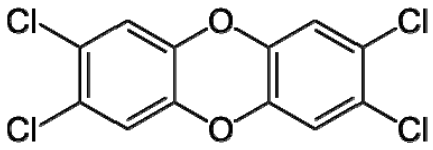
BACWA Guidance Document

Part II: Assessing Data Quality and Reporting Guidance

for

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS By Method 1613 Revision B (October 1994)



March 1, 2010

Table of Contents

1.0 Procedures for Laboratory Report Review

1.1. Key Definitions and Focus Areas for Laboratory Report Review

Effectively reviewing Dioxin/Furan laboratory reports from subcontract laboratories requires a thorough knowledge of several terms commonly used for this specialized testing area. This section will serve to identify those terms and acronyms to support a better understanding of the data generated and its application for regulatory compliance. Ultimately, being knowledgeable about the specific nuances of Dioxin/Furan testing will support the objective of only using valid, defensible data or clearly stating when data are 'estimated'.

The guidance provided in this document is based on Tentative Order No R2-2009 from the California Regional Water Quality Control Board (San Francisco Bay Region), '"Attachment G"' for NPDES Wastewater Discharge Permits (March 2010). This tentative order is referred to as '"Attachment G"' for the remainder of this guidance document. The reader is also urged to apply any additional instructions from its Agency's permit when interpreting the usability of subcontract laboratory data in support of Dioxin/Furan testing. The information provided in this document is intended as guidance.

While there are specific instructions for handling Dioxin/Furan data based on '"Attachment G"', background information for common terms customarily associated with Dioxin/Furan testing are presented in this guidance document.

1.1.1 WHO Toxic Equivalency Factors (TEFs) and Toxicity Equivalent (TEQ)

Dioxin is the abbreviated term for a family of 210 related chlorine compounds known collectively as chlorinated dibenzo-p-dioxin and chlorinated dibenzo furans (See Section A. 2. of Part I of this Guidance Document). Seventeen of the possible 210 chlorine congeners of dioxin and furans are substituted at the 2,3,7,8-positions with chlorine atoms. The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).

Unless otherwise instructed, all detected Dioxin/Furans in a laboratory report are typically converted to the toxicity relative to 2,3,7,8-TCDD through the use of Toxicity Equivalent Factors (TEFs) from the World Health Organization (WHO). This conversion occurs by multiplying the detected amount of the congener by the associated TEF. The assumption is that toxic effects are additive. Due to that assumption, the total of the concentrations detected of each congener are multiplied by the TEF to obtain a Toxicity Equivalent (TEQ).

$$\sum_{n=1}^{k} TEF_n \times C_n = TEQ$$

Where,

- ***C_n equals the concentration of the individual congener in the complex mixture under analysis.***
- ***TEF is determined by inspection of the available congener-specific data and an assignment of an 'order of magnitude estimate' of relative toxicity when compared to 2,3,7,8-TCDD as provided by the World Health Organization (WHO). See Table 1.***
- ***n equals the number of positive results***

Due to the specific reporting requirements adopted in '"Attachment G"', one additional factor for the Dioxin-TEQ calculation is used (BEF) which is discussed under Section 1.1.3 below. The purpose of Section 1.1.1 is to focus on defining TEF and TEQ.

The approach of relating toxicity to 2,3,7,8-TCDD was initiated in the United States in 1986 as a way to estimate potential health risks associated with a PCB transformer fire in Binghampton, NY. The original recommendation of this approach came from Canada in 1983 because the Ontario Ministry of the Environment produced a Scientific Criteria Document that advanced the concept that development of human health concerns should be based on a toxic equivalency approach with 2,3,7,8-TCDD. This recommendation was accepted by the EPA in 1984 as the best way to assign risk for complex mixtures to establish environmental standards for human health concerns. In other words, risk should be based on a "toxic equivalency" approach with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) as the prototype to transform various concentrations of PCDDs and PCDFs into equivalent concentrations of 2,3,7,8-TCDD. Hence, concentrations of PCDDs and PCDFs are analytically determined, the concentration of each congener is multiplied by its respective TEF value, and all the products are summed to give a single 2,3,7,8-TCDD equivalent.

1.1.2 The World Health Organization and TEFs

The overall approach for assigning risk for complex mixtures relative to 2,3,7,8-TCDD has been adopted globally. The World Health Organization (WHO) established TEFs for the 17 congeners in 1998 and updated them in 2005. TEFs are determined by inspection of the available congener-specific data and an assignment made of an 'order of magnitude' estimate of relative toxicity compared to 2,3,7,8-TCDD. These are considered reasonable estimates of the relative toxicity. Table 1 below details the TEFs assigned in 1998 and 2005.

Table 1: 1998 and 2005 WHO TEFs for 17 CDD/CDF Congeners

Congener	World Health Organization 1998 Toxicity Equivalence Factor (TEF)	World Health Organization 2005 Toxicity Equivalence Factor (TEF)
2,3,7,8-tetra CDD	**1**	**1**
1,2,3,7,8-penta CDD	**1**	**1**
1,2,3,4,7,8-hexa CDD	**0.1**	**0.1**
1,2,3,6,7,8-hexa CDD	**0.1**	**0.1**
1,2,3,7,8,9-hexa CDD	**0.1**	**0.1**
1,2,3,4,6,7,8-hepta CDD	**0.01**	**0.01**
octa CDD	***0.0001***	***0.0003****
2,3,7,8-tetra CDF	**0.1**	**0.1**
1,2,3,7,8-penta CDF	***0.05***	***0.03****
2,3,4,7,8-penta CDF	***0.5***	***0.3****
1,2,3,4,7,8-hexa CDF	**0.1**	**0.1**
1,2,3,6,7,8-hexa CDF	**0.1**	**0.1**
1,2,3,7,8,9,-hexa CDF	**0.1**	**0.1**
2,3,4,6,7,8-hexa CDF	**0.1**	**0.1**
1,2,3,4,6,7,8-hepta CDF	**0.01**	**0.01**
1,2,3,6,7,8,9-hepta CDF	**0.01**	**0.01**
octa CDF	***0.0001***	***0.0003****

Note: * *TEFs Updated in 2005.*

Based on requirements detailed in '"Attachment G"', the Dioxin-TEQ (Toxicity Equivalent) is to be calculated based on the 1998 TEFs. Agencies can choose to have the subcontract laboratory apply the 1998 TEFs to calculate a traditional Dioxin-TEQ or the subcontract laboratory can report the data as 'concentration only' so the Agency can apply the 1998 WHO TEF in its final report.

The following generic 'laboratory report page' is presented in Figure 1 below to show how data look when TEFs have been applied to calculate a traditional Dioxin-TEQ. In this example, the Agency has instructed the laboratory to calculate the Dioxin-TEQ based on the 1998 WHO TEFs. The laboratory has calculated Dioxin-TEQ for each result above the 'DL'. The result for each Dioxin or Furan above the laboratory's 'DL' is multiplied by the 1998 WHO TEF to get a Dioxin-TEQ result. The data highlighted in figure 1's yellow boxes in Figure 1 below were used by the laboratory for its calculations. The Dioxin-TEQ's are summed to get the Total Toxicity Equivalency which is highlighted in yellow on the last line of the example laboratory report page (0.465 pg/L):

Figure 1: Example Lab Report Page with Dioxin-TEQ Calculations

Sampling Date: 08/14/2007		Laboratory ID: U1598743				
DIOXINS/FURANS by Method 1613	**Units**	**Results**	**DL**	**1998 TEF (WHO)**	**TEQ (DL)**	
2,3,7,8-tetra CDD	pg/L	<0.601	0.601	1.00	0	
1,2,3,7,8-penta CDD	pg/L	<0.594	0.594	1.00	0	
1,2,3,4,7,8-hexa CDD	pg/L	0.934	0.587	0.1	0.0934	+
1,2,3,6,7,8-hexa CDD	pg/L	0.834	0.638	0.1	0.0834	+
1,2,3,7,8,9-hexa CDD	pg/L	1.20	0.632	0.1	0.120	+
1,2,3,4,6,7,8-hepta CDD	pg/L	1.51	0.629	0.01	0.0151	+
octa-CDD	pg/L	3.85	1.60	0.0001	0.000385	+
Total Tetra CDD	pg/L	1.14	0.601			
Total Penta	pg/L	3.28	0.594			
Total Hexa	pg/L	2.97	0.624			
Total Hepta	pg/L	1.51	0.629			
2,3,7,8-tetra CDF	pg/L	<0.626	0.626	0.1	0	
1,2,3,7,8-penta CDF	pg/L	<0.607	0.607	0.05	0	
2,3,4,7,8-penta CDF	pg/L	<0.574	0.574	0.5	0	
1,2,3,4,7,8-hexa CDF	pg/L	0.881	0.607	0.1	0.0881	+
1,2,3,6,7,8-hexa CDF	pg/L	0.644	0.644	0.1	0.0644	+
2,3,4,6,7,8-hexa CDF	pg/L	<0.698	0.698	0.1	0	
1,2,3,7,8,9,-hexa CDF	pg/L	<0.957	0.957	0.1	0	
1,2,3,4,6,7,8-hepta CDF	pg/L	<0.919	0.919	0.01	0	
1,2,3,6,7,8,9-hepta CDF	pg/L	<1.31	1.31	0.01	0	
octa-CDF	pg/L	3.57	1.29	0.0001	0.000357	+
Total Tetra CDF	pg/L	2.69	0.673			
Total Penta CDF	pg/L	0.896	0.590			
Total Hexa CDF	pg/L	1.52	0.631			
Total Hepta CDF	pg/L	<1.12	1.12			
TOTAL TOXIC EQUIVALENCY	pg/L				= 0.465	

Note 1: The reviewer is suggested to clarify the use of the 'DL' term with the lab. See Section 1.1.5 of this report for additional guidance regarding detection limit terminology.

Note 2: Rows ending with a '+' are the data used for calculating the "Total Toxic Equivalency" whose sum is located in the last row of this example.

Upon further inspection of this example laboratory page in Figure 1 above, there are detection limit terms used by the laboratory as indicated by red arrows, DL and TEQ (DL), that need to be thoroughly understood by the data reviewer. Instructions adopted by the RWQCB SF Bay Region as of March 2010 require a clear understanding because '"Attachment G"' directs the Discharger to set any congener concentrations below the 'ML' to zero when calculating the Dioxin-TEQ results. In other words, data that are 'estimated' or 'detected not quantified' because results are below the lowest calibration standard are considered 'zero' per "Attachment G" and are not used for the Dioxin-TEQ calculations.

The key questions for the data reviewer from Figure 1's example laboratory report page should focus on the following areas.

a. How is the laboratory defining the term Detection Limit or 'DL'?
b. What does TEQ (DL) mean by this laboratory?
c. Is the 'DL' above or below the lowest level of the calibration curve (ML)?
d. How is the 'DL' derived by this laboratory?
e. What is the lowest calibration curve level (ML)?

