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STATE OF MINNESOTA
Office Memorandum

TO: NPDES Permittees and Contract Laboratories

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SUBJECT: Reporting NPDES Data to MPCA

The MPCA NPDES permit Program requires all NPDES analytical values reported to MPCA that are below the analytical method Reporting Limit (RL) be reported as < RL (less than the reporting limit). Previously these values were reported as *nondetectable* which is no longer acceptable.

Example:

My Ammonia as N analysis indicates that my wastewater sample contains 0.008 mg/L Ammonia. My Method Detection Limit (MDL) study determined that for my analytical instrument and method my MDL for Ammonia as N is 0.004 mg/L.

My Sample analysis value of 0.010 mg/L is greater than my MDL of 0.004 mg/L so I report an Ammonia as N value of 0.008 mg/L, right? **Wrong!**

I've determined the MDL for this analysis, instrument, and method but what I'm really interested in is finding out what my Reporting Limit (RL) is for the analysis, instrument, and method.

The RL value will **always** be greater than the MDL value because the RL is a multiple of the MDL. Guidance on how to calculate your MDL is given in part V below.

I. Determining the MDL for a Specific Analysis and Using a Specific Instrument and Method

Determining the MDL can be a bit complicated. It requires analyzing at least seven aliquots of a wastewater sample or of a certified sample, determining the standard deviation of the seven values, and multiplying the product by the student-t value for seven replicates. The student-t value for seven replicates is 3.143 and varies depending upon how many aliquots of a sample you analyze. Thus if you always analyze exactly seven sample aliquots your student-t value will always be 3.143.

Number of Sample Aliquots Analyzed	Student-t Value (99% Confidence Level)
7	3.143
8	2.998
9	2.896
10	2.821
11	2.764
12	2.718

If you prefer to have these calculations performed for you and the MDL determined for you, contact the person whose name is at the top of this memorandum. You will also be sent my mail or email and Excel spreadsheet calculator that will calculate your MDL for you. All you need to do is enter your seven replicate values and your MDL value will appear.

II. More About Reporting Your NPDES Data

Following is information about what to do with values you get that are below the RL when calculating your monthly average that you report on your DMR.

Averaging Monthly Values When One or More is <RL.

1. If **some** values are less than (<) the RL:

Substitute zero for all values < RL when calculating your monthly average.

Example:

The RL = 2.0 and the values for the month are: 5.0 mg/L, 4.0 mg/L, 3.0 mg/L, and <2.0 mg/L

Report as your monthly average: $(5.0 + 4.0 + 3.0 + 0.0) \div 4 = 12.0 \div 4 = 3.0$ mg/L

2. If **all** values are less than (<) the RL, the value to report is always '<RL'.

Ignore the < sign, calculate the average value, and report this average value using the < sign.

Example:

The RL = 3.5 and the values for the month are: < 3.5 mg/L, <3.5 mg/L, <3.5 mg/L, and 3.5 mg/L

Report as your monthly average: $(3.5 + 3.5 + 3.5 + 3.5) \div 4 = 14.0 \div 4 = < 3.5$ mg/L

III. Calculating Fecals – Using the Geometric Mean

Example:

Values for the month are: < 4.0 cfu/100 mL, < 4 cfu/100mL, and 25 cfu/100 mL

Ignoring any '<', the product of the values = $4 \times 10 \times 25 = 1000$. Since this example has three values, the geometric mean is the cube root of 1000 = $1000^{\frac{1}{3}} = 10$.

If you have two values for the month you will take the square root of the product; if you have four values for the month you will take the 4th root of the product, and so on.

Generally, most calculators calculate roots as follows:

1. Enter the product of the values into your calculator
2. Press the 'INV' key on your calculator
3. Press the 'Y^x' key on your calculator
4. Enter the number of the root to be taken. (If you have 3 values, enter "3"; if you have 5 values enter '5'.
5. Press the '=' sign.
6. The appropriate value to report as the geometric mean of your monthly fecal analyses will appear.

Different calculators may be manipulated differently to perform these mathematical functions. To determine how to calculate roots of numbers using your calculator, consult your calculator instruction booklet.

To have your geometric mean calculated for you, contact the person whose name appears at the top of this memo. You will also be sent by mail or email an Excel spreadsheet calculator that will calculate the geometric mean of up to seven samples for you. You can store this spreadsheet calculator on your computer for future use.

IV. Calculating Monthly Average or Daily Mass Loading Concentrations That Are Below the RL

To calculate a mass loading with a < RL concentration, use the RL value in the calculation and then add the '<' to the product of the concentration and the volume. Zero cannot be used in place of the <RL concentration because that would result in a zero mass loading because zero x the volume = zero.

