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## **DMMP CLARIFICATION PAPER**

### **POLYCHLORINATED DIOXINS AND FURANS (PCDD/F): REVISIONS TO THE SUPPLEMENTAL QUALITY ASSURANCE PROJECT PLAN (SQAPP)**

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## **INTRODUCTION AND BACKGROUND**

In 2007, the DMMP agencies presented a clarification paper (DMMP, 2007a) and supplemental QAPP (DMMP, 2007b) discussing procedures for collection and analysis of PCDD/F data.

In the past 3 years, the program has gained significant experience reviewing PCDD/F data, both from dredging projects and from the 2008 OSV BOLD Survey of Puget Sound. In addition, a public issue paper was presented at the 2009 SMARM (EcoChem, 2009), recommending changes to the 2007 guidance. Based on DMMP experience and input received at the 2009 SMARM, the agencies are implementing minor revisions to the procedures for analyzing PCDD/F to assure that the highest quality of data are being generated for suitability determinations.

## **CLARIFICATION**

The following revisions are being implemented for the PCDD/F Supplemental QAPP:

- All projects will be required to analyze a sediment reference material such as NIST SRM#1944 with each analytical batch. Acceptance criteria for the reference material results (based on the 95% confidence interval) must be included in the sampling and analysis plan. If results fall outside the acceptance range, the laboratory may be required to reanalyze.
- It is strongly recommended that dioxin raw data be subjected to Stage 4 validation (EPA, 2009). Because of the complexity of dioxin analysis, the extremely low reporting limits, and the high potential for interfering compounds such as chloro diphenyl ethers, it is in the best interest of the project proponent to conduct this validation. The Corps of Engineers Seattle District validates all of its PCDD/F testing results for federal navigation dredging at this highest level.

As with other DMMP example plans, the SQAPP will need to be made project-specific by the project proponent (or its consultant). Deviations from procedures in the SQAPP will be considered by the DMMP agencies on a project-specific basis.

## **References**

DMMP, 2007a. Polychlorinated Dioxins and Furans (PCDD/F): Clarification of Procedures for Acquiring Sediment Data.

DMMP, 2007b. Supplemental Information on Polychlorinated Dioxins and Furans (PCDD/F) for use in Preparing a Quality Assurance Project Plan (QAPP).

EcoChem, 2009. Dioxin Data – Clarification of SRM Analysis and Validation Requirements. Presented at the 2009 Sediment Management Annual Review Meeting.

EPA, 2009. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use.

**REVISED SUPPLEMENTAL INFORMATION ON  
POLYCHLORINATED DIOXINS AND FURANS (PCDD/F) FOR USE  
IN PREPARING A QUALITY ASSURANCE PROJECT PLAN (QAPP)**

**November 8, 2010**

**1.0 INTRODUCTION AND BACKGROUND**

This document contains supplemental information to assist applicants in preparing a QAPP for projects when PCDD/F in sediment is of concern. A QAPP provides guidance and information for the laboratory that is to conduct the analysis of samples.<sup>1</sup> The information presented in this document supplements the Dredged Material Management Program (DMMP) guidance on preparing sampling and analysis plans. Its purpose is to assure that all PCDD/F data collected are of sufficient quality and are comparable throughout the program.

Under the DMMP, dredging project proponents are required to conduct analysis of PCDD/F in sediment when there is a reason to believe that anthropogenic sources may be present. The reason to believe includes information about nearby current or historical PCDD/F sources, such as chlor-oxide bleach process pulp mills, chlor-alkali or chlorinated solvent manufacturing plants, phenoxy herbicide use and handling, former wood treatment sites, or areas with high PCB concentrations.

PCDD/F comprise a family of toxic chemicals that have a similar chemical structure and a common mechanism of toxic action. PCDDs and PCDFs are not usually intended chemical products, but are trace-level byproducts of many forms of combustion and several industrial chemical processes. PCDD/F are widely distributed throughout the environment, are persistent and bioaccumulative. These chemicals have been characterized by EPA as “class B2,” or probable human carcinogens, and are thus considered to increase the risk of cancer. At body burdens ten times or less above those attributed to average background exposure, adverse non-cancer health effects have been observed in both animals and humans. In animals, these effects include changes in hormonal systems, alterations in fetal development, reduced reproductive capacity, and immunosuppression (EPA 2003).