Section 1.1.5 will define detection limit terms as used by Dioxin/Furan testing laboratories so they can be correctly understood for properly reporting the Dioxin-TEQ under '"Attachment G"' instructions.

1.1.3 Bioaccumulation Equivalency Factors (BEFs)

The RWQCB SF Bay Region has added the concept of 'Bioaccumulation Equivalency Factors' when determining Dioxin-TEQ. Prior to the adoption of this approach, the calculation detailed in Section 1.1.1 of this guidance document was used. The following is a summary of the meaning of 'Bioaccumulation Factors' and the history behind that approach.

In 1995, EPA developed the Bioaccumulation Equivalency Factors (BEFs) for the Dioxin/Furans congeners in support of the Great Lakes Water Quality Initiative to assess risk associated with congener concentrations in effluents in this system. Bioaccumulation is the net accumulation of a substance by an organism as a result of uptake from all environmental sources. Just as the different Dioxin/Furan congeners exhibit different levels of toxicity, they also exhibit different levels of bioaccumulation potential. To account for the different levels of bioaccumulation potential, each congener is assigned a bioaccumulation equivalency factor (BEF) relative to 2,3,7,8-TCDD.

As stated above, the U.S. Environmental Protection Agency adopted the approach of using both TEFs and BEFs in 1995 to calculate Dioxin-TEQ for the Great Lakes System (40 CFR 132, Appendix F). In the absence of site-specific BEFs, the U.S. Environmental Protection Agency supports the use of national BEFs, stating, "…EPA believes that national bioaccumulation factors are broadly applicable to sites throughout the United States and can be applied to achieve an acceptable degree of accuracy when estimating bioaccumulation potential at most sites." Because of this stance by the EPA, BEFs from the Great Lakes System are used in "Attachment G" whose application is to the San Francisco Bay Region.

Biota-sediment accumulation factors (BSAFs) are calculated from fish and sediment data to determine the relative bioavailability of each Dioxin/Furan congener to an organism of interest. A 'Biota-Sediment Accumulation Factor' (BSAF) is the ratio (in kg of organic carbon/kg of lipid) of a substance's lipid-normalized concentration in tissue of an aquatic organism to its organic carbon-

normalized concentration in surface sediment. This applies in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism. A 'Bioaccumulation Factor' (BAF) is the ratio (in L/Kg) of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time. BSAFs are used to calculate location-specific bioaccumulation equivalency factors (BEFs) for each Dioxin/Furan congener, which provide an indication of bioaccumulation potential relative to the most toxic Dioxin/Furan congener, 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD).

The TEFs for the 17 CDDs/CDFs (Dioxin/Furans) address the toxicity of various chemicals as compared to 2,3,7,8-TCDD, but do not address differences in bioaccumulation potential between the chemicals. The first approach presented by EPA recognized these differences in the bioaccumulation potentials of Dioxin/Furans by including specific bioaccumulation equivalency factors (BEFs) for the 17 CDD/CDF congeners. These 17 BEFs for Dioxin/Furan congeners were updated and the new values were provided in an August 30, 1994 notice of data availability for public comment (59 FR 44687).

For ease of reference, the BEFs required for the Dioxin-TEQ calculation as detailed in "Attachment G'' for each Dioxin/Furan Congener has been presented in Table 2 below:

Table 2: 1998 WHO TEFs and BEFs for 17 CDD/CDF Congeners

Congener	World Health Organization 1998 Toxicity Equivalence Factor (TEF)	Bioaccumulation Equivalency Factor (BEF)
2,3,7,8-tetra CDD	1	1.0
1,2,3,7,8-penta CDD	1	0.9
1,2,3,4,7,8-hexa CDD	0.1	0.3
1,2,3,6,7,8-hexa CDD	0.1	0.1
1,2,3,7,8,9-hexa CDD	0.1	0.1
1,2,3,4,6,7,8-hepta CDD	0.01	0.05
octa CDD	0.0001	0.01
2,3,7,8-tetra CDF	0.1	0.8
1,2,3,7,8-penta CDF	0.05	0.2
2,3,4,7,8-penta CDF	0.5	1.6
1,2,3,4,7,8-hexa CDF	0.1	0.08
1,2,3,6,7,8-hexa CDF	0.1	0.2
1,2,3,7,8,9,-hexa CDF	0.1	0.6
2,3,4,6,7,8-hexa CDF	0.1	0.7
1,2,3,4,6,7,8-hepta CDF	0.01	0.01
1,2,3,6,7,8,9-hepta CDF	0.01	0.4
octa CDF	0.0001	0.02

1.1.4 Dioxin-TEQ Reporting as Defined by the California RWQCB San Francisco Bay Region

With the adoption of '"Attachment G"' by the RWQCB SF Bay Region in March 2010, the concept of incorporating 'BEFs' into the Dioxin-TEQ results has been introduced. This approach involves multiplying each TEF value for each congener by a corresponding bio-concentration equivalency factor (BEFs) to calculate a Dioxin-TEQ for the mixture. This approach is being used by water quality programs in New York and several other Great Lakes states. The Oregon DEQ is considering adopting a similar approach. Based on '"Attachment G"', the formula for traditionally calculating Dioxin-TEQ has been expanded to the following equation:

$$\sum_{n=1}^{k} TEF_n \times C_n \times BEF_n = \text{Dioxin-TEQ Concentration}$$

Where,

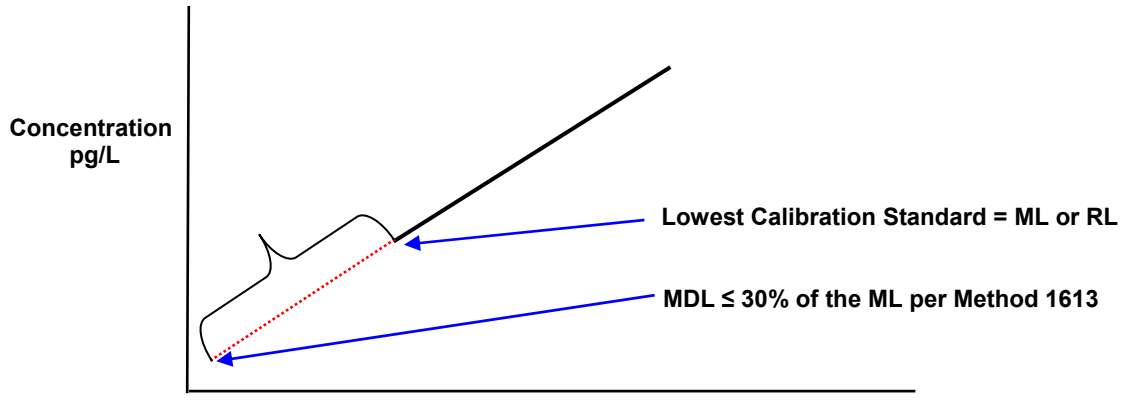
- ***C_n equals the concentration of the individual congener in the complex mixture under analysis.***
- ***TEF_n is determined by inspection of the available congener-specific data and an assignment of an 'order of magnitude estimate' of relative toxicity when compared to 2,3,7,8-TCDD as provided by the World Health Organization (WHO, 1998). See Table 1 in this guidance document.***
- ***n equals the number of positive results ≥ML***
- ***BEF_n equals the bioaccumulation equivalency factor for each congener. See Table 2 in this guidance document for BEFs associated with each Dioxin/Furan congener.***

1.1.5 Detection Limit Terminology

Laboratories performing Dioxin/Furans testing may employ several terms regarding detection limits for target analytes. This can be a difficult area for data assessment of Dioxin/Furans data because these laboratories may use terms that are not defined in the reference method (i.e. Method 1613) or other supporting documents or regulations such as '"Attachment G"'. These terms may also have different meanings compared to traditional environmental testing methods. The issue may be further complicated by laboratories using the same term to mean different levels for detection. The following is a summary of the major terms associated with detection limits and their formal definitions for Dioxin/Furans testing to help clarify the relationship of the terms.

As an Agency works with its subcontract laboratory, it is highly recommended to understand the laboratory's basis for its detection limit terms to assure the data are of appropriate quality for reporting under "Attachment G". Figure 2 is a graphical representation of the relationship of the most common Dioxin/Furans detection limit terms that are further defined in this section.

Figure 2. Detection Limit Relationships for Dioxin Testing



Range where data are considered 'Quantitated'

Range where data are considered 'Estimated' so 'J' or 'DNQ' flags are used

'EMPC' Range which is the Estimated Maximum Potential Concentration Range used by Hazardous Waste testing protocols.

Sample Specific Estimated Detection Limit Range ('EDL', 'DL', 'RDL')

1.1.5.1 Method Detection Limit (MDL)

'"Attachment G"' specifies the use of Method 1613 for Dioxin/Furans testing. This guidance document is using Method 1613, Revision B, October 1994 for its definitions and discussion.

Method 1613 requires, as part of the initial demonstration of capability and each time a modification is made to the method, that the laboratory performs a Method Detection Limit (MDL) Study that is in compliance with 40 CFR Part 136, Appendix B. Per Section 9.1.2.1 of Method 1613, the laboratory is required to demonstrate that the MDL generated is lower than one-third the regulatory compliance level or one-third the ML for this method, whichever is higher:

9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-third the regulatory compliance level or one-third the ML in this method, whichever is higher. If calibration will be affected by the change, the analyst must recalibrate the instrument per Section 10.

Laboratories should use the term 'MDL' for Dioxin/Furan testing to represent the results of the study required by EPA's 40 CFR Part 136, Appendix B but the Agency is recommended to check with its subcontract laboratory to assure how the MDL data are generated and that they are generated for each Dioxin/Furan of interest. MDL studies are to be performed annually or when there are significant changes to the system or staff in accordance with Method 1613's instructions to Dioxin/Furan testing laboratories. The Agency should routinely check with its subcontract laboratory to assure it has the current set of MDL study data from Method 1613.

For traditional data assessment purposes, results between the MDL and the lowest calibration standard (ML) are flagged as 'estimated' since testing is significantly less accurate below the lowest calibration standard (ML) which is where the MDL is traditionally calculated. Conventions for local permits are to use 'DNQ' for 'Detected Not Quantified' when results are detected at or above the MDL but below the lowest calibration standard (ML). However, for Dioxin-TEQ calculations, all results below the lowest calibration level (ML) and the MDL are not to be used.

1.1.5.2 Sample-Specific Estimated Detection Limit (DL)

The "Sample-Specific Estimated Detection Limit" may often abbreviated as 'DL' in laboratory reports for Dioxin/Furans testing. This may also be called the 'Sample Specific EDL', 'RDL', or 'EDL' by Dioxin/Furans laboratories. For traditional environmental testing procedures (non-Dioxin), the term 'DL' is usually meant as the 'Reporting Limit' or 'Lowest Calibration Standard' or 'ML'. However, the term 'DL' for Dioxin/Furans testing has a significantly different meaning and care should be taken to understand the guidance provided in this discussion.

