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

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.[1] 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 [Online 2007], 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). [2]

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1 The dredging program has retained the prior terminology of Sampling and Analysis Plan / Quality Assurance Project Plan; this is what is 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).

[2] 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 Mammals, Humans	TEF-F Fish	TEF-W Birds
PCDD			
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
S1,2,3,7,8,9-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
PCDF			
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°C $\pm$ 2°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°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.

The DMMP agencies concluded that Method 1613B, a High-Resolution Gas Chromatographic/High Resolution Mass Spectrophotometric method, when conducted by trained and experienced analysts, is the most suitable method for sediment, because it incorporates additional $^{13}C_{12}$-labelled reference compounds so that each 2,3,7,8-substituted congener can be related to a unique reference standard for identification and quantification. It affords better traceability than EPA Method 8290. In addition, several EPA and Corps of Engineers (USACE) documents have recommended Method 1613B over 8290 for the analysis of dioxins in dredged material for this reason (EPA/USACE 1998, EPA 1995). Generally, Method 1613B has produced suitably low detection and reporting limits. For more information on available methods for PCDD/F analysis, please see the DMMP Clarification Paper, "Polychlorinated Dioxins and Furans (PCDD/F): Clarification of Procedures for Acquiring Sediment Data (2007)." Use of another method or modifications to this method requires DMMP agency approval.

Target reporting limits are presented in Table 2.

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

Dioxins and Furans	Reporting Limit (ng/kg Dry Wt)
PCDD	
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
PCDF	
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 the extraction, cleanup and analysis of dioxins. The criteria presented in Tables 3 and 4 must be met in order to verify that extraction, cleanup and analytical methods are being performed correctly. Laboratories will be required to meet these performance criteria as well as take the specified corrective action if performance criteria are not met.

Deviations from the specified performance criteria will be considered by the DMMP agencies on a project-specific basis. Justification for alternative performance criteria must be submitted in writing and receive agency approval prior to initiation of testing, preferably during the sampling and analysis plan approval process. In addition to the QC requirements presented in Tables 3 and 4, 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

Because of the complexity of the method, the extremely low reporting limits, and the high potential for interfering compounds such as chloro diphenyl ethers, it is strongly suggested that dioxin raw data be validated. If the applicant chooses not to validate the data, the primary method of data evaluation will consist of analysis of a traceable sediment reference material. Such a sediment reference material (SRM) is NIST SRM#1944 (see NIST citation in References). Other SRMs may be identified at a later time. Based upon review of precision, accuracy, representativeness, and completeness measures as well as the SRM, further validation of the dioxin raw data may be required in accordance with EPA *National Functional Guidelines for Chlorinated Dioxin/Furan Data Review* (EPA 2005), which revises the methods for verification and validation of environmental samples. The DMMP will review the primary results against the Method 1613B acceptance limits and those in the project QAPP, and against the sediment reference material. Should the DMMP request validation, the project must provide it, using as validator a person with demonstrated experience accomplishing validation for PCDD/F.

Should validation of raw data be required, it shall include review of all chromatograms and recalculation of at least 10% of the results. If problems are found in the recalculation of this data sample, all data must be recalculated. This validation is more than a review of summary data. This validation must conform to the requirements of the EPA Functional Guidelines described above.

6.0 REPORTING OF DATA

The laboratory should report each of the 2,3,7,8-chlorine substituted PCDD/F congeners on a dry-weight basis as well as the summation of each homolog group (e.g., all HxCDDs). (Reporting of homolog groups is standard practice, but the homologs are not used in calculating TEQs.) The 17 congeners of interest should be tabulated as TEQ, both with nondetected values (U) = ½ detection limit and with U = 0. (The difference between these values gives data reviewers an idea of how much the 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.

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, 2002) and must be followed unless preempted by the following.

Table 3. Summary of Quality Control Procedures

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action*
Ongoing Precision And Recovery (Takes the place of the Laboratory Control Standard)	1 per analytical batch (≤ 20 samples)	Recovery within acceptance criteria in Table 4 of this SQAPP	1. Check calculations 2. Reanalyze batch 3. All data in analytical batch rejected
Stable-isotope-labeled compounds (Takes the place of the Matrix Spike)	Spiked into each sample for every target analyte	Recovery within limits in Table 4 of this SQAPP	1. Check calculations 2. Qualify all associated results as estimated
Stable-isotope-labeled compounds (Takes the place of the Matrix Spike)	Spiked into each sample for every target analyte	Ion abundance ratios must be within criteria in Table 9 of method 1613B	1. Re-analyze 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.
Blind field duplicate	5% or 1 per batch (≤ 20 samples)	Relative percent Difference ≤ 50%	None; it is a guideline and not a requirement.
Method blank	1 per analytical batch (≤ 20 samples)	Detection ≤ minimum level in Table 2 of Method 1613B	1. Report project samples as non-detected for results ≤ to the reported method blank values 2. Samples may be re-analyzed if method blank results high enough to cause exceedance of

			criteria 3. Report method blank results for analytical batches of similar matrices analyzed during the previous 30 days.
Mass calibration/Mass Spectrometer Resolution	Check required at the beginning and end of each 12-hour analytical period	Must meet method 1613B requirements and Table 4 of this SQAPP	1. Re-analyze affected samples 2. Reject all data not meeting method 1613B requirements
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	Failure to verify presence of 2,3,7,8-TCDF by second column confirmation requires qualification of associated 2,3,7,8-TCDF results as non-detected at the associated value.
Dilution of extracts upon not achieving target reporting limits or method performance in presence of possibly interfering compounds	Not applicable	Not applicable	Before sample dilution, it is recommended that the lab re-analyze samples, employing all method 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.
Standard Reference Material	One per project	Result must be within reference range	Data validation will be required

* 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[1]	IPR[2]		OPR[3] (%)	I-CAL[4] %	CAL/VER[5] (%) (Coeff. of Variation)	Labelled Cmpd %Rec. in Sample	
		RSD (%)	Recovery				Warning Limit	Control Limit
Native Compound								
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	-	-
Labelled Compounds								
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-130	35	72-130	40-120	23-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130
$^{13}C_{12}$-OCDD	200	48	20-138	25-130	35	70-130	25-120	17-130
Cleanup Standard								
$^{37}Cl_4$-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)

[1] QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
[2] IPR: Initial Precision and Recovery demonstration
[3] OPR: Ongoing Precision and Recovery test run with every batch of samples.
[4] Initial Calibration
[5] 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[1]	TEQ U=1/2 DL	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
Total TEQ:				1.62	1.50

[1]Laboratory Qualifiers
U: Analyte was not detected at or above the reported result.

References

EPA (online) 2007. Persistent Bioaccumulative and Toxic (PBT) Chemical Program. http://www.epa.gov/pbt/pubs/dioxins.htm

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 SRM References:

- A PDF of SRM #1944 will be posted on the website with the TQAPP
- http://www-naweb.iaea.org/nahu/nmrm/nmrm2003/material/ni1944.htm -- ordering information and nominal concentrations
- https://srmors.nist.gov/referencelinks/view_referencelinks.cfm?srm=1944 – references regarding analytical ranges

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/