There are 75 PCDD and 135 PCDF congeners, compounds distinguished by the number and position of their chlorine atoms. These can be grouped as homologs, or congener classes, compounds which have the same number of chlorine atoms per molecule. Homologs can be abbreviated as follows, with the number of chlorines shown in parentheses. Dioxins: TCDD (4), PeCDD (5), HxCDD (6), HpCDD (7), and OCDD (8). Furans: TCDF (4), PeCDF (5), HxCDF (6), HpCDF (7), and OCDF (8).<sup>2</sup>

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<sup>1</sup> The dredging program has retained the prior terminology of Sampling and Analysis Plan / Quality Assurance Project Plan; this is what is used here. EPA consolidated both of these plans into a document also called a QAPP (e.g., “G5 Guidance” at <http://www.epa.gov/Region10/offices/oea/epaqag5.pdf>).

<sup>2</sup> Homologs are molecules with the same chemical formula but different structural configuration. These designations are mainly relevant here because labs will report sums of, for example, all HxCDD.

PCDD/F are bioaccumulative compounds, although the toxicity of the various congeners varies considerably. The 17 congeners that have chlorine atoms located in the 2,3,7,8 positions (*e.g.*, 2,3,7,8-TCDD or 1,2,3,7,8-PeCDF) are the dioxins of known concern for health effects in fish, wildlife, and humans. Of these, 2,3,7,8-TCDD is considered the most toxic and is used as a benchmark (Toxic Equivalency Factor (TEF) of 1.0) for estimating the toxicity of the other dioxins. WHO (2005, published 2006) updated the toxicities for the 17 PCDD/F congeners. Table 1 summarizes the latest update of TEFs. The Toxicity Equivalence (TEQ) is calculated by multiplying the TEF by the concentration of the compound, and summing the results (as shown in Table 5). The resulting TEQ may be useful for risk assessment purposes. Data are typically reported to DMMP using the mammalian TEF.

**Table 1. Summary of WHO 2005 Mammalian Toxicity Equivalency Factors for PCDD/F and the Van den Berg et al. 1998 - Fish and Avian Toxicity Equivalence Factors**

Dioxins and Furans	TEF-M	TEF-F	TEF-W
	Mammals, Humans	Fish	Birds
<i>PCDD</i>			
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1
1,2,3,4,7,8-HxCDD	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.01	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.001	<0.0001
OCDD	0.0003	<0.0001	0.0001
<i>PCDF</i>			
2,3,7,8-TCDF	0.1	0.05	1
1,2,3,7,8-PeCDF	0.03	0.05	0.1
2,3,4,7,8-PeCDF	0.3	0.5	1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,6,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0003	<0.0001	0.0001

## 2.0 SEDIMENT SAMPLING AND ANALYSIS

In the field, sediment samples should be placed in wide-mouth glass jars with sufficient headspace to prevent breakage during freezing of the sample, placed into coolers with ice, and maintained at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until delivery to the laboratory. Sediment samples should be maintained in the dark while in transport and once in the laboratory. At the laboratory, the samples should be frozen at  $-18^{\circ}\text{C}$  until extraction. Frozen samples may be held for one year prior to extraction. After one year, results may still be reported, but they will be qualified as estimates unless the DMMP agrees that this qualifier is not necessary. Analysis of extracted sediments must be completed within 30 days of extraction (EPA 2005). However, if the sediment extracts are frozen, they must be analyzed within one year (EPA 1994).

## 3.0 ANALYTICAL METHODOLOGY

Because of the difficulty identifying PCDD/PCDF congeners at low concentrations and the significant possibility of interfering compounds (such as diphenyl ether) causing the reporting of artificially elevated values, it is important that a highly specific and sensitive method be employed for the analysis of PCDD/PCDF congeners.

