Detection Limits

An explanation of detection limit requirements for Regulation 85 nutrient monitoring and reporting

The Water Quality Control Division (Division) has discovered that some facilities are not deriving and/or reporting their method detection limits (MDL) and minimum level (ML, formerly lower reporting limit) values correctly. This is particularly frequent for facilities which use their in-house (or other) laboratory and/or employ testing kits, such as those manufactured by HACH, to measure the concentrations of the various nutrient components. The division has developed this document in order to facilitate understanding of detection limit requirements and to aid facilities in the correct determination of their MDL and ML.

Background

Regulation 85.6(4)(c) indicates that all analytical procedures must be performed using methods specified in, or approved by EPA in accordance with, 40 C.F.R. Part 136 or approved by the division. This same section also details the maximum values for the MDL, as follows:

Nitrate + nitrite (NO_5)	0.02 mg/L (reported as N)
Total Kjeldahl nitrogen (TKN)	0.1 mg/L (reported as N)
Total nitrogen (TN)	0.1 mg/L (reported as N)
Total phosphorus (TP)	0.01 mg/L (reported as P)

The regulation also defines the practical quantitation limits (PQL) that must be achieved by analytical methods as those PQLs defined in Regulation 61. These PQL values have been replaced by the PQL values published in the new Water Quality Control Division Policy CW6. The PQL values for nutrient monitoring parameters (and components), as reported in Policy CW6[1], are:

Ammonia (NH_3)	0.2 mg/L (reported as N)
Nitrate (NO_3)	0.1 mg/L (reported as N)
Nitrate + nitrite (NO_5)	0.1 mg/L (reported as N)
Nitrite (NO_2)	0.05 mg/L (reported as N)
Total inorganic nitrogen (TIN)	0.2 mg/L (reported as N)
Total Kjeldahl nitrogen (TKN)	0.5 mg/L (reported as N)
Total nitrogen (TN)	0.5 mg/L (reported as N)
Total phosphorus (TP)	0.05 mg/L (reported as P)

The analytical methods used for nutrient monitoring must be capable of reporting with a ML at or below these PQL values.

Definitions[1]

MDL (method detection limit): the minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined by the procedure set forth in appendix B of 40 CFR Part 136.

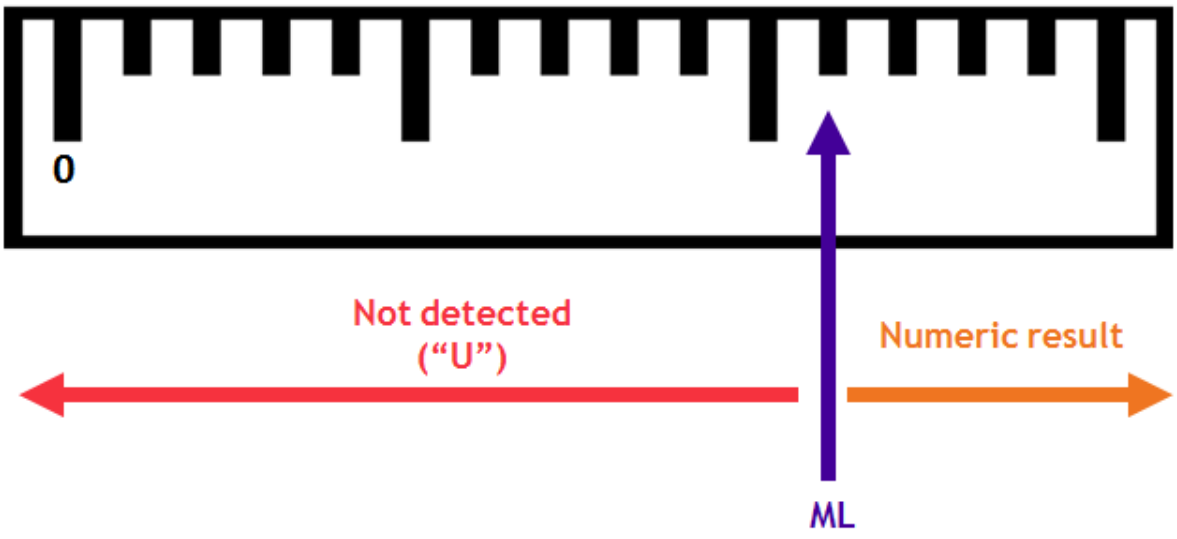
ML (minimum level): *synonymous with lower reporting limit (LRL):* the lowest concentration of an analyte that can be accurately and precisely quantified using a given method, as determined by the laboratory. This term differs from PQL because ML refers to the capability of your analytical method while PQL is a maximum value of ML for regulatory reporting purposes.