Example:

Daily or Monthly Average Concentration = < 2.0 mg/L

Daily or Monthly average flow = 7 million gallons per day

Daily or Monthly Average Mass Loading = 2mg/L x 7 million gallons per day x 3.78 kg/gallon = < 53 kg/day

If you calculate loading on a daily basis and you average the daily loading to obtain a monthly average loading, use one of the procedures in **Average Monthly Values When One or More is < RL**, above.

V. Determining Report Limit (RL)

The reporting limit (RL) is typically 2 – 10 times the method detection limit (MDL) and can never be less than the MDL. The MDL is calculated according to 40 CFR part 136, Appendix B. The MDL must be calculated for all analytical methods used for NPDES reporting **except for dissolved oxygen, pH, total suspended solids, all volatile solids, and fecal coliform**. You must determine the MDL for analyses you perform in-house. If you use a contract laboratory to perform analyses for one or more of your parameters, it is responsible for determining the MDL for those parameters.

If you are required to report Total Residual Chlorine (TRC) on your DMR Report, you **must** perform this analysis in-house because it must be analyzed **immediately** after sampling.

This does apply to total residual chlorine (TRC), which is currently not certified by the State of Minnesota Laboratory Certification program. Listed below are directions for calculating an MDL for and analytical method.

1. Obtain an estimated MDL from the instrument manufacturer. Table 1 shows the estimated MDLs for various TRC instruments and methods.
2. Obtain a commercially prepared certified standard or use your own wastewater effluent. The certified standard or effluent concentration you use for your MDL determination must be 1 – 5 times the estimated MDL concentration. Certified standards may be obtained from commercial manufacturers. A list of certified standard manufacturers is given in Table 2. These are the same companies that manufacture standards for the annual NPDES DMRQA Study in which major NPDES dischargers and various other complies are required to participate. You may have to dilute the certified standard to obtain the appropriate concentration for your MDL Study. This dilution step may introduce measurement error into your MDL Study. If you use effluent for your MDL Study, pour the effluent sample into seven vials of appropriate size and fill them to overflowing before capping so there is no headspace. Place the vials in ice water while they await analysis to minimize TRC degradation by any matter in the effluent that may cause TRC degradation. Determine the concentrations of the seven effluent portions as quickly as possible.
3. Record the values of the seven portions of certified standard or effluent. Calculate the standard deviation of the seven samples. The standard deviation can be easily calculated on a scientific calculator. Consult your calculator guidebook for directions for calculating standard deviation. If you do not have a calculator you may contact the person whose name appears at the top of this memo who will calculate the standard deviation for you. He can also provide you with an electronic MDL calculator in Excel spreadsheet form that you may use for future standard deviation calculations. This Excel spreadsheet calculator can be emailed to you and you can save it in a file on your computer. If you do not have access to email, a disk containing the Excel spreadsheet calculator can be mailed to you free of charge. The Excel spreadsheet calculator also automatically calculates the Reporting Limit (RL) and the Percent Recovery. To obtain this information using the Excel spreadsheet calculator you merely need to enter the seven sample values onto the spreadsheet.
4. As mentioned above, the RL value is typically 2 – 10 times the MDL value. The larger the number you use, the larger the RL value will be and thus the more '<' values you will be reporting on your DMRs. To minimize the number of '<' reported, MPCA recommends using a factor of 2 to determine the RL value ($MDL \times 2 = RL$).
5. The value of the certified sample or the average value of your effluent sample should be no more than 10 times the calculated MDL value. If it is, too much error has been introduced into your MDL Study and it will have to be repeated until the value of the certified sample or the average value of your effluent sample is less than 10 times the MDL value.
6. If you used a certified sample for your MDL Study, calculate the percent recover as follows. (If you use effluent for your MDL Study, you cannot determine the percent recovery because the true value of the effluent is unknown.).

Average of the seven sample values \div the certified value $\times 100 =$ percent recovery.

For your MDL Study to be valid, the percent recovery must be between 70% and 130% of the certified value. If it is not, you must repeat the MDL Study.

EPA Approved TRC Methods and Their Estimated MDLs

Analytical Method	EPA	Standard Method	Other Methods	Estimated MDL
Amperometric Direct Titration	330.01	4500-Cl D		0.01 mg/L
Iodometric Direct Titration	330.3	4500-Cl B		0.1 mg/L
Back Titration Ether End-Point Titration	330.2	4500-Cl C		0.01 – 0.1 mg/L
DPD FAS Titration	330.4	4500-Cl F		0.05 mg/L
Electrode			Orion Electrode 97-70	0.01 mg/L
DPD Spectro-photometric	330.5	4500-Cl G	Hach 8167 – using the following: Pocket Colorimeter DR-700, DR-800, DR-2000, DR-2010, DR-3000, and DR-4000.	0.02 mg/L
DPD Spectro-photometric			Hach 8167 – using the following: DR-100	0.1 mg/L
DPD Spectro-photometric Low Level	330.5	4500-Cl G	Hach 8370 – can only be done using the following equipment: DR 2012 and DR 4000	0.002 mg/L