EPA Method 1613B, a High-Resolution Gas Chromatographic/High Resolution Mass Spectrophotometric method, is the most commonly used method for DMMP projects. Method 1613B incorporates  $^{13}\text{C}_{12}$ -labelled reference compounds for each 2,3,7,8-substituted congener, providing unique reference standards for identification and quantification. EPA Method 8290 can provide the same traceability as 1613B with the addition of labeled compounds to cover all 17 congeners of interest. In reality, the actual methodology used by many labs is a hybrid of these two methods. The analytical technology and methodology have evolved since methods 1613B and 8290 were written. Both methods, as written, have deficiencies and should not be followed verbatim. Rather, data quality objectives need to be specified for the analytical laboratory to meet. In the remainder of this paper QA guidelines for method 1613B are referenced due to its predominant use. If other methods are used, appropriate QA guidelines will need to be documented in the SAP.

It is critical for reporting limits to be sufficiently low when analyzing dredged material for dioxin. Target reporting limits for DMMP projects are presented in Table 2.

**Table 2. Summary of Target Reporting Limits for PCDD/F**

Dioxins and Furans	Reporting Limit (ng/kg Dry Wt)
<i>PCDD</i>	
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	1.0
1,2,3,4,7,8-HxCDD	2.5
1,2,3,6,7,8-HxCDD	2.5
1,2,3,7,8,9-HxCDD	2.5
1,2,3,4,6,7,8-HpCDD	2.5
OCDD	5.0
<i>PCDF</i>	
2,3,7,8-TCDF	1.0
1,2,3,7,8-PeCDF	2.5
2,3,4,7,8-PeCDF	1.0
1,2,3,4,7,8-HxCDF	2.5
1,2,3,6,7,8-HxCDF	2.5
1,2,3,7,8,9-HxCDF	2.5
2,3,4,6,7,8-HxCDF	2.5
1,2,3,4,6,7,8-HpCDF	2.5
1,2,3,6,7,8,9-HpCDF	2.5
OCDF	5.0

#### **4.0 METHOD QUALITY CONTROL**

The DMMP agencies are recommending QC performance criteria rather than providing a step-by-step protocol for extraction and cleanup. Such criteria are needed to verify that extraction and cleanup are being performed correctly. The QC performance criteria must be presented in the sampling and analysis plan and approved by the DMMP agencies. Laboratories will be required to meet these performance criteria as well as take the specified corrective action if performance criteria are not met. Example criteria and corrective actions are provided in Tables 3 and 4.

All projects will be required to analyze a sediment reference material such as NIST SRM#1944 with each analytical batch. Acceptance criteria for the reference material results (based on the 95% confidence interval) must be provided by the laboratory and included in the sampling and analysis plan. If results fall outside the acceptance range, the laboratory may be required to reanalyze. A laboratory duplicate must also be analyzed with each analytical batch.

In addition to the project-specific QC requirements presented in the sampling and analysis plan, the laboratory shall implement all quality control procedures discussed in Method 1613B and meet all associated performance criteria.

The laboratory shall provide identification of sources and lot numbers for all reference materials and analytical standards to be used to perform analyses. Copies of certificates for certified reference materials and analytical standards shall be provided the DMMP with the laboratory results. In addition, the raw data associated with the analysis of dioxins shall be made available to the DMMP agencies upon their request.

#### **5.0 VALIDATION OF DATA**

It is strongly recommended that all TCDD/F data be subjected to Stage 4 validation (EPA, 2009). Because of the complexity of Method 1613B, the extremely low reporting limits, and the high potential for interfering compounds such as chloro diphenyl ethers, it is in the best interest of the project proponent to conduct this validation. Validation must be performed in accordance with EPA *National Functional Guidelines for Chlorinated Dioxin/Furan Data Review* (EPA 2005). The validator must have demonstrated experience accomplishing validation for PCDD/F. Details related to validation, including the name of the validator or validation subcontractor, must be included in the sampling and analysis plan.

