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DMMP CLARIFICATION PAPER

POLYCHLORINATED DIOXINS AND FURANS (PCDD/F): CLARIFICATION OF PROCEDURES FOR ACQUIRING SEDIMENT DATA

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INTRODUCTION AND BACKGROUND

While the DMMP agencies are developing a dioxin interpretive framework, a need has been identified to assure that all PCDD/F data collected are of sufficient quality and are comparable through out the program. Under the Dredged Material Management Program, dredging project proponents are required to conduct analysis of PCDD/F in sediment when there is a reason to believe that 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 unintentional byproducts of most 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 chlorines. 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). [1]

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

[1] 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.

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 and some PCBs. WHO (2005, published 2006) updated the toxicities for the 17 PCDD/F congeners as well as the PCBs for which a similar mode of toxicity has been identified.[2] Additivity of these PCBs is appropriate to PCDD/F to calculate a joint TEQ. Table 1 summarizes the latest update of TEFs. The TEQ is calculated by multiplying the TEF by the concentration of the compound, and summing the results (as shown in Table 2).

Table 1. Summary of WHO 2005 Toxicity Equivalency Factors for PCDD/F and PCB

Dioxins and Furans	TEF
PCDD	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
S1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
PCDF	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,6,7,8,9-HpCDF	0.01
OCDF	0.0003

Polychlorinated Biphenyls	TEF
non-ortho substituted PCBs	
3,3',4,4'-TCB (PCB 77)	0.0001
3,4,4',5-TCB (PCB 81)	0.0003
3,3',4,4',5-PeCB (PCB 126)	0.1
3,3',4,4',5,5'-HxCB (PCB 169)	0.03
mono-ortho substituted PCBs	
2,3,3',4,4'-PeCB (PCB 105)	0.00003
2,3,4,4',5-PeCB (PCB 114)	0.00003
2,3',4,4',5-PeCB (PCB 118)	0.00003
2',3,4,4',5-PeCB (PCB 123)	0.00003
2,3,3',4,4',5-HxCB (PCB 156)	0.00003
2,3,3',4,4',5'-HxCB (PCB 157)	0.00003
2,3',4,4',5,5'-HxCB (PCB 167)	0.00003
2,3,3',4,4',5,5'-HxCB (PCB 189)	0.00003

PROPOSED CLARIFICATION

Specifying data analysis procedures for PCDD/F is considerably more difficult than for other chemicals in the DMMP list, due to the analytical complexity. The DMMP agencies wish to assist projects that may have to accomplish PCDD/F sampling and

[2] PCBs will continue to be measured by the Aroclor method in most cases, and there are papers suggesting summary TEQ for commercial Aroclor mixtures; however, if there is reason to believe that PCBs and PCDD/F are both present and contributing to a bioaccumulation hazard on a case-specific basis, the DMMP will consider congener PCB analysis.

analysis to assure that defensible PCDD/F data are acquired. To clarify procedures for collection and analysis of PCDD/F data, a Supplemental Quality Assurance Project Plan (SQAPP) is being prepared and will be placed on the SMARM website before the meeting. The public will have up to 30 days following the SMARM to comment on the SQAPP. The goals of the SQAPP are to:

a) Assure that sampling and holding procedures are documented,

b) Specify best available method,

c) Specify method quality control procedures,

d) Describe data evaluation and validation methods, and

e) Describe data reporting formats.

The SQAPP will provide a tool for the project proponent and laboratory that specifies protocols for obtaining high quality data that are comparable and of known quality. 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. Justification for alternative performance criteria will be submitted in writing to receive agency approval prior to initiation of testing, preferably during the sampling and analysis plan approval process.

What follows is a brief summary of elements of the SQAPP. It has been developed based on review of current PCDD/PCDF methods, discussions with laboratories, and review of EPA and USACE guidance documents.

a) **Sediment sampling and holding**. These procedures are generally similar to semivolatile chemicals in the DMMP. 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).

b) **Analytical methods.** Three solid-phase EPA methods are available for PCDD/F analysis. The identification of PCDD/F congeners at low concentrations is difficult, and there is significant possibility of interfering compounds (such as diphenyl ethers) causing the reporting of artificially elevated values.

   - EPA Method 8280: *The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans.* EPA Method 8280 is a high-resolution gas chromatography/low resolution mass spectrometry method for determining all seventeen 2,3,7,8-substituted congeners in a range of environmental matrices including sediment at a parts-per-billion (ug/kg) level. It is not sufficiently sensitive for sediment work in a regulatory context, which requires parts-per-trillion reporting limits (ng/kg).

- EPA Method 8290: *Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry.* EPA method 8290 is a method employing stable-isotope dilution that provides procedures for the detection and quantitative measurement of 2,3,7,8-substituted PCDDs and PCDFs (congeners and tetra- through octa-chlorinated homologs) in a variety of environmental matrices, including sediments, at a ng/kg level.
- EPA Method 1613B: *Tetra- Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry*. Method 1613B provides procedures for determining 2,3,7,8-substituted PCDDs and PCDFs (congeners and tetra- through octa-chlorinated homologs) in various environmental matrices, including sediments, at a ng/kg level. Stable-isotope standards for all congeners are injected into each sample and accounted.

The DMMP agencies concluded that Method 1613B, 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. This affords better traceability than EPA Method 8290. In addition, several EPA and Corps of Engineers (USACE) documents recommend Method 1613B over 8290 for the analysis of dioxins in dredged material (EPA/UACE 1998, EPA 1995). Generally, Method 1613B has produced suitably low detection and reporting limits. Some examples of achievable limits are provided in the SQAPP.

c) Method quality control procedures. Tables of QC procedures are indicated in the SQAPP in order to supplement and clarify the method requirements and to clarify the analyst's actions when acceptance ranges are exceeded or interfering chemicals are believed to be present.

d) Data evaluation/validation methods. 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 is NIST SRM#1944 (see NIST citation in References). Others may be identified. 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 or

those in the SQAPP, and against the sediment reference material. Should the DMMP request validation, the project must provide it, using a person with demonstrated experience accomplishing validation for PCDD/F.

e) Data Reporting. 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). (This latter is standard practice, but the homologs are not used in calculating TEQ.) 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 2. 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	K	0.1	0.1
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	K	0.0915	0.0915
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	K	0.0294	0.0294
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:				1.731	1.726

[1]Laboratory Qualifiers:

K: peak detected but did not meet quantification criteria; result reported represents the estimated maximum possible concentration. Results flagged with a K were considered valid results when calculating the TEQ since nothing in the validation report indicated otherwise.

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/

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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

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/