Proposed MDL procedure for Chapter 6 **March 17, 2017**

Red text added since March 5, 2017 conference call.

2. Method Detection Limits

2.1 The method detection limit (MDL) is the minimum concentration of a substance that can be reported with 99% confidence that the concentration can be distinguished from a blank. The determination of a realistic detection limit is significant when studying trends in natural systems containing very low concentrations of the analytes of interest.

2.2 MDLs must be determined prior to reporting data from a method. After an initial determination, MDLs are then verified or re-determined annually or if there is a significant change in the operating parameters of the method or instrumentation. Other factors which may require an MDL study include new matrix, change of analyst, or change in operating range.

2.3 The procedure for determining the MDL will be dictated by the method and/or the accreditation requirements for the laboratory. The accepted procedure for performing the MDL is outlined in 40 CFR 136 Appendix B and is the method stated in several EPA procedures. This method is subject to update any time the Federal Register is updated so it is important to use the most recent accepted version.

2.3.1 An alternative method for determining the MDL has been published by the EPA and listed as, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. The document number is "EPA 821-R-16-006".

2.3.2 It is expected that laboratories performing analysis for the CBP will use the most recent accepted version of the MDL procedure in the Federal Register.

2.4 The MDL may be determined using spiked reagent water or an environmental sample representative of the samples normally analyzed by the lab. A suggested procedure for analytes that cannot be spiked, such as particulate nitrogen and carbon, is presented in section 8.5.

2.4.1 The analyte concentration range used for the MDL determination will be based on the method used to perform the study as described in section 8.4.

2.4.1.1 Environmental samples may be used to perform the study can be diluted or fortified into the proper range for the study.

2.4.2 The analysis must include all steps performed for the method and use the same calibration curve that will be used for routine samples.

2.4.3 A minimum seven replicates should be used for the determination and the individual measurements spread over multiple runs and days to account for variation from run to run.

2.4.4 Use the appropriate T statistic, based on the number of replicates and n-1 degrees of freedom, for the final calculation as dictated in the procedure used.

2.4.5 The data points used for the determination should be a continuous set and a justification for removal of any point must be kept on file. Examples for deleting a point may be assignable cause, such as the solution being made at the wrong concentration, or a statistical test showing the point as an outlier to the population

2.5 Analytes that cannot be spiked such as particulate nitrogen and carbon, particulate phosphorus and TSS do not have a requirement for a MDL to be performed and are not covered by the procedure listed in 40 CFR 136 Appendix B. It is the preference of the CBP that laboratories design a procedure with which they can assess standard deviation on a uniform sample near the bottom of the range of analysis. The standard deviation can then be used to assimilate an MDL determination. Additionally, the laboratory should assess the calculated MDL against the blank contribution from the filter media. If the calculated MDL is lower than this determination then the process for determining the MDL should be investigated. The quoted MDL should not be lower than the value of blanks for the test to avoid false positives. It may be more appropriate to use the blank procedure in the reference in 8.3.1. if the blanks are higher than the MDL. The following procedure is an example.

2.5.1 Combine previously analyzed samples, preferably using equal volumes, from several sampling locations. Determine the concentration of the combined sample. Alternatively a very low concentration sample for the analytes of interest may be used if it meets the criteria of 8.5.2.

2.5.2 If necessary, dilute the sample with reagent water to bring the analyte concentration to a level of approximately 1 to 20 times the theoretical or current MDL. Make sure the final diluted volume is adequate for at least 8 filtrations.

2.5.2.1 Filter a portion and analyze to verify the correct range.

2.5.3 If the range is correct then proceed with filtering an additional seven aliquots for the analyte of interest.

2.5.4 Analyze seven of the aliquots in the same manner as routine samples and distribute among several runs to account for run variance.

2.5.5 Calculate the MDL as follows: (Online calculator available at: http://www.chemiasoft.com/mdl_by_epa.html)

MDL = (t)(S), where:

S = the standard deviation of the replicate analyses,

t = Student's t value for n-1 degrees of freedom at the 99% confidence limit; where

t = 3.143 for six degrees of freedom

2.5.6 This process will provide a precision statement for reproducibility at the bottom of the analytical range but may not correlate with the lowest amount of analyte that can be seen by a particular instrument or method.

2.5.7 A table of MDL and PQL values shall be submitted annually. When values change, a revised table of MDL and PQL values and their effective dates should be included with the next data submittal. To determine if an MDL is statistically different from the existing MDL multiply the existing MDL by 0.5 and then by 2.0. This forms the upper and lower limits of the 95% confidence interval. A new calculated MDL within that interval is considered to be within the same population and would not require for MDL to be changed.