Dioxins, Furans, and PCBs:
Addressing Non-Detects and Establishing PQLs

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Abstract

The purpose of this poster presentation is to document a Department of Ecology interpretation for evaluating detection limits and non-detects for purposes of summing congeners for site evaluations (for the purposes of comparison with cleanup levels), and establishing a Practical Quantitation Limit (PQL) for dioxin-like congeners, specifically for:

- Chlorinated dibenzo-p-dioxins (PCDDs) (TCDD is a member of this class);
- Chlorinated dibenzofurans (PCDFs); and
- Dioxin-like polychlorinated biphenyls (PCBs)

This poster is specific as it pertains to Ecological Risk Assessment and the Terrestrial Ecological Evaluation (WAC 173-340-7490 through 7494).

Background and Definitions

Data sets that contain values that are below-detection limit (BDL) are known as censored data sets. Censored data sets present difficulties for many standard estimation procedures and statistical tests. For example, the mean cannot be estimated unless numerical values are assigned to the BDL data. Thus, the values assigned to BDL data can significantly impact the calculated mean of the data set (Ecology, 1992).

When a laboratory reports a target analyte as not detected (ND or <), they also give a numeric reporting limit. In other words, they are saying that the analyte is not present at or above the stated reporting limit. However, the analyte could be present at a lower concentration. In fact, the laboratory may even have positively identified it – but not reported it – at a lower concentration (Scholz and Flory, 1999).

Limit of Linearity (LOL): The concentration at or above the upper end of the calibration curve at which the relationship between the quantity present and the instrument response ceases to be linear. The LOL is set at the concentration of the highest standard analyzed even though it could extend beyond this (Scholz and Flory, 1999).

Practical Quantitation Limit (PQL): The lowest concentration that can be reliably measured within specified limits of precision, accuracy, representativeness, completeness, and comparability during routine laboratory operating conditions, using department approved methods (Ecology, 2007a).

Method Detection Limit (MDL): The minimum concentration of a compound that can be measured and reported with a ninety-nine percent (99%) confidence that the value is greater than zero (Ecology, 2007a).

Estimated Detection Limit (EDL): The minimum concentration required to produce a specified signal to noise (S/N) ratio. The SW-846 Method 8290 for dioxins/furans by CCMS requires that EDLs be used for reporting limits. The EDLs are explicitly determined by the laboratory for each analyte in each sample. The noise in the vicinity of the absent analyte is measured then multiplied by an S/N ratio of 2.5. This labor-intensive procedure is used in order to obtain the lowest possible reporting limits for these highly toxic compounds [dioxins/furans]. It could be specially requested for other GCMS analyses as well (Scholz and Flory, 1999).

The (EDL) is the concentration required to produce a signal with a peak height of at least 2.5 times the background signal ("noise") level. When using High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) it is important to require the reporting of this level in order to report detected analytes in the sample.

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Figure 1: Diagram of Laboratory Limits for Dioxin Analytes for Site Managers

Region of Less Certain Quantitation ("LOL" – Concentrations at or above the LOL (upper end of the calibration curve) at which the relationship between the quantity present and the instrument response ceases to be linear.)
Region of Known Quantitation and Identification of Analyte ("PQL" – Concentrations at or above the PQL that can be reliably measured during routine laboratory operating conditions)
Region that Represents Estimated Quantitation and Positive Identification of Analyte ("EDL" – Calculated at 2.5 times the Signal-to-Noise Ratio)
Region of Unknown Identification and Quantitation ("Noise") Unable to differentiate between the Blank and the Sample

What is the Detection Limit?

Low concentration data are reported to the user in one of three ways – quantified, estimated, or censored – based on the LOL, QL, and EDL. Based on these terms:

- If an analyte is present above the PQL and below the LOL, it is identified, quantified, and unqualified.
- If an analyte is present below the PQL and above the EDL, it is identified and the concentration is estimated with a qualifier ("J" Flag).
- If an analyte is not detected above the EDL, it is considered not-detected/censored ("U" Flag).

As a result, values that are detected above the EDL are considered identified in the sample of concern. Therefore, the congener-specific detection limit in a sample is at the EDL, which is expressed as 2.5 times the signal-to-noise ratio. Detecting a concentration above the EDL is not the only criteria needed to positively identify an analyte. The criteria needed to unambiguously identify a gas chromatograph peak are (USEPA, 2011a):

- Retention Times and Relative Retention Times
- Peak Identification
- Signal-to-Noise Ratio
- Ion Abundance Ratios
- Polychlorinated Diphenyl Ether Interferences

Figure 2: Example of Data Qualifiers Based on USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (USEPA, 2011a)

U	The analyte was analyzed for, but not detected. The value preceding the "U" may represent the adjusted Contract Required Quantitation Limit of the sample specific estimated detection limit.
J	The analyte was positively identified. The associated numerical value is the approximate concentration of the analyte in the sample (due either to an issue with the quality of the data generated because certain QC criteria were not met, or the concentration of the analyte was below the adjusted CRQL).
UJ	The analyte was not detected (see definition of "U" flag, above). The reported value should be considered approximate.
R	The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.