The "Sample-Specific Estimated Detection Limit" is not defined in Method 1613 or in "Attachment G". However, it is a commonly used term because Dioxin/Furans laboratories perform testing under other regulatory programs where the "Sample-Specific Estimated Detection Limit" is required for reporting Dioxin/Furans results. It is a term driven by hazardous waste testing programs which use procedures from Solid Waste-846 (SW-846) or the Superfund Protocols from EPA's Contract Laboratory Program (CLP). The procedures from SW-846 and CLP protocols have some differences compared to Method 1613 but the vernacular from SW-846 and CLP testing has made its way into Method 1613 reporting for wastewater testing. The outcome may be a lack of clarity by some Dioxin/Furans testing laboratories about detection limit terminology needed by wastewater Agencies in the San

Francisco Bay Area. The consequence can be that an Agency reports results that are lower than the 'ML' or even lower than the MDL which is inconsistent with current instructions under "Attachment G". Please note that the use of the terminology 'DL' is common to High-Resolution GC/MS (HR GC/MS) testing, so the Agency is suggested to clarify the application of this terminology when any HR GC/MS procedures are needed.

As shown in Figure 2 above, the term 'DL' as used for Dioxin/Furans testing, is generally below the ML depending on the performance of the individual sample during analysis. The exception is if there are dilutions applied to the sample and that is a special case. The 'DL' calculation for Dioxin/Furans testing under the hazardous waste testing protocols is specific to the individual sample and takes into consideration several factors but the term is not defined in Method 1613. It is an estimate made by the laboratory of the concentration of a given analyte that is present to produce a signal with a peak height of at least 2.5 times (2.5x) the background noise signal level. It can be above or below the MDL depending on the performance of the sample.

This "Sample-Specific Estimated Detection Limit" is unique to the individual sample and will be affected by sample size, dilution, instrument stability at the time of analysis, etc. The estimate also takes into consideration the %Recoveries for the spiked, isotope-labeled internal standards (see isotope dilution discussion under Section 1.1.7). As such, no two samples in a single report will have the same DL (e.g. Sample-Specific Estimated Detection Limit). The same is true for all quality control checks (i.e. Method Blanks, Laboratory Control Samples, or Matrix Spike/Matrix Spike Duplicates, etc).

For example, if Method Blanks from two different batches are provided in the same report by a laboratory performing Method 1613 using hazardous waste terminology, the DL's will not be the same. In traditional environmental testing, the data reviewer can rely on the 'Reporting Limit' or 'ML' to be the same even if multiple Method Blanks are reported within a project and between projects. However, Reporting Limit and Detection Limit are not the same as in traditional environmental testing for Dioxin/Furans testing. The consequence of the application of hazardous waste testing conventions for the definition of detection limits can result in the use of results by an Agency that are below the 'ML' or even the MDL.

The Agency is recommended to require that its laboratory clearly identify the level of the ML (see 1.1.5.3 for more information) and the MDL as concentration in pg/L in its reports. It is further suggested that the wastewater agency require the laboratory to remove any use of hazardous waste detection limit terminology from its reports and only use those terms defined in Method 1613 which are ML (see below) and MDL. By allowing the Dioxin/Furans laboratory to report levels down to the 'DL' or 'Sample-Specific Estimated Detection Limit', the Agency may get results below the MDL which is inconsistent with reporting conventions under "Attachment G".

1.1.5.3 Minimum Level (ML)

As stated in Method 1613, the Minimum Level is equivalent to the calibration point at which the entire analytical system must give a recognizable signal with definable accuracy for the target analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

The RWQCB SF Bay Region has defined Minimum Levels (ML) in the same manner and has instructed Agencies to set congener concentrations below the ML to 'zero' for calculating

Dioxin-TEQ results. That means any congener result 'at or above the ML' shall be used for calculating Dioxin-TEQ and shall incorporate the appropriate TEF and BEF for each Dioxin/Furan in the formula. Table A in "Attachment G" summarizes all data required for the Dioxin-TEQ calculation and is provided below for ease of review.

Table 3
"Attachment G" - Table A:
Minimum Levels, Toxicity Equivalency Factors, and Bioaccumulation Equivalency Factors

Congener	Minimum Level (pg/L)	World Health Organization 1998 Toxicity Equivalence Factor (TEF)	Bioaccumulation Equivalency Factor (BEF)
2,3,7,8-tetra CDD	10	1	1.0
1,2,3,7,8-penta CDD	50	1	0.9
1,2,3,4,7,8-hexa CDD	50	0.1	0.3
1,2,3,6,7,8-hexa CDD	50	0.1	0.1
1,2,3,7,8,9-hexa CDD	50	0.1	0.1
1,2,3,4,6,7,8-hepta CDD	50	0.01	0.05
octa CDD	100	0.0001	0.01
2,3,7,8-tetra CDF	10	0.1	0.8
1,2,3,7,8-penta CDF	50	0.05	0.2
2,3,4,7,8-penta CDF	50	0.5	1.6
1,2,3,4,7,8-hexa CDF	50	0.1	0.08
1,2,3,6,7,8-hexa CDF	50	0.1	0.2
1,2,3,7,8,9,-hexa CDF	50	0.1	0.6
2,3,4,6,7,8-hexa CDF	50	0.1	0.7
1,2,3,4,6,7,8-hepta CDF	50	0.01	0.01
1,2,3,6,7,8,9-hepta CDF	50	0.01	0.4
octa CDF	100	0.0001	0.02

The Agency is recommended to assure that its subcontract laboratory uses the ML's specified in Table A from "Attachment G" and MDL's as specified in Method 1613 so that it is clear to the Agency how a positive detect is to be handled for the Dioxin-TEQ calculation. The laboratory should also be instructed to not report data below the MDL as defined by 40 CFR Part 136, Appendix B. This instruction is important because most programs under which Dioxin/Furans laboratories participate require results to be reported above the "Sample-Specific Estimated Detection Limit" (DL) for Dioxin-TEQ calculations. The ML and MDL are actually the critical levels for a local Agency to calculate the Dioxin-TEQ under "Attachment G".

It is important for Agencies reviewing data to know that Dioxin/Furans testing laboratories may calculate a Dioxin-TEQ for results below the lowest calibration level (ML) without applying the 'DNQ' flag or even identifying that data between the ML and MDL are considered 'estimated'. The staff assigned to perform data review of Dioxin/Furans data is suggested to carefully review results to assure this practice does not allow data to be accepted because there were no flags.

1.1.6 Estimated Maximum Possible Concentration (EMPC)

Because some laboratories use Method 1613 in the context of other regulatory programs (i.e. Hazardous Waste testing under the Resource Conservation and Recovery Act, Superfund's Contract Laboratory Program) the term 'Estimated Maximum Possible Concentration' or EMPC

may be used to report data. The laboratory may also use the term 'Maximum Possible Concentration' to mean the same term. EMPC is not a term used in Method 1613 which can make it difficult for a data reviewer to assess Dioxin data and its meaning for what looks to be a 'positive' detection.

This value is reported by a laboratory because all identification criteria (retention times, internal standard performance, etc) have been met except the ion ratio criteria. When this happens, the identification of the isomer has higher uncertainty. However, under hazardous waste remediation programs, this information proves a very conservative level of reporting to protect public health. This term was added to Figure 2 to illustrate that an Estimated Maximum Possible Concentration can occur at any point in the working range because this term relates to CDD/CDF-like compounds whose identification has more uncertainty. That uncertainty about identification can happen at any level because all of the identification criteria have not been met but these types of results still provide useful information to data users under hazardous waste testing programs.

Laboratories may analyze samples with an EMPC on a second column to assess whether the result is confirmed. Confirmation occurs when the identification criteria are all met on the second column which may have better specificity for the isomer in question. The Estimated Maximum Possible Concentration (EMPC) value is applied to a sample when the signal-to-noise (S/N) ratio is at least 2.5:1 for both quantitation ions, but the ion abundance ratio criteria are not met.

The Agency is suggested to require that its subcontract laboratory remove any reference to EMPC results from its laboratory reports since it is not a term defined in Method 1613.

1.1.7 Isotope Dilution Technique

The Isotope Dilution technique is introduced in this Guidance Document because it is a significant aspect of Method 1613 for assessing data. In essence, the performance of 15 spiked isotopes are used to correct detection limits. All results and detection limits for any quality control or samples are adjusted for the performance of isotopically-labeled analogues for each CDD/CDF. Therefore, no two analyses will have the same 'DL' because instrument conditions vary from run-to-run or day-to-day.

The performance data for the 15 labeled chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) are usually presented in the laboratory report with control limits that come from Method 1613. The recovery of these compounds, along with the recovery of the clean-up standard (see definition in Section 1.1.8 below), is a critical measure of the effectiveness of the laboratory and method to extract the compounds of interest.

For those who wish more details, the isotope dilution calibration technique is essentially a special case of internal standard calibration. In isotope dilution, the internal standards are stable isotopically-labeled analogs of the target analytes *and* they are added to the sample prior to any sample handling steps, including sample extraction. Because the spiked compounds differ from the target compounds only in the presence of the stable isotopes, the physical and chemical behavior of each labeled compound is virtually the same as its unlabeled "native" analog. Thus, any losses of the target compound that may occur during any of the sample preparation, extraction, cleanup, or determinative steps will be mirrored by a similar loss of the labeled standard. Similarities between the labeled compounds and their native analogs means that the response factors and relative retention times for the unlabeled compounds are both very close to 1.0.

The labeled compounds are spiked into the sample at a constant amount, and that amount of labeled standard is also present in the calibration standards. The response factors developed from the calibration standards assume that all of the labeled compound added to the sample reaches the instrument. Thus, for example, if one adds 100 units of labeled analog to the sample, then there must be 100 units of the labeled analog in each of the calibration standards, and the calibration routine assumes that all 100 units are present in the aliquot that is analyzed. This assumption allows one to correct the observed concentration of the target compound for the loss (or apparent gain) of the labeled compound. This correction is termed the recovery correction.

The degree to which the labeled compounds meet this assumption is monitored through the use of traditional internal standards that are added to the sample extract immediately prior to injection. Separate response factors relate the concentrations of the labeled compounds to the traditional internal standards. Most isotope dilution methods include some limits on the apparent recovery of the labeled compounds. However, those limits are often consensus limits that may be overly conservative. As long as the responses for both the native and labeled compounds can be distinguished from the background instrumental noise, isotope dilution calibration can provide excellent results, even when the apparent recovery of the labeled compound is as low as 5 to 10% of its spiked concentration. The limits allow labeled compound recoveries over 100% as well. Such recoveries can occur as a result of the inherent variability in the calibration of the labeled compounds themselves, and are not indicative of contamination or other problems.

The built-in recovery correction is one of the principal advantages of isotope dilution analyses, isotope dilution generally produces data that are more precise as well as with less bias. The use of isotope labeled analogues of Dioxin congeners is a significant reason for the high cost of this test. The control limits for the performance of this quality control check are located in Table 7 of Method 1613.