If the project proponent should decide not to do the validation up front, the DMMP agencies will review the primary results against the Method 1613B acceptance limits and those in the project QAPP. Based on the results of this review, the DMMP agencies may require validation. Should the DMMP require validation, the project proponent must provide it, using the validation specifications provided in the previous paragraph.

## 6.0 REPORTING OF DATA

The laboratory shall report each of the 2,3,7,8-chlorine substituted PCDD/F congeners on a dry-weight basis. Method detection limits, estimated detection limits and reporting limits shall be reported for each of these congeners. The 17 congeners of interest shall be tabulated as TEQ, both with nondetected values (U) = ½ estimated detection limit and with U = 0. (The difference between these values gives data reviewers an idea of how much the estimated detection limit substitution affects the TEQ summation.) Table 5 presents the specified mammalian TEFs for each of the 17 congeners and provides an example of the calculations necessary to derive the TEQ. For the purpose of TEQ summation, estimated maximum potential concentrations (EMPCs) shall be reported as nondetects (U) at the EMPC value. Details regarding estimated detection limits are provided in Attachment 1.

This summary of QC requirements is not all-inclusive of method 1613B requirements. Other method-required QC checks, criteria and corrective actions can be found in the EPA *National Functional Guidelines for Chlorinated Dioxin/Furan Data review* (EPA, 2005) and must be followed unless preempted by the following.

**Table 3. Summary of Quality Control Procedures**

QC Check	Minimum Frequency	Acceptance Criteria	Laboratory Corrective Action*
Ongoing Precision And Recovery	1 per analytical batch (≤ 20 samples)	Recovery within acceptance criteria in Table 4 of this QAPP guidance document	1. Check calculations 2. Reanalyze batch
Stable-isotope-labeled compounds	Spiked into each sample for every target analyte	Recovery within limits in Table 4	1. Check calculations 2. Qualify all associated results as estimated
		Ion abundance ratios must be within criteria in Table 9 of method 1613B	1. Reanalyze specific samples. 2. Reject all affected results outside the criteria 3. Alternatively, use of secondary ions that meet appropriate theoretical criteria is allowed if interferences are suspect. This alternative must be approved by the DMMP agencies.
Laboratory duplicate	5% or 1 per batch (≤ 20 samples)	Relative percent Difference ≤ 30%	1. Evaluation of the homogenization procedure and evaluation method 2. Reanalyze batch

Method blank	1 per analytical batch ( $\leq$ 20 samples)	Detection $\leq$ minimum level in Table 2 of Method 1613B	1. If the method blank results are greater than the reporting limit, halt analysis and find source of contamination; reanalyze batch. 2. Report project samples as non-detected for results $\leq$ to the reported method blank values
GC/MS Tune	At the beginning of each 12 hour shift. Must start and end each analytical sequence.	$>10,000$ resolving power @ $m/z304.9825$ Exact mass of $380.9760$ within 5 ppm of theoretical value.	1. Re-analyze affected samples 2. Reject all data not meeting method 1613B requirements
Initial Calibration	Initially and when continuing calibration fails.	Five point curve for all analytes. RSD must meet Table 4 requirements for all target compounds and labeled compounds. Signal to noise ratio (S/N) $>10$ . Ion abundance (IA) ratios within method specified limits.	
Window Defining/Column Performance Mix	Before every initial and continuing calibration.	Valley $<25\%$ for all peaks near 2378-TCDD/F peaks.	
Continuing Calibration	Must start and end each analytical sequence.	%D must meet Table 4 limits for target compounds & labeled compounds. S/N $>10$ . IA ratios within method specified limits.	
Confirmation of 2,3,7,8- TCDF	For all primary-column detections of 2,3,7,8-TCDF	Confirmation presence of 2,3,7,8-TCDF in accordance with method 1613B requirements	
Sample data not achieving target reporting limits or method performance in presence of possibly interfering compounds	Not applicable	Not applicable	Rather than simply dilute an extract to reduce interferences, the lab should perform additional cleanup techniques identified in the method to insure minimal matrix effects and background interference. Thereafter, dilution may occur. If re-analysis is required, the laboratory shall report both initial and re-analysis results.