Detection Limit Use and Censorship of Data

Because of the limited number of samples with full dioxin/furan congener analysis and the difficulty of applying the default approach to mixtures, actual practice at most dioxin/furan contaminates sites is to use the following alternative statistical procedure under WAC 173-340-740(7)(f)(v) (Ecology, 2007b):

- For congeners that occur at the site but not in the sample of concern, assign one-half the detection limit for compliance calculations; and
- For congeners not detected in any samples at a site, assign a value of zero for compliance calculations (assuming Ecology-approved detection limits were used).

Note: This does not preclude Ecology Site Managers from following other alternative statistical procedures, such as the Kaplan Product Limit Estimator (Helsel, 2009).

Summary of Procedures

Congeners should be assigned or labeled as non-detected in a sample only if the detection limit (threshold for assignment of non-detect) is at 2.5 times the signal to noise ratio. The laboratory should be required to report the sample-specific EDL for each congener. The sample-specific EDL is at 2.5 times the signal-to-noise ratio.

- If the congener is labeled as non-detected in a specific sample, but detected in other samples at the site, then assign one-half the detection limit (2.5 times the signal-to-noise ratio) for the congener.
- If the congener is labeled as non-detected in a specific sample, and also not detected in any other samples at the site, then assign a value of zero.

Note: Before Ecology determines the laboratory is qualified to conduct the analysis, review the Laboratory Quality Assurance Project Plan to verify that the Laboratory Quantitation (QL) for each dioxin-like congener is at (or below) the QL for each congener listed in Table 1.

Quantitation Limits for Soil Investigations Under MTCA

MTCA states:
WAC 173-340-700(6) (d) Natural background and analytical considerations. In some cases, cleanup levels calculated using the methods specified in this chapter are less than natural background levels or levels that can be reliably measured. In those situations, the cleanup level shall be established at a concentration equal to the practical quantitation limit or natural background concentration, whichever is higher. See WAC 173-340-707 and 173-340-709 for additional information.

Essentially, this means that the final cleanup value for the terrestrial ecological exposure pathway is the highest of one of three values (Ecology, 2007a):

- A value calculated to represent protectiveness of receptors (plants, soil biota, and wildlife);
- A value calculated to represent natural background;
- A value calculated to represent the practical quantitation limit.

As a result, the PQL is an important factor when determining cleanup levels. But what is the Quantitation Limit?

In 1993, Ecology issued "Implementation Memo No. 3" which provided a summary of the PQLs that were able to be achieved by lab surveys at that time. Until the 1993 memo is updated, the recommended PQL for PCDDS, PCDFs, and PCBs in soil are listed in Table 1.

Table 1: Congener-Specific (and sum) Median Soil Quantitation Limits and Toxicity Equivalency Factors for Mammals, Avians, and Fish for PCDD, PCDF, and PCB Dioxin-Like Congeners (based on laboratory survey in Table 2). TEFs were derived from Van den Berg (et al) (1998, 2006).

Analyte	Quantitation Limit (QL) (ppt)	Mammalian TEF	Avian TEF	Fish TEF	TEF Adjusted QL (Mammals) (ppt)	TEF Adjusted QL (Avian) (ppt)	TEF Adjusted QL (Fish) (ppt)	Sum QL (Mammals) - 2,3,7,8 (TEQ)	Sum QL (Avian) - 2,3,7,8 (TEQ)	Sum QL (Fish) - 2,3,7,8 (TEQ)
2,3,7,8 TCDD	0.605	1	1	1	0.605	0.61	0.605			
1,2,3,7,8 PeCDD	1.945	1	1	1	1.945	1.95	1.945			
1,2,3,4,7,8 HxCDD	2.5	0.1	0.05	0.5	0.25	0.13	1.25			
1,2,3,6,7,8 HxCDD	2.5	0.1	0.01	0.01	0.25	0.03	0.025			
1,2,3,7,8,9 HxCDD	2.5	0.1	0.1	0.01	0.25	0.25	0.025			
1,2,3,4,6,7,8 HpCDD	2.5	0.01	0.001	0.001	0.025	0	0.003			
1,2,3,4,6,7,8,9 OCDD	5	0.0003	0.0001	1E-04	0.002	0	5E-04			
2,3,7,8 TCDF	0.665	0.1	1	0.05	0.067	0.67	0.033			
1,2,3,7,8 PeCDF	2.5	0.03	0.1	0.05	0.075	0.25	0.125			
2,3,4,7,8 PeCDF	2.5	0.3	1	0.5	0.75	2.5	1.25			
1,2,3,4,7,8 HxCDF	2.5	0.1	0.1	0.1	0.25	0.25	0.25			
1,2,3,6,7,8 HxCDF	2.5	0.1	0.1	0.1	0.25	0.25	0.25			
2,3,4,6,7,8 HxCDF	2.5	0.1	0.1	0.1	0.25	0.25	0.25			
1,2,3,7,8,9 HxCDF	2.5	0.1	0.1	0.1	0.25	0.25	0.25			
1,2,3,4,6,7,8 HpCDF	2.5	0.01	0.01	0.01	0.025	0.03	0.025			
1,2,3,4,7,8,9 HpCDF	2.5	0.01	0.01	0.01	0.025	0.03	0.025			
1,2,3,4,6,7,8,9 OCDF	5	0.0003	0.0001	1E-04	0.002	0	5E-04			
	43.2							5.3	7.4	6.3
3,3',4,4' TetraCB (77)	10.5	0.0001	0.05	1E-04	0.001	0.53	0.001			
3,4,4',5 TetraCB (81)	10.5	0.0003	0.1	5E-04	0.003	1.05	0.005			
2,3,3',4,4' PeCB (105)	10.5	3E-05	0.0001	5E-06	3E-04	0	5E-05			
2,3,4,4',5 PeCB (114)	10.5	3E-05	0.0001	5E-06	3E-04	0	5E-05			
2,3',4,4',5 PeCB (118)	10.5	3E-05	1E-05	5E-06	3E-04	0	5E-05			
2',3,4,4',5 PeCB (123)	10.5	3E-05	1E-05	5E-06	3E-04	0	5E-05			
3,3',4,4',5 PeCB (126)	10.5	0.1	0.1	0.005	1.05	1.05	0.053			
2,3,3',4,4',5 HxCB (156)	10.5	3E-05	0.0001	5E-06	3E-04	0	5E-05			
2,3,3',4,4',5' HxCB (157)	10.5	3E-05	0.0001	5E-06	3E-04	0	5E-05			
2,3',4,4',5,5' HxCB (167)	10.5	3E-05	1E-05	5E-06	3E-04	0	5E-05			
3,3',4,4',5,5' HxCB (169)	10.5	0.03	0.001	5E-05	0.315	0.01	5E-04			
2,3,3',4,4',5,5' HpCB (189)	10.5	3E-05	1E-05	5E-06	3E-04	0	5E-05			
	126.0							1.4	2.6	0.1