1.1.8 Clean up Standard or Clean up Surrogate

The ^{37}Cl-labeled clean-up standard is used to monitor the efficiency of the individual sample clean-up step. It is added to the sample extracts after extraction and before any clean-up steps. Low recoveries of the labeled compounds and the clean-up standard suggest that losses may be due to the performance of the clean-up steps. Thus, re-extraction and reanalysis of the sample may yield better results. If the labeled compound recoveries are low and the clean-up standard recovery is not, the recovery problems may be associated with the extraction procedures or related to a particularly difficult matrix. In this case, reanalysis may only serve to confirm a "matrix effect".

Laboratories may use the term ‘CRS’, ‘Cleanup Surrogate’, or $^{37}Cl_4$-2,3,7,8-TCDD to identify that specific QC measure in their reports. The control limits are specified in Method 1613 as %Recovery from 35%-197% from Table 7 of Method 1613. Results need to fall within that range to be acceptable.

1.1.9 Precision and Recovery Standard (PAR)

In simple language, the Precision and Recovery Standard (PAR) is same as the Laboratory Control Sample or the Laboratory Fortified Blank for traditional environmental testing methods. It is a spiking solution used to prepare quality control checks called either the ‘Initial Precision and Recovery’ standard (IPR) or the ‘Ongoing Precision and Recovery’ standard (OPR) for Dioxin testing depending on when this check is performed by the laboratory. The PAR is used as a standard to assess precision and accuracy for the laboratory.

The initial capability of the laboratory to acceptably perform Method 1613 is demonstrated through an 'Initial Precision and Recovery' study which is called an IPR. The PAR is analyzed in replicate and results must achieve Method 1613 requirements for accuracy and precision provided in Table 6 and Table 7 of Method 1613. For this initial precision and accuracy, all cleanup steps used in processing samples shall be included in the IPR study. This study is exactly the same as that required for traditional environmental testing procedures where the Laboratory Control Sample is analyzed four (4) times to determine accuracy and precision.

The demonstration of continuing ability to perform the analysis is accomplished by analyzing the PAR solution with every batch and is called the 'OPR' for the 'Ongoing Precision and Recovery' standard. It is a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery (Method 1613 -Table 6 and Table 7). This sample is extracted and analyzed with each preparatory batch of samples.

As part of measuring system performance, Methods 1613 requires that samples and standards be measured within require QC limits. QC criteria such as required relative retention times of labeled and native isomers, theoretical ion abundance ratios, recovery limits for the OPR, and recovery limits for spiked labeled target compounds must be met in order to demonstrate that the measurement system is within control limits. These limits are provided in Tables 6 and 7 in Method 1613.

1.1.10 Calibration Verification Standard (VER)

The Calibration Verification (VER) standard is a mid-point calibration standard check that is performed each day of testing to assure the stability of the instrumentation since the last 5-point initial calibration curve was performed. This is similar to the concept of the 'Initial Calibration Verification' standard or 'Continuing Calibration Verification' standard that is an unprocessed, mid-level standard analyzed at the beginning of the workday for traditional environmental testing. Table 6 of Method 1613 provides the control limits for the performance of that standard.

1.1.11 GC Retention Time Window Defining Solution and Isomer Specificity Test Standard

This quality control check is used to define the beginning and ending retention times for the dioxin and furan isomers and to demonstrate isomer specificity of the GC columns employed for determination of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The method specifies which compounds must be included to assure the system is operating in the correct retention time window range to detect all of the isomers.

2.0 Data Review Focus Points for Method 1613

Review of laboratory reports for Dioxin/Furans testing needs to focus on several key areas to assure data are properly used for calculating the Dioxin-TEQ. The purpose of the previous section was to establish a foundation for understanding commonly used terms or acronyms in Dioxin/Furans testing laboratory reports or when discussing technical issues with the subcontract laboratory. There are several vitally important facts to understand from the laboratory report when there are positive detections for any Dioxin/Furan compounds. They can be summarized as follows:

2.1 Detection Limit Review

Because "Attachment G" sets the Dioxin-TEQ calculation at the ML and laboratories who traditionally test for Dioxin/Furans have adopted practices directed by hazardous waste testing protocols, this is an area that requires detailed scrutiny of laboratory data and extensive communication with the laboratory. This effort is to assure that data are reported in accordance with "Attachment G" which uses 'ML' levels for calculating a Dioxin-TEQ.

2.1.1 What is the laboratory's definition of Detection Limit?

Guidance: The data reviewer is suggested to consider if the Dioxin/Furans positively detected are above or below the lowest calibration standard (ML) and to not use the 'DL' provided by the laboratory without clarification. Dioxin/Furans testing reports may not include the ML so pre-planning with the laboratory to require reporting at this level is recommended. Generally Dioxin/Furans testing laboratories report results above the 'Sample-Specific Estimated Detection Limit' or 'DL'. This is where a result has a signal to noise ratio of at least 2.5 to 1. A laboratory may or may not flag results between the 'Sample-Specific Estimated Detection Limit' and the lowest calibration standard (ML) because it is using hazardous waste protocols. The level of accuracy and precision at the 'Sample-Specific Estimated Detection Limit' is less than for results at or above the ML by definition in Method 1613.

The following conventions are recommended to be adopted when communicating with the laboratory:

- "Attachment G" does not explicitly define 'Reporting Limit' but it is interpreted in this Guidance document to be equivalent to the ML since the Reporting Limit is referred to as the 'quantifiable limit' on Page G-16 of "Attachment G".
- The Agency is recommended to require the laboratory to use the ML's provided in "Attachment G".
- The laboratory must provide in the report a column with the MDL for each Dioxin/Furan of interest. Results below the MDL, as calculated using 40 CFR Part 136 B and Method 1613, are not to be reported.
- Results reported between the MDL and the ML are to qualified as 'detected but not quantified' or 'DNQ'.
- The Agency is recommended to request that the laboratory remove and not use any extraneous detection limit language associated with terms like 'DL', 'EDL', 'RDL', 'Sample-Specific Estimated Detection Limit', or 'Estimated Maximum Potential Concentration' to reduce confusion for data-users.

2.1.2 What is the laboratory's level for its lowest calibration standard (ML) for the detected Dioxin/Furan?

Guidance: Since the lowest calibration standard level (ML) or reporting limit (RL) for each Dioxin/Furan may not be provided with laboratory reports, readers are urged to require its subcontract laboratory to generate its reports using the ML value as required under "Attachment G" and MDL. The ML should be the same level as the Reporting Limit.

2.2 Results Review

"Attachment G" from the RWQCB San Francisco Bay Region has incorporated the use of 'BEF' in the Dioxin-TEQ calculation. The data reviewer is suggested to work with its laboratory pro-actively to assure results are reported in a usable form. Since "Attachment G" is unique to the San Francisco Bay Region, specific discussions about reporting needs are suggested. Below are focus areas that require communication to assure data quality objectives are met.

2.2.1 What is the concentration of the Dioxin/Furan detected in pg/L without any corrections for toxicity or bioaccumulation?

Guidance: Agencies are suggested to keep Dioxin/Furans data simple by having results reported in concentration (pg/L) with the ML and MDL clearly specified in the laboratory report. A spreadsheet for calculating Dioxin-TEQ using 1998 WHO TEF and BEF values adopted under "Attachment G" is provided in Appendix 3 of this Guidance document.

If the laboratory is to calculate the Dioxin-TEQ, it should be provided with the MLs, 1998 WHO TEFs, and BEFs specified by "Attachment G". The Agency is suggested to verify the calculations during the data review process to assure the correct factors are used.

2.2.2 How do positive concentrations reported by the Laboratory relate to any positive concentrations in the Method Blank?

Guidance: The data reviewer is suggested to consider the following when reviewing any positive results associated with environmental testing:

- How do the positive concentrations reported by the laboratory relate to any positive concentrations in the Method Blank? In other words, what type of factor is observed between positive results in the sample and positive results in the Method Blank?

- Did the laboratory report detections in its Method Blank that are >1/3 the regulatory level or > ML (whichever is higher)?

Whenever there are positive detects either >1/3 the regulatory level or >ML, carefully review the results for the corresponding congeners in the Method Blanks. Data users must especially keep that relationship in mind when the sample's results are over the ML and the Method Blank also has similar detections below the ML. That is because the results may be actually due to background contamination from the laboratory. By flagging the similarity in results between the samples and associated Method Blank(s), the Agency can pro-actively work with the laboratory to properly qualify its results.

It is recommended that Agencies insist on good laboratory practices to avoid background contamination either >1/3 the regulatory level or >ML (whichever is higher) since Method 1613

explicitly requires corrective action in this case and not just flagging for compliance monitoring. See the following section taken from Method 1613:

9.5.2 If any 2,3,7,8-substituted CDD/CDF (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance level, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each level of chlorination given in Table 2 (assuming a response factor of 1 relative to the ^{13}C -1,2,3,4-TCDD internal 12 standard for compounds not listed in Table 1), analysis of samples is halted until the blank associated with the sample batch shows no evidence of contamination at this level. All samples must be associated with an uncontaminated method blank before the results for those samples may be reported for regulatory compliance purposes.

Data reviewers need to be aware that Dioxin/Furans laboratories reporting data under hazardous waste testing may qualify data when sample levels are greater than 5 times positive detections in associated Method Blanks or that they may simply flag data as 'estimated' by convention. This should not be the case for performance under wastewater testing and is not provided as an option under "Attachment G". This potential scenario is of concern because higher biased data due to background contamination can push an Agency into exceeding Water Quality Objectives since the Dioxin-TEQ is so low.

A general rule of thumb is to reject sample results that do not meet the requirements of Section 9.5.2 of Method 1613 or if any positive detects in samples are reported at levels similar to the Method Blank. In addition, the Agency needs to assess the impact of sample detections that may be due to laboratory contamination when calculating the Dioxin-TEQ.

If there are detections in the Method Blank below the lowest calibration standard and the sample results are above the ML, data reviewers need to use professional judgment and to provide a narrative with the data if there are concerns when reporting to a regulatory body. It is important to know that Method 1613 requires a laboratory to reject a batch if there are detections >ML or >1/3 the regulatory limit, whichever is higher. Since laboratories may not be aware of the Agency's requirements to the multitude of regions served, the Agency needs to assure this relationship is met before accepting and reporting data for Dioxin/Furans testing.

2.3 Calculations and Report Review

2.3.1 What source is the laboratory using for the TEF (1998 WHO, 2005 WHO, etc) to calculate the Dioxin-TEQ for positive detections?

Guidance: In order to assure the requirements of the permit are met, verify what TEF version is being used for each positive detection to calculate the Dioxin-TEQ. Only apply TEF factors to results that are ≥ML. The Agency needs to assure that the laboratory has been provided a summary of "Attachment G" for this calculation to assure that data are correctly reported, calculated, and/or flagged. Along with the summary, the Agency is suggested to instruct its subcontract laboratory to use WHO TEFs from 1998 for the Dioxin-TEQ calculations.