Sediment Reference Material	One per analytical batch	Result must be within 20% of the 95% confidence interval	<ol style="list-style-type: none"> <li>1. Extraction and analysis should be evaluated by the lab and re-analysis performed of the entire sample batch once performance criteria can be met.</li> <li>2. If analysis accompanies several batches with acceptable RM results, then the laboratory can narrate possible reason for RM outliers.</li> </ol>
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If re-analysis is required, the laboratory shall report initial and re-analysis results

**Table 4. QC Acceptance Criteria for PCDD/F**

	Test Conc., ng/mL <sup>1</sup>	IPR <sup>2</sup>		OPR <sup>3</sup> (%)	I-CAL <sup>4</sup> %	CAL/VER <sup>5</sup> (%) (Coeff. of Variation)	Labeled Cmpd %Rec. in Sample	
		RSD (%)	Recovery				Warning Limit	Control Limit
<b>Native Compound</b>								
2,3,7,8-TCDD	10	28	83-129	70-130	20	78-129	-	-
2,3,7,8-TCDF	10	20	87-137	75-130	20	84-120	-	-
1,2,3,7,8-PeCDD	50	15	76-132	70-130	20	78-130	-	-
1,2,3,7,8-PeCDF	50	15	86-124	80-130	20	82-120	-	-
2,3,4,7,8-PeCDF	50	17	72-150	70-130	20	82-122	-	-
1,2,3,4,7,8-HxCDD	50	19	78-152	70-130	20	78-128	-	-
1,2,3,6,7,8-HxCDD	50	15	84-124	76-130	20	78-128	-	-
1,2,3,7,8,9-HxCDD	50	22	74-142	70-130	35	82-122	-	-
1,2,3,4,7,8-HxCDF	50	17	82-108	72-130	20	90-112	-	-
1,2,3,6,7,8-HxCDF	50	13	92-120	84-130	20	88-114	-	-
1,2,3,7,8,9-HxCDF	50	13	84-122	78-130	20	90-112	-	-
2,3,4,6,7,8-HxCDF	50	15	74-158	70-130	20	88-114	-	-
1,2,3,4,6,7,8-HpCDD	50	15	76-130	70-130	20	86-116	-	-
1,2,3,4,6,7,8-HpCDF	50	13	90-112	82-122	20	90-110	-	-
1,2,3,4,7,8,9-HpCDF	50	16	86-126	78-130	20	86-116	-	-
OCDD	100	19	86-126	78-130	20	79-126	-	-
OCDF	100	27	74-146	70-130	35	70-130	-	-
<b>Labelled Compounds</b>								
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130
<sup>13</sup> C <sub>12</sub> -2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-130	35	72-130	40-120	23-130
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130
<sup>13</sup> C <sub>12</sub> -OCDD	200	48	20-138	25-130	35	70-130	25-120	17-130
<b>Cleanup Standard</b>								
<sup>37</sup> Cl <sub>1</sub> -2,3,7,8-TCDD	10	36	39-154	31-130	35	79-127	40-120	35-130

(Table shown with permission from AXYS Analytical Services LTD (2005), Vancouver, British Columbia, Canada. *Analysis of Polychlorinated Dioxins and Furans by Method 1613B* -- MSU-018 Rev. 5, 07-Jun-2005)

<sup>1</sup> QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume

<sup>2</sup> IPR: Initial Precision and Recovery demonstration

<sup>3</sup> OPR: Ongoing Precision and Recovery test run with every batch of samples.