Table 2: Median Congener-Specific (and sum) Dioxin values calculated from prior Laboratory Survey Results and Ecology Proposed Values.

Congener	Survey Laboratory 1	Survey Laboratory 2	Survey Laboratory 3	Survey Laboratory 4	Survey Laboratory 5	Survey Laboratory 6	Survey Laboratory 7	Survey Laboratory 8	Survey Laboratory 9	Survey Laboratory 10	Survey Laboratory 11	Proposed Minimum Value	Congener-Specific Median Value
2,3,7,8 TCDD	1	1	1	1	0.2	0.5	0.5	1	0.71	0.2	0.2	0.2	0.605
1,2,3,7,8 PeCDD	5	5	5	5	1	2.5	2.5	1	1.39	1	1	1	1.945
1,2,3,4,7,8 HxCDD	5	5	5	5	1	2.5	2.5	2.5	2.24	1	1	1	2.5
1,2,3,6,7,8 HxCDD	5	5	5	5	1	2.5	2.5	2.5	2.33	1	1	1	2.5
1,2,3,7,8,9 HxCDD	5	5	5	5	1	2.5	2.5	2.5	2.53	1	1	1	2.5
1,2,3,4,6,7,8 HpCDD	5	5	5	5	1	2.5	2.5	2.5	10.3	1	1	1	2.5
1,2,3,4,6,7,8,9 OCDD	10	10	10	10	2	5	5	5	21.2	2	2	2	5
2,3,7,8 TCDF	1	1	1	1	0.2	0.5	0.5	1	0.83	0.2	0.2	0.2	0.665
1,2,3,7,8 PeCDF	5	5	5	5	1	2.5	2.5	2.5	2.33	1	1	1	2.5
2,3,4,7,8 PeCDF	5	5	5	5	1	2.5	2.5	2.5	2.06	1	1	1	2.5
1,2,3,4,7,8 HxCDF	5	5	5	5	1	2.5	2.5	2.5	1.9	1	1	1	2.5
1,2,3,6,7,8 HxCDF	5	5	5	5	1	2.5	2.5	2.5	1.8	1	1	1	2.5
2,3,4,6,7,8 HxCDF	5	5	5	5	1	2.5	2.5	2.5	1.95	1	1	1	2.5
1,2,3,7,8,9 HxCDF	5	5	5	5	1	2.5	2.5	2.5	2.61	1	1	1	2.5
1,2,3,4,6,7,8 HpCDF	5	5	5	5	1	2.5	2.5	2.5	3.41	1	1	1	2.5
1,2,3,4,7,8,9 HpCDF	5	5	5	5	1	2.5	2.5	2.5	4.84	1	1	1	2.5
1,2,3,4,6,7,8,9 OCDF	10	10	10	10	2	5	5	5	17.6	2	1	2	5
			Low PQL (removed)										43.22
			High PQL (removed)										
			Median of PQLs (minus removed PQLs)										

Laboratory Statement of Work

See Appendix A of memorandum titled "Dioxins, Furans, and PCBs: Laboratory Analysis and Non-Detected Values" (Ecology, 2014) for general, qualifiers, and analyte identification requirements.