2.3.2 What source is the laboratory using for the BEF to calculate the Dioxin-TEQ for positive detections?

Guidance: In order to assure the requirements of "Attachment G" are met, the Agency will need to provide or reference the "Attachment G" Bioaccumulation Equivalency Factors to calculate the Dioxin-TEQ. Only apply BEF factors to results that are ≥ML. The Agency needs to assure that the laboratory has been provided the correct BEFs to assure that data are correctly reported, calculated, and/or flagged based on the instructions provided by "Attachment G".

Along with the summary, the Agency is suggested to provide its subcontract laboratory with the new formula in case the laboratory is tasked with preparing the Dioxin-TEQ under “Attachment G”.

2.3.3 Dioxin/Furans Data Review Worksheet

In order to support training through this Guidance document and consistency in reviewing quality control parameters associated with Dioxin/Furan data by Method 1613, a ‘Dioxin/Furans Data Review Worksheet’ has been developed. This template is intended to be modified for use by an Agency to support its data quality objectives. See Figure 3 on Page 20 of this Guidance Document.

Figure 3: Dioxin/Furans Data Review Worksheet

Agency: _____	**Date(s) Sampled:** _____ **Date(s) Extracted:** _____ **Date(s) Analyzed:** _____		
Laboratory: _____ **Permit/'Attachment G' (March 2010) Submitted to Lab?** ❑ Yes ❑ No	**Sample ID's:** _____ **Batch #/Test:** _____ _____		
COC#: _____	**Data Reviewer(s):** _____ _____	**Date Lab Report Received?** _____	**Laboratory Report Number(s):** _____ _____

Data Quality Element Reviewed	Issues Flagged by the Laboratory?	Data Usable? Yes	No	NA	Guidance
1. Chain of Custody Complete?		❑	❑	❑	
2. Required Analysis Reported?		❑	❑	❑	
3. Holding Times Met and Transport Temperatures Acceptable?		❑	❑	❑	Flag 'J' (Estimated): ❑ Yes ❑ No Flag 'R' (Rejected): ❑ Yes ❑ No Re-Sample/Re-Analyze: ❑ Yes ❑ No
4. Laboratory Report Complete, Signed, Dated, On Time?		❑	❑	❑	
5. Equipment Blank(s)		❑	❑	❑	Use judgment if positive detections
6. Field Blank(s)		❑	❑	❑	Use judgment if positive detections
7. Field Duplicates		❑	❑	❑	Use replicate data to trend system precision over time
8. Positive Sample Results Reported?		❑	❑	❑	Use Section 19 Worksheet to evaluate positive results. Results ≥MDL and <ML need 'DNQ' flags. Lab to use only Method 1613 detection limit terms. Positive results ≥ML are used for Dioxin-TEQ.
9. Laboratory Method Blank(s)		❑	❑	❑	Use Section 19 Worksheet to evaluate positive results in all samples and associated Method Blanks. Laboratory must re-extract and re-analyze if Dioxin/Furans ≥ ML or 1/3 regulatory compliance level per Method 1613. Table A in "Attachment G" is used for the ML.
10. OPR Results (e.g. LCS)		❑	❑	❑	Laboratory must meet Table 6 limits from Method 1613
11. Matrix Spike/Matrix Spike Duplicates		❑	❑	❑	Use MS/MSD data to trend system accuracy and precision over time
12. Internal Standards		❑	❑	❑	Laboratory must meet Table 6 limits from Method 1613
13. Labeled Isotopes		❑	❑	❑	Laboratory must meet Table 7 limits from Method 1613
14. Cleanup Surrogate or Standard (e.g. $^{37}Cl_4$-2,3,7,8-TCDD, CRS)		❑	❑	❑	Laboratory must meet %Recovery (35-197%) requirement stated in Table 7
15. Any Estimated Maximum Concentration Results Reported? (EMPC's are detects that do not meet all of the identification criteria so ID is less certain)		❑	❑	❑	The Guidance is to require the laboratory to remove any reference to "EMPC" terminology from its laboratory reports. EMPC's is a hazardous waste testing term not defined in Method 1613.

Data Quality Element Reviewed	Issues Flagged by the Laboratory?	Data Usable? Yes	No	NA	Guidance
16. TEFs used and Dioxin-TEQ Calculation Correct?		❑	❑	❑	Confirm 1998 WHO TEFs used for the Dioxin-TEQ Calculation.
17. BEFs used and Dioxin-TEQ Calculation Correct?		❑	❑	❑	Confirm 1995 GLI BEFs used for the Dioxin-TEQ Calculation.
18. Other issues identified by the laboratory?		❑	❑	❑	Laboratory should meet all QC requirements specified by Method 1613 for compliance monitoring.
19. Are data properly flagged based on permit instructions?		❑	❑	❑	Confirm laboratory has followed permit instructions for reporting.

Congener	MDL (pg/L)	Minimum Level (ML) Table A (pg/L)	Sample Congener Results (pg/L) Batch #: _____	Method Blank Results (pg/L) Batch #: _____	Flag Sample Result if: < ML = DNQ; ≥ML = No Flag; < MDL = ND; 'B' = Positive Detection for the same Congener in the associated Method Blank*
2,3,7,8-tetra CDD		10			
1,2,3,7,8-penta CDD		50			
1,2,3,4,7,8-hexa CDD		50			
1,2,3,6,7,8-hexa CDD		50			
1,2,3,7,8,9-hexa CDD		50			
1,2,3,4,6,7,8-hepta CDD		50			
octa-CDD		100			
2,3,7,8-tetra CDF		10			
1,2,3,7,8-penta CDF		50			
2,3,4,7,8-penta CDF		50			
1,2,3,4,7,8-hexa CDF		50			
1,2,3,6,7,8-hexa CDF		50			
1,2,3,7,8,9,-hexa CDF		50			
2,3,4,6,7,8-hexa CDF		50			
1,2,3,4,6,7,8-hepta CDF		50			
1,2,3,6,7,8,9-hepta CDF		50			
octa-CDF		100			

***Consider qualifying or rejecting results using professional judgment when Method Blank data are not significantly different from sample results. The laboratory should be contacted for determining next steps.**

2.3.4 Calculating the Dioxin-TEQ Using Excel

The following conventions are recommended to be adopted for use with the spreadsheet provided in Appendix 3 of this Guidance document:

- The Agency is recommended to handle results below the ML as 'zero' for calculating the Dioxin-TEQ results based on "Attachment G" instructions.
- Results below the MDL are considered 'not detected' due to their high level of uncertainty.
- Results reported ≥MDL and <ML should be qualified as 'detected but not quantified' (DNQ). Results between the MDL and ML are set to 'zero' and not used for the Dioxin-TEQ calculation.
- The data reviewer is recommended to have the MDL provided by the laboratory for each Dioxin/Furan and to have results reported down to the MDL as defined by Method 1613.
- "Attachment G" does not explicitly define 'Reporting Limit' but it is interpreted in this Guidance document to be equivalent to the 'ML' since the 'Reporting Limit' is referred to as the 'quantifiable limit' on Page G-16 of "Attachment G".

The following provides an example Excel spreadsheet to guide the reader through the Dioxin-TEQ calculation under the '<ML=0' scenario. The Excel spreadsheet provided with this Guidance document is located in Appendix 3 for review. The tab identified as '<ML=0' in the Excel spreadsheet is used for calculating the Dioxin-TEQ result by applying 1998 WHO TEFs and 1995 GLI BEF factors. Concentrations below the ML are set to zero by the data-user in accordance with instructions from "Attachment G".

Figure 4

WWTP Effluent pg/L: Dioxin-TEQ Calculation (Use all results ≥ML)						
				< ML = 0		
Congener	Minimum Level (pg/L)	WHO 1998 TEF	GLI 1995 BEF	Conc. ≥ML	TEQ w/o BEF	TEQ w/BEF
2,3,7,8-TCDD	10	1.0	1.0	0	0	0
1,2,3,7,8-PeCDD	50	1.0	0.9	0	0	0
1,2,3,4,7,8-HxCDD	50	0.1	0.3	0	0	0
1,2,3,6,7,8-HxCDD	50	0.1	0.1	0	0	0
1,2,3,7,8,9-HxCDD	50	0.1	0.1	0	0	0
1,2,3,4,6,7,8-HpCDD	50	0.01	0.05	0	0	0
OCDD	100	0.0001	0.01	0	0	0
2,3,7,8-TCDF	10	0.1	0.8	0	0	0
1,2,3,7,8-PeCDF	50	0.05	0.2	0	0	0
2,3,4,7,8-PeCDF	50	0.5	1.6	0	0	0
1,2,3,4,7,8-HxCDF	50	0.1	0.08	0	0	0
1,2,3,6,7,8-HxCDF	50	0.1	0.2	0	0	0
1,2,3,7,8,9-HxCDF	50	0.1	0.6	0	0	0
2,3,4,6,7,8-HxCDF	50	0.1	0.7	0	0	0
1,2,3,4,6,7,8-HpCDF	50	0.01	0.01	0	0	0
1,2,3,4,7,8,9-HpCDF	50	0.01	0.4	0	0	0
OCDF	100	0.0001	0.02	0	0	0
			Total:	0	0.000	0.000

2.4 Example Case Studies

In the following case studies, Dioxin/Furan data were randomly selected from reports posted on the internet for California-based projects. The laboratory reports were reviewed by a BACWA consultant for areas that would be helpful in training the users of this Guidance document. Volunteer laboratories were interviewed to clarify findings and to identify areas that may be unclear for BACWA member data reviewers:

2.4.1: Data are reported below the ML but not flagged as 'DNQ'

In one example reviewed, the laboratory report calculated the Dioxin-TEQ from results that were below the lowest calibration level (ML) but did not apply any flagging. That is because any results above its 'Sample-Specific Estimated Detection Limit' or 'DL' are reported based on the laboratory's own policy and not based on "Attachment G".

No ML or lowest calibration level information was provided for the reviewer to identify that issue in the report. The laboratory used the term 'DL' as the criteria for reporting results above that value. The 'DL' as defined by the laboratory was below the ML. Data below the lowest calibration level (ML) should have been be flagged as 'DNQ' and the final Dioxin-TEQ calculated from results ≥ML to be consistent with "Attachment G".

In the absence of specific instructions to the subcontract laboratory, a subcontract laboratory may report all results above its 'DL' without flags because of requirements for testing under other programs such as hazardous waste testing. In this case, the laboratory defaulted to its policy in the absence of instructions from the data-user.

The laboratory's use of detection limits (DL) that were below the ML's stated in Table A should prompt a call to the laboratory to change its reporting protocol to only include detection limit terminology used in Method 1613 (e.g. MDL, ML) and from "Attachment G". In addition, the laboratory should be required to flag in accordance with wastewater testing conventions. One final note for this case study was that the example laboratory report reviewed used the term 'RDL' to mean the same as 'DL' so that both terms mean they are at the level of the 'Sample-Specific Estimated Detection Limit' level. This means data that was below the ML and are not usable under "Attachment G" because of the higher levels of uncertainty.