<sup>4</sup> Initial Calibration

<sup>5</sup> CAL/VER: Calibration Verification test run at least every 12 hours

**Table 5. Example Results of Dioxin/Furan TEQ Calculation**

Analyte	TEF (WHO 2005)	Sample C-1			
		Conc. ng/kg-dw	LQ <sup>1</sup>	TEQ U=1/2 EDL	TEQ U=0
2,3,7,8-TCDD	1	0.1	U	0.05	0
1,2,3,7,8-PeCDD	1	0.4		0.4	0.4
1,2,3,4,7,8-HxCDD	0.1	0.4		0.04	0.04
1,2,3,6,7,8-HxCDD	0.1	2.4		0.24	0.24
1,2,3,7,8,9-HxCDD	0.1	1.3		0.13	0.13
1,2,3,4,6,7,8-HpCDD	0.01	39.3		0.393	0.393
OCDD	0.0003	253		0.0759	0.0759
2,3,7,8-TCDF	0.1	0.7		0.07	0.07
1,2,3,7,8-PeCDF	0.03	0.224		0.00672	0.00672
2,3,4,7,8-PeCDF	0.3	0.305	U	0.0458	0
1,2,3,4,7,8-HxCDF	0.1	0.433		0.0433	0.0433
1,2,3,6,7,8-HxCDF	0.1	0.294	U	0.0147	0
2,3,4,6,7,8-HxCDF	0.1	0.321		0.0321	0.0321
1,2,3,7,8,9-HxCDF	0.1	0.087	U	0.00435	0
1,2,3,4,6,7,8-HpCDF	0.01	6.61		0.0661	0.0661
1,2,3,4,7,8,9-HpCDF	0.01	0.409		0.00409	0.00409
OCDF	0.0003	15.1		0.00453	0.00453
<b>Total TEQ:</b>				1.62	1.50

<sup>1</sup>Laboratory Qualifiers

U: Analyte was not detected at or above the reported result.

## References

EPA 2009. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund use. <http://www.epa.gov/superfund/policy/pdfs/EPA-540-R-08-005.pdf>

EPA 2005. *Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Review*. EPA-540-R-05-001. September, 2005. <http://www.epa.gov/superfund/programs/clp/download/dlm/dlm2nfg.pdf>

EPA 2003. *National Academy of Sciences Review Draft of Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds*. <http://www.epa.gov/ncea/pdfs/dioxin/nas-review/>

EPA/USACE 1998. *Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. – Testing Manual (Inland testing Manual)*. EPA Number 823B98004. <http://www.epa.gov/waterscience/itm/ITM/>

EPA 1995. *QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations - Chemical Evaluations*. EPA Number 823B95001. <http://yosemite.epa.gov/water/owrccatalog.nsf/e673c95b11602f2385256ae1007279fe/fa5420ee832b630485256b0600724b38!OpenDocument>

EPA 1994. Method 1613: *Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS*. Revision B. EPA Number 823B95001. <http://www.epa.gov/waterscience/methods/1613.html>

NIST 2010 (online). SRM 1944 – New York/New Jersey Waterway Sediment; from National Institute of Standards and Technology. [https://www-s.nist.gov/srmors/view\\_detail.cfm?srm=1944](https://www-s.nist.gov/srmors/view_detail.cfm?srm=1944)

Van den Berg, Martin et al. 1998. *Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife*. Environmental Health Perspectives Volume 106, Number 12, December 1998.

World Health Organization (WHO) 2005. *Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds*. ToxSci Advance Access published online July 7, 2006. [http://www.who.int/ipcs/assessment/tef\\_update/en/](http://www.who.int/ipcs/assessment/tef_update/en/)

## Attachment 1 Estimated Detection Limits

The estimated detection limit is a sample- and analyte-specific detection limit that is based on the signal-to-noise ratio present in the sample for each analyte at the time of analysis. This is the best value to use to get the lowest defensible TEQ values.

The estimated detection limit is defined as follows:

$$\text{EDL} = \frac{2.5 \times H_x \times Q_{is}}{H_{is} \times W \times \overline{\text{RF}}_n}$$

where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

$H_x$  = sum of the height of the noise level for each quantitation ion for the unlabeled PCDDs/PCDFs.

$H_{is}$  = sum of the height of the noise level for each quantitation ion for the labeled internal standard.

W = weight, in g, of the sample.

$\overline{\text{RF}}_n$  = calculated mean relative response factor for the analyte (with n = 1 to 17 for the seventeen 2,3,7,8-substituted PCDDs/PCDFs).

$Q_{is}$  = quantity, in pg, of the internal standard added to the sample before extraction.