2.4.2 Result is higher than the 'DL', so why is there a flag?

Figure 5 below may be helpful when reviewing data to understand 'DL' terminology and 'J' flags as applied for Dioxin/Furans testing. In this example, the laboratory uses the term 'DL' to mean the "Sample-Specific Estimated Detection Limit". The laboratory uses the term MDL in accordance with 40 CFR Part 136, Appendix B. The MDL for octa-CDD is 0.473 pg/L. It is unclear if the laboratory is reporting down to the ML or the 'DL'.

The octa-CDD result for this sample is 40.1 pg/L and it might be confusing why there is a 'J' flag. The result of 40.1 pg/L is flagged with a 'J' because it is below the laboratory's ML but the ML is not stated in this report. The unstated ML for OCDD is 50 pg/L and 40.1 pg/L is below that level. Since Dioxin/Furan testing laboratories do not generally provide their ML's, the reviewer needs to understand the relationship between the MDL, the DL, and the ML to properly assess the 'J' flag assigned by the laboratory. Figure 5 below details how to evaluate this issue from an example laboratory report page.

Figure 5: Example Detection Limit Relationship for Flagging

Sampling Date: 08/14/2007		Laboratory ID: U1598744			
DIOXINS/FURANS by Method 1613	**Units**	**Conc**	**DL**	**Qual**	**MDL**
2,3,7,8-tetra CDD	pg/L	ND	1.76		0.0843
1,2,3,7,8-penta CDD	pg/L	ND	2.27		0.0843
1,2,3,4,7,8-hexa CDD	pg/L	ND	3.53		0.185
1,2,3,6,7,8-hexa CDD	pg/L	ND	3.99		0.196
1,2,3,7,8,9-hexa CDD	pg/L	ND	4.09		0.199
1,2,3,4,6,7,8-hepta CDD	pg/L	ND	6.88		0.161
octa-CDD	pg/L	40.1	-	J	0.473
2,3,7,8-tetra CDF	pg/L	ND	1.48		0.808
1,2,3,7,8-penta CDF	pg/L	ND	2.80		0.0923
2,3,4,7,8-penta CDF	pg/L	ND	3.04		0.102
1,2,3,4,7,8-hexa CDF	pg/L	ND	1.44		0.0623
1,2,3,6,7,8-hexa CDF	pg/L	ND	1.41		0.0600
2,3,4,6,7,8-hexa CDF	pg/L	ND	1.62		0.0675
1,2,3,7,8,9,-hexa CDF	pg/L	ND	2.40		0.0945
1,2,3,4,6,7,8-hepta CDF	pg/L	ND	1.98		0.0800
1,2,3,6,7,8,9-hepta CDF	pg/L	ND	3.48		0.119
octa-CDF	pg/L	75.2	5.08		0.360

Note:
Why is 40.1 pg/L flagged with a 'J'? What is the lab reporting down to (MDL or DL?)

The lab uses 40 CFR Part 136 for the MDL which is acceptable. Lab defines 'DL' as the 'Sample-Specific Estimated Detection Limit' which is above the MDL. However, the ML is not stated on the lab report page. After further review, the lab is using an ML of 50 pg/L for octa-CDD which is why the 40.1 pg/L result is flagged with a 'J'.

Note: The octa-CDF result is 75.2 pg/L but it is not flagged with 'DNQ' per "Attachment G", Table A (octa-CDF's ML is 100 pg/L). The laboratory is using 50 pg/L as its ML.

2.4.3: Checking sample results (<ML) against method blank data

One final example of real data relates to the reviewer being very careful to check Method Blank data when there are any positive detections in the Agency's samples. The following summary from an example laboratory report has been entered onto the "Dioxin/Furan Data Review Worksheet" provided in this Guidance. By entering the Method Blank results along with the sample results, ML's, and MDL's, the data reviewer can easily identify a problem with the laboratory's background levels for Dioxin/Furan testing. The data highlighted in yellow with a 'B' flag is of concern:

From Figure 3: Dioxin and Furan Data Review Worksheet for Method Blank Review					
Congener	MDL (pg/L)	Minimum Level (ML) Table A (pg/L)	Sample Congener Results (pg/L) Batch #: _____	Method Blank Results (pg/L) Batch #: _____	Flag Sample Result if: < ML = DNQ ≥ ML = No Flag < MDL = ND 'B' = Positive Detection for the same Congener in the associated Method Blank*
2,3,7,8-tetra CDD	0.560	10	<0.560	<0.560	
1,2,3,7,8-penta CDD	0.572	50	<0.572	1.04	
1,2,3,4,7,8-hexa CDD	*0.504*	*50*	*0.934*	*1.26*	B
1,2,3,6,7,8-hexa CDD	*1.01*	*50*	*0.834*	*<1.01*	B
1,2,3,7,8,9-hexa CDD	*0.542*	*50*	*1.20*	*1.34*	B
1,2,3,4,6,7,8-hepta CDD	*0.571*	*50*	*1.51*	*1.78*	B
octa-CDD	*1.11*	*100*	*3.85*	*4.49*	B
2,3,7,8-tetra CDF	0.584	10	<0.584	<0.584	
1,2,3,7,8-penta CDF	0.578	50	<0.578	0.821	
2,3,4,7,8-penta CDF	*0.546*	*50*	*0.549*	*0.548*	B
1,2,3,4,7,8-hexa CDF	*0.554*	*50*	*0.881*	*1.09*	B
1,2,3,6,7,8-hexa CDF	*0.589*	*50*	*0.644*	*0.970*	B
1,2,3,7,8,9,-hexa CDF	0.584	50	<0.584	<0.584	
2,3,4,6,7,8-hexa CDF	0.583	50	<0.583	<0.583	
1,2,3,4,6,7,8-hepta CDF	1.04	50	<1.04	<1.04	
1,2,3,6,7,8,9-hepta CDF	0.585	50	<0.585	<0.585	
octa-CDF	*1.20*	*100*	*3.57*	*5.36*	B

As can be readily observed this example, there were a significant number of positive detects highlighted in yellow above the laboratory's MDL in the Method Blank. None of the detects are greater than the "Attachment G" ML's (lowest calibration standard) which is acceptable under Method 1613. However, a careful review of the associated Method Blank data against the sample results raises concerns that need to be addressed with the laboratory. These data were not flagged as 'estimated' on the laboratory report provided to the data-user due to the laboratory's policy to allow the data reviewer to handle qualifiers. Since the levels detected in the sample were so close to levels detected in the Method Blank, this should raise a concern that low-level Dioxin/Furan results in the client sample data may be a consequence of laboratory background contamination. In this example, a 'B' flag was assigned due to the Agency's policy and the laboratory contacted.

3.0 Suggested Instructions to Subcontract Laboratories from Agencies

Dioxin/Furan data generated under Method 1613 must meet all of the quality control requirements stated in the method for the data to be used for compliance monitoring. That, along with other instructions, are paramount to the success of the effort between the Agency and the subcontract laboratory. This section provides guidance to the Agency on what language to include in its agreements with its certified laboratory for performing Dioxin/Furan testing. The following recommendations should be considered:

A. The laboratory must be certified for Method 1613 and a copy of the certificate submitted to the Agency. Other supporting documentation for the Agency's file is the laboratory's QA Manual and at least 2 years of Performance Testing/Performance Evaluation results for a non-potable water matrix. Reviewing the last certification audit report and response for Dioxin/Furan testing is helpful for gauging the laboratory's quality system.
B. The laboratory should receive a copy of "Attachment G" with reporting instructions clearly stated as part of the contract for performing services.
C. Only data meeting the quality control requirements of Method 1613 should be accepted by the Agency for Dioxin/Furan monitoring. Minor excursions that do not affect data precision, accuracy, or confidence in identification should be narrated by the laboratory. However, the Agency should reserve final judgment on the usability of the results for monitoring before accepting qualified results beyond those flags related to the level of positive detections (e.g. DNQ).
D. Detections of Dioxin congeners below the lowest calibration level (ML) should be reported with a flag (DNQ).
E. ~~'J' or~~ Detections of congeners ≥ML should be considered 'quantitative' and can be used without qualification for monitoring in the absence of other flags by the subcontract laboratory.
F. Detections of Dioxin/Furans below the MDL should be reported as 'Non-Detect' since results below the MDL have a higher uncertainty that a value is 'non-zero' which could lead to use of false positives.
G. Laboratory reports should clearly state the ML and MDL levels for each congener in all samples analyzed and all associated batch quality control (Method Blank, MS/MSD's, OPR's, etc) to facilitate the evaluation of positive detections against permit requirements.
H. Any detections of congeners in Method Blanks ≥MDL must be flagged in the associated sample results if there are positive detections in samples also ≥MDL. Detections in the Method Blank may be an indication of background contamination from the laboratory that may artificially increase Dioxin/Furan detections above the ML.

    Note: *The Agency is encouraged to develop a policy for what factor is needed between any positive detection and levels in the Method Blank should that event occur. The policy should detail the Agency's response if background levels indicated by the laboratory's Method Blank have the possibility of biasing Dioxin-TEQ calculations. It is recommended that the contract language between an Agency and the laboratory identify data quality objectives for Method Blanks to assure the laboratory's compliance and consistency in the Agency's decision-making process.*

I. The laboratory is only to use terminology defined in Method 1613 for reporting. Use of terminology such as EMPC's, "Sample-Specific Estimated Detection Limits", DL's, and RDL are not terms defined in Method 1613 and should not be incorporated in laboratory reports used for an Agency's NPDES compliance testing purposes to avoid confusion by data-users.

4.0 Handling Qualified Data

The outcome of this systematic data review process is a thorough assessment of the usability of data generated by a subcontract laboratory for Dioxin/Furans testing. Through use of the 'Dioxin/Furans Data Review Worksheet' provided in this Guidance, an Agency can assess its data against its own data quality objectives and decide how to use data for monitoring.

Should there be a serious doubt about the validity of Dioxin/Furans data generated by a subcontract laboratory, the Agency may need to consider the use of a third-party for an opinion. The second-opinion may include 'Data Validation' which involves collection and review of all raw data (i.e. method review, sample receipt, sample preparation, MDL studies, calibration data, instrument performance checks, samples, and quality control) supporting the Laboratory Report. The use of a second-opinion to assess the ramifications of data quality issues should be considered if data may need to be 'rejected'. Simpler objective reasons for rejection of data by an Agency may include:

- ❑ Gross exceedance of holding time
- ❑ No preservation (de-chlorination, storage/transport temperature problems)
- ❑ Positive detections in Agency samples and associated Method Blanks resulting in similar congeners and levels detected
- ❑ Laboratory narratives which point to rejection of data due to the Laboratory's own doubt

Areas less clear-cut than the above scenarios may require additional objective evidence for why the Agency 'rejected' positive results from a sampling event. The best way to develop that objective evidence is suggested through a third-party.

As such, not all sampling events will produce 'perfect' results (no qualifications, flags, or narratives) and a significant amount of judgment may be needed for how to proceed. The effort for handling qualified data is most effectively implemented using this Guidance, the Agency's policies, the Agency's data quality objectives, and "Attachment G" language. These four elements formalized into a procedure can greatly assist an Agency before qualified data are received from a subcontract laboratory. The Guidance provided to this point will go a significant way in helping the laboratory staff provide a meaningful assessment of the usability of results.

A rule-of-thumb for reporting under any regulatory program is to narrate or discuss issues around the generation and/or subsequent usage of data. If data are generated with any known excursions from sampling, methodology, Agency policy, or permit requirements, it is always prudent to provide a discussion regarding the situation and how it may impact (or is believed to not impact) the results.

If the data assessment process at the Agency level produces doubt about the accuracy, precision, or identification of the reported results, a discussion should be provided with the data if the Agency's circumstances result in being unable to re-sample and re-analyze. In an era driven by the process of electronic data uploading and the limitations of providing information due to electronic fields or set formatting, the Agency must always be communicative by alternative actions such as correspondence with supporting information. This additional effort assures that clarifications or qualifications are documented and traceable at a future date.

4.1 Frequently Asked Questions

The next level of Guidance provided in this section is how to handle scenarios such as when samples from the same collection event are analyzed at different times or handling unexpected positive detections or what to do with two sets of data. The following section provides recommendations for options an Agency can pursue based on the scenario described:

4.1.1 Under what circumstances should an Agency consider analysis of back-up samples?

Guidance: The most usual circumstance is batch-level quality control failures that require re-extraction and re-analysis and the laboratory has insufficient sample. However, unexpected positive detections may drive an Agency to consider analysis of back-up samples or to initiate re-sampling and re-analysis. The occurrence of Dioxin/Furan results just below the ML in Method Blanks and an Agency's Dioxin/Furans results being just above the ML may also be a reasonable basis to prompt a second round of testing. That is because Dioxin/Furan detections below the ML have the possibility of creating a high bias leading to detections over the ML.

The indicators of whether or not the positive detects are random or 'real' comes from a review of raw data for method blanks, calibration blank checks, instrument performance checks, and levels in other samples analyzed along with the Agency's sample. Checking the results from all samples tested in an analytical sequence (particularly immediately before the Agency's samples) can provide insight as to whether or not there was cross-contamination or 'carry-over' from one sample to another. It is usual that a Dioxin/Furans testing laboratory will detect this problem during the data review process. When detected, a Dioxin/Furans laboratory will initiate re-analysis before releasing data if it is suspect to eliminate that possibility. However, the request for copies of this raw data by an Agency will assure that an additional review is conducted. The outcome of that review will drive the decision whether to initiate a second round of sampling and/or testing.

The re-analysis can be performed by the same laboratory or a second laboratory depending on the trends for the laboratory's performance. However, re-testing from the same sampling event should also include related quality control samples (i.e. equipment blanks, field blanks, etc).

Another strategy for addressing unexpected Dioxin/Furan results is to send a double blind check sample prepared by a certified PT Provider. PT Providers for traditional environmental testing have the capability of preparing and sending the Agency a whole-volume sample which can be used to evaluate the occurrence of false positives for Dioxin/Furans above the ML.

4.1.2 Can an Agency still report data as the same "sampling event" when samples are tested at different times?

Guidance: In other words, if an Agency collects replicate containers for Dioxin/Furans testing and retains backup samples, is that still the same sampling event? The unique stability of Dioxin/Furans chemistry allows the samples to function as if they are from the same sampling event because the holding time for Dioxin testing is 1 year. Within the normal variability between effluent samples collected in the same timeframe, replicate containers can be considered as part of the same sampling event. Keeping as many factors as consistent as possible and providing documentation supporting consistency is helpful for assessing the usability of data generated under this situation. Factors such as consistency between storage conditions, sample handling, transport temperature, bottle lot numbers, preservative lot numbers, and percent solids results between replicates can be included in the supporting documentation when retained samples are used for re-extraction and re-analysis at a date within 1 year of sampling.

4.1.3 Does the Agency send the set of back-up samples plus associated quality control (Equipment Blanks, Field Blanks, MS/MSD's, Duplicates, etc) to another laboratory if there are positive detections with the first laboratory or does it remain with the same laboratory and send retained samples for the second round?

Guidance: The strategy depends on the nature of the subcontract laboratory's performance over time. If the history of the subcontract laboratory has been to generate method-complaint and contract-

compliant data, then it is usual and customary to send the back-up samples and associated quality control to the same laboratory.

Even with the best laboratories, random contamination at the facility can occur through handling, processing, and analyzing samples due to the ultra-low nature of Dioxin/Furans testing. As such, it is possible that a follow up round of testing from replicate containers representing the same sampling event will not reproduce the same results and the Agency is left with how to handle both sets of data (discussed below in Section 4.1.4).

Unexpected 'positive' detects above the ML that are not reproduced by the same laboratory or a second laboratory is a very serious matter. The Guidance provided to the Agency under this circumstance may be to have all raw data reviewed by a third-party validation company to develop objective evidence supporting the actions of the Agency to either accept the positive detections above the ML or to reject those data. All documentation and the justification for the Agency's actions must be provided to the Regional Board when data are finally reported for compliance monitoring.

4.1.4. How are 'rejected' data or multiple sets of data handled for reporting compliance samples (average between both sampling rounds, pick one set over another, report all data/include an explanation with objective evidence for action, etc)?

Guidance: This can be a common situation in which Agencies can be found when there is qualified and/or rejected data generated for Dioxin/Furans testing. Permit instructions may be to report results as a monthly average of all samples without mention of what to do with qualified or rejected data. The key is to gather objective evidence for why a result needs to be 'rejected' or not included in the monthly average. Objective evidence can be from the Agency's own review of the subcontract laboratory's report which points to laboratory error, holding time violations, or sample handling issues. A letter from the laboratory stating its own doubt about the results or an opinion from a second party can also be pursued to support the Agency's case for not including the 'rejected' data into the report to the Board.

The most prudent action is to report all data which must include the objective evidence generated by the Agency for assessing its situation. In that context, the Agency may propose an action or actions supported by the collective outcome of the information gathered (average, select one set over another, report both sets with qualification, etc). However, in order for data to not be used for reporting, there must be some process that objectively supports its rejection and why.

Appendix 1: Definitions Commonly Used for Dioxin/Furans Testing

BIOACCUMULATION: The net accumulation of a substance by an organism as a result of uptake from all environmental sources.

BIOACCUMULATION EQUIVALENCY FACTOR (BEF): A factor used to account for the different levels of bioaccumulation potential for each congener. Assigned a bioaccumulation equivalency factor (BEF) are relative to bioaccumulation for 2,3,7,8-TCDD.

BIOACCUMULATION FACTOR (BAF): The ratio (in L/kg) of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time.

BIOTA-SEDIMENT ACCUMULATION FACTOR (BSAF): The ratio (in kg of organic carbon/kg of lipid) of a substance's lipid-normalized concentration in tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment, in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism.

CALIBRATION SOLUTION: solutions containing known amounts of selected analytes, internal standards and recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CALIBRATION VERIFICATION (VER): a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time window for each homologue.

CDD: Chlorinated Dibenzo-p-Dioxin. The isomers and congeners of tetra- through octa-chlorodibenzo-p-dioxin.

CDF: Chlorinated Dibenzofuran. The isomers and congeners of tetra- through octa-chlorodibenzofurans.

CLEAN-UP STANDARD: only one labeled analyte (2,3,7,8-TCDD) is added to all samples extracts prior to any Clean-up procedure. This standard is used to differentiate between losses of analytes or internal standards during extraction and losses that occur during the various Clean-up procedures.

CONGENER: synonymous with the word “homologue” which is a member or members of a particular homologous series (i.e. Dioxin/Furans) that has the same molecular weight but not necessarily the same structural arrangement. The term “Congener’ and ‘Homologue’ are often used interchangeably in the literature. See “HOMOLOGUE”.

ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC): the concentration of a given analyte that would produce a signal with a given area peak. The EMPC is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and/or confirmation ions has signal to noise in excess of 2.5 times the background level but does not meet identification criteria.

FIELD BLANK: An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC: Gas chromatograph or gas chromatography.

GEL PERMEATION CHROMATOGRAPHY (GPC): removes many high molecular weight interferences that cause GC column performance to degrade. It may be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds.

HOMOLOGUE: a member or members of a particular homologous series that has the same molecular weight but not necessarily the same structural arrangement. For example, the 28 pentachlorinated dibenzofurans are homologues.

HPLC: high performance liquid chromatography

HRGC/HRMS: high resolution gas chromatography/ high resolution mass spectrometry.

INITIAL CALIBRATION STANDARD SOLUTION (CS1-CS5): analysis of analytical standards for a series of different specified concentrations. The initial calibration is used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INITIAL PRECISION AND RECOVERY (IPR): must be performed by the laboratory to establish the ability to generate acceptable precision and accuracy by analyzing four aliquots of the diluted PAR standard. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6). An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

INTEGRATED ION CURRENT: electronic output to computer from instrument to provide a hard copy of area and height of a peak that may or may not be an analyte of interest.

INTERNAL STANDARDS (IS): labeled analytes are added to every sample and are present at the same concentration in every blank, quality control sample, and calibration solution. The IS are added to the sample before extraction and are used to measure the concentration of the analytes. In Method 1613, the IS's are 13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD.

ION ABUNDANCE RATIO: mathematical comparison of selected pair of ions stipulated by the method for each target analyte. The ratio between each pair of ions must fall within established limits. These ions are needed for the identification and quantitation of target analytes.

ISOMER: chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

LABELED ANALYTE (or analog): an analyte that has isotopically carbon added to its chemical structure. These compounds are used to established identification (retention time) and used for quantitation of unlabeled analytes.

MASS/CHARGE: usually expressed as m/z.

METHOD BLANK (MB): an analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The MB is used to define the level of laboratory background contamination.

MINIUMUM LEVEL (ML): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point to the analyte. It is equivalent to the concentration of the lowest calibration

standard, assuming that all method-specified sample weights, volumes, and clean up procedures have been employed. Interpreted in “Attachment G” to be the same as the Reporting Limit.
NON-CONGENER: elements not from the same group in the periodic table.

NON-2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure have positions other than 2,3,7,8.

ONGOING PRECISION AND RECOVERY (OPR): must be performed by the laboratory to establish the ability to maintain on a continuous basis, acceptable precision and accuracy. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6).
PAR: Precision and Recovery standard. Secondary standard that is diluted and spiked to form IPR and OPR. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6).

PERCENT VALLEY: see Resolution

PERFLUOROKEROSENE (PFK): compound used to establish mass spectral instrument performance for dioxin/furan analysis.

PERFORMANCE EVALUATION (PE)/PERFORMANCE TEST (PT) SAMPLE: a chemical waste, soil or water sample containing known amounts of unlabeled CDDs/PCDFs used for Quality Assurance programs.

PCDPE: Polychlorinated Diphenylether: isomers having the same SICP and ion ratios identical to furan isomers and are monitored for interference in furan qualitative and quantitative analysis.

QUALITY CONTROL CHECK SAMPLE (QCS): A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

RECOVERY: a determination of the accuracy of the analytical procedure made by comparing measured values from a fortified (spiked) sample against the known spiked values.

RELATIVE RETENTION TIME (RRT): ratio of the retention time of the analyte versus the retention time of the corresponding internal standard. RRT for each analyte must be within range established by the method.

RELATIVE RESPONSE (RR): the ratio of the area response of the mass spectrometer to a known amount of an analyte (unlabeled to labeled) versus a known concentration in standard solution, plotted using linear regression. The RR is used to determine instrument performance and is used in the quantitation calculations.

RELATIVE STANDARD DEVIATION (RSD): The standard deviation times 100 divided by the mean. Also termed “coefficient of variation”.

REPORTING LIMIT – Interpreted in this Guidance document to be the same as the ML since Page G-16 of “Attachment G” references the Reporting Limit as the lowest quantifiable limit.

RESPONSE FACTOR (RF): the ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of internal standard as measured in the initial and continuing

calibrations. The RF is used to determine instrument performance using correlation coefficient and is used in the quantitation calculations.

RESOLUTION: the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RINSATE: a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SELECTED ION MONITORING (SIM): a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SICP: A plot of ion abundance versus time for each ion which provides the retention time, peak area and height. This information is used for identification and quantitation of target analyte.

SIGNAL TO NOISE (S/N) RATIO: the ratio of analyte signal to random background signal. To determine the ratio, display each characteristic ion using a window 100 scans wide, and draw a base line from the lowest point in the 100 scan window. The noise is defined as the height of the largest signal (excluding signal due to CDDs/PCDFs or other chemicals) within the 100 scan window. The signal is defined as the height of the PCDD/PCDF peak. If the data system determines the ratio, the Contractor shall demonstrate comparability between the above criteria and the automated S/N determination. Chemical noise is left to the judgment of the analyst.

2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure has other positions as well as the 2,3,7,8 positions.

TOXICITY EQUIVALENCY FACTOR (TEF): a method of converting concentrations of CDDs/PCDFs to an equivalent concentration of 2,3,7,8-TCDD to obtain an estimation of the toxicity of the entire sample.

TWELVE HOUR TIME PERIOD: the 12 hour time period begins with the injection of the CS3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12 hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be injected with 12:00 hours of the CS3 solution or the column performance solution.

UNLABEL ANALYTE: target compound that has not been isotopically altered.

WINDOW DEFINING MIXTURE (WDM): a mixture containing the first and last eluting isomer for each congener. The retention time for each first and last eluting isomer establishes the retention time window for each congener. All analytes in the standards (calibrations, internal standards, recovery standards, Clean-up standard) and identified analytes in samples must have a reported retention time within the established window. It is analyzed before any calibration standard, at the beginning of each 12 hour time period or when there is a shift greater than 10 seconds between retention time of recovery standards in standards or any analysis from retention time in recent calibration verification.

Appendix 2. References

1. Method 1613 “Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994
2. USEPA ‘National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDD’s) and Chlorinated Dibenzofurans (CDF’s) Data Review’, OSWER 9240.1-51, EPA-540-R-05-001, September 2005.
3. Los Alamos National Laboratory “Routine Validation of Dioxin Furan Analytical Data (EPA Method 1613 and SW-846 Method 8290), SOP-5169, 6/3/2008.
4. USEPA “Data Validation SOP for EPA Method 1613, Revision B Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilutions (HRGC/HRMS), Region II, SOP HW-25, Revision 3, September 2006.
5. USEPA “Dioxin/Furan Data Validation Guidance”, Region III, Draft March 1999.
6. ‘Data Validation Standard Operating Procedures for Chlorinated Dioxin/Furan Analysis by High Resolution Gas Chromatography” EPA Region IV, Revision 3.0, May 2002.
7. USEPA Analytical Operations/Data Quality Center (AOC) “National Functional Guidelines for Chlorinated Dioxin/Furan Data Review, Final, OSWER 9240.1-37, EPA 540-R-02-003, August 2002.
8. USEPA Region 10 “SOP For the Validation of Polychlorinated Dibenzodioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data”, Environmental Services Division, Revision 2.0, January 31, 1996.
9. Tentative Order No R2-2009, California Regional Water Quality Control Board, San Francisco Bay Region, Attachments F and G, March 2010.

Appendix 3. Dioxin-TEQ Calculation Excel Spreadsheet Example

WWTP Effluent pg/L: Dioxin-TEQ Calculation (Use all results ≥ML)						
				< ML = 0		
Congener	Minimum Level (pg/L)	WHO 1998 TEF	GLI 1995 BEF	Conc. ≥ML	TEQ w/o BEF	TEQ w/BEF
2,3,7,8-TCDD	10	1.0	1.0	0	0	0
1,2,3,7,8-PeCDD	50	1.0	0.9	0	0	0
1,2,3,4,7,8-HxCDD	50	0.1	0.3	0	0	0
1,2,3,6,7,8-HxCDD	50	0.1	0.1	0	0	0
1,2,3,7,8,9-HxCDD	50	0.1	0.1	0	0	0
1,2,3,4,6,7,8-HpCDD	50	0.01	0.05	0	0	0
OCDD	100	0.0001	0.01	0	0	0
2,3,7,8-TCDF	10	0.1	0.8	0	0	0
1,2,3,7,8-PeCDF	50	0.05	0.2	0	0	0
2,3,4,7,8-PeCDF	50	0.5	1.6	0	0	0
1,2,3,4,7,8-HxCDF	50	0.1	0.08	0	0	0
1,2,3,6,7,8-HxCDF	50	0.1	0.2	0	0	0
1,2,3,7,8,9-HxCDF	50	0.1	0.6	0	0	0
2,3,4,6,7,8-HxCDF	50	0.1	0.7	0	0	0
1,2,3,4,6,7,8-HpCDF	50	0.01	0.01	0	0	0
1,2,3,4,7,8,9-HpCDF	50	0.01	0.4	0	0	0
OCDF	100	0.0001	0.02	0	0	0
			Total:	0	0.000	0.000

Appendix 4: Dioxin/Furans Data Review Worksheet

Agency: _____	**Date(s) Sampled:** _____ **Date(s) Extracted:** _____ **Date(s) Analyzed:** _____		
Laboratory: _____ **Permit/'Attachment G' (March 2010) Submitted to Lab?** ❑ Yes ❑ No	**Sample ID's:** _____ **Batch #/Test:** _____ _____		
COC#: _____	**Data Reviewer(s):** _____ _____	**Date Lab Report Received?** _____	**Laboratory Report Number(s):** _____ _____

Data Quality Element Reviewed	Issues Flagged by the Laboratory?	Data Usable? Yes	No	NA	Guidance
1. Chain of Custody Complete?		❑	❑	❑	
2. Required Analysis Reported?		❑	❑	❑	
3. Holding Times Met and Transport Temperatures Acceptable?		❑	❑	❑	Flag 'J' (Estimated): ❑ Yes ❑ No Flag 'R' (Rejected): ❑ Yes ❑ No Re-Sample/Re-Analyze: ❑ Yes ❑ No
4. Laboratory Report Complete, Signed, Dated, On Time?		❑	❑	❑	
5. Equipment Blank(s)		❑	❑	❑	Use judgment if positive detections
6. Field Blank(s)		❑	❑	❑	Use judgment if positive detections
7. Field Duplicates		❑	❑	❑	Use replicate data to trend system precision over time
8. Positive Sample Results Reported?		❑	❑	❑	Use Section 19 Worksheet to evaluate positive results. Results ≥MDL and <ML need 'DNQ' flags. Lab to use only Method 1613 detection limit terms. Positive results ≥ML are used for Dioxin-TEQ.
9. Laboratory Method Blank(s)		❑	❑	❑	Use Section 19 Worksheet to evaluate positive results in all samples and associated Method Blanks. Laboratory must re-extract and re-analyze if Dioxin/Furans ≥ ML or 1/3 regulatory compliance level per Method 1613. Table A in "Attachment G" is used for the ML.
10. OPR Results (e.g. LCS)		❑	❑	❑	Laboratory must meet Table 6 limits from Method 1613
11. Matrix Spike/Matrix Spike Duplicates		❑	❑	❑	Use MS/MSD data to trend system accuracy and precision over time
12. Internal Standards		❑	❑	❑	Laboratory must meet Table 6 limits from Method 1613
13. Labeled Isotopes		❑	❑	❑	Laboratory must meet Table 7 limits from Method 1613
14. Cleanup Surrogate or Standard (e.g. $^{37}Cl_4$-2,3,7,8-TCDD, CRS)		❑	❑	❑	Laboratory must meet %Recovery (35-197%) requirement stated in Table 7
15. Any Estimated Maximum Concentration Results Reported? (EMPC's are detects that do not meet all of the identification criteria so ID is less certain)		❑	❑	❑	The Guidance is to require the laboratory to remove any reference to "EMPC" terminology from its laboratory reports. EMPC's is a hazardous waste testing term not defined in Method 1613.

Data Quality Element Reviewed	Issues Flagged by the Laboratory?	Data Usable? Yes	No	NA	Guidance
16. TEFs used and Dioxin-TEQ Calculation Correct?		❑	❑	❑	Confirm 1998 WHO TEFs used for the Dioxin-TEQ Calculation.
17. BEFs used and Dioxin-TEQ Calculation Correct?		❑	❑	❑	Confirm 1995 GLI BEFs used for the Dioxin-TEQ Calculation.
18. Other issues identified by the laboratory?		❑	❑	❑	Laboratory should meet all QC requirements specified by Method 1613 for compliance monitoring.
19. Are data properly flagged based on permit instructions?		❑	❑	❑	Confirm laboratory has followed permit instructions for reporting.

Congener	MDL (pg/L)	Minimum Level (ML) Table A (pg/L)	Sample Congener Results (pg/L) Batch #: _____	Method Blank Results (pg/L) Batch #: _____	Flag Sample Result if: < ML = DNQ; ≥ML = No Flag; < MDL = ND; 'B' = Positive Detection for the same Congener in the associated Method Blank*
2,3,7,8-tetra CDD		10			
1,2,3,7,8-penta CDD		50			
1,2,3,4,7,8-hexa CDD		50			
1,2,3,6,7,8-hexa CDD		50			
1,2,3,7,8,9-hexa CDD		50			
1,2,3,4,6,7,8-hepta CDD		50			
octa-CDD		100			
2,3,7,8-tetra CDF		10			
1,2,3,7,8-penta CDF		50			
2,3,4,7,8-penta CDF		50			
1,2,3,4,7,8-hexa CDF		50			
1,2,3,6,7,8-hexa CDF		50			
1,2,3,7,8,9,-hexa CDF		50			
2,3,4,6,7,8-hexa CDF		50			
1,2,3,4,6,7,8-hepta CDF		50			
1,2,3,6,7,8,9-hepta CDF		50			
octa-CDF		100			

***Consider qualifying or rejecting results using professional judgment when Method Blank data are not significantly different from sample results. The laboratory should be contacted for determining next steps.**