Generally, detection limit values should follow this pattern: **MDL < ML ≤ PQL.**

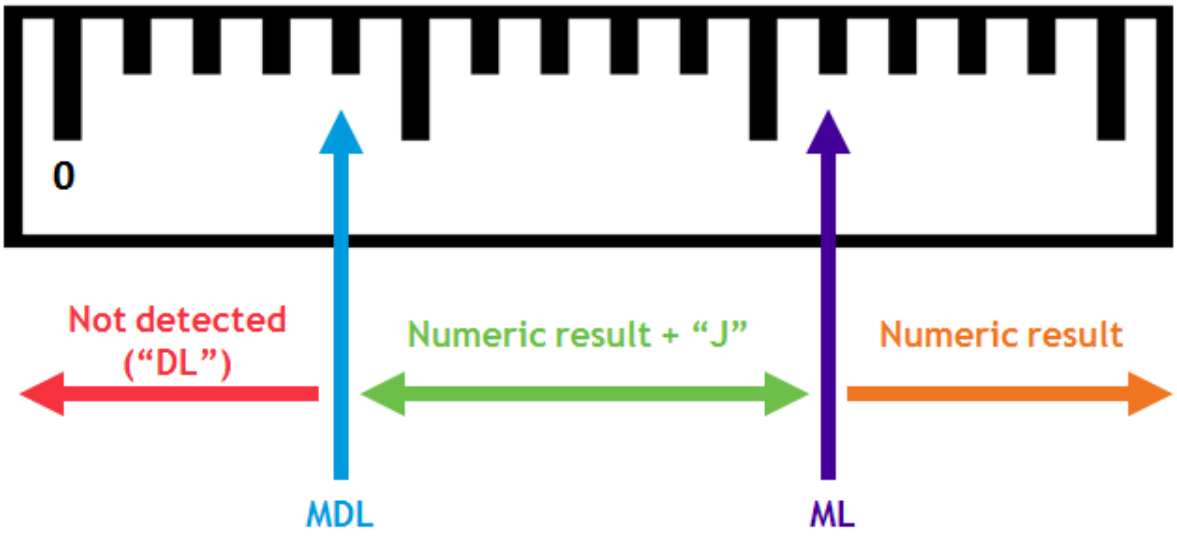
Why is nutrient monitoring data reported down to the MDL or the ML?

The regulation states that all ambient (in-stream) samples above the MDL must be reported as values, and that all effluent samples above the PQL (ML) must be reported as values. In other words, in-stream samples, where we expect lower concentrations and less interfering compounds, must be evaluated against the MDL while effluent samples (where higher concentrations are expected) must be evaluated against the ML. The following figure summarizes the reporting requirements:

a) effluent data



b) in-stream data



To summarize, for effluent data, a numeric result should be reported down to the LRL, but for in-stream data, a numeric result should be reported down to the ML.

Range of values stated in kit documentation

The analytical method kits typically include a range of concentrations which can be accurately measured. For instance, the HACH Nitrate TNTplus low range kit has a published range of 0.23 to 13.50 mg/L (nitrate as N). The lower value of this range, here 0.23 mg/L, is equivalent to the ML for Regulation 85 reporting. It is ***not*** equivalent to the MDL and should not be reported as such.

Other analytical methods, such as those offered by Lachat, publish both a concentration range and a MDL value. In these cases, the the low end of the concentration range is equivalent to the ML and the published MDL can be utilized for reporting. Keep in mind that some Lachat methods are dual range methods, such as 10-107-04-1-C for nitrate+nitrite, and the values for the ML and MDL differ depending on which range you utilize.

Determining the MDL

The procedure for determining the MDL for you method is described in appendix B of 40 C.F.R. Part 136. A brief procedure is summarized here:

1. Determine your "near-blank" concentration
    a. Measure your lowest standard 3 times
    b. Calculate the standard deviation of those three samples
        i. Microsoft Excel formula: STDEV
        ii. Formula provided in appendix B of 40 C.F.R. Part 136
    c. Multiply this standard deviation by 3 to derive your "near-blank" concentration

2. Make a solution with the exact concentration of the "near-blank" calculated in Step 1
    a. Use serial dilution to dilute standard solution to the approximate concentration of "near-blank"
    b. For example, if the "near-blank" concentration is 1 ug/L for nitrate but the nitrate standards in the HACH kit only go down 50 ug/L, the division would recommend the following procedural steps :
        i. Place 1 mL of the 50 ug/L standard into a vial and add 4 mL of reagent water. Thus, the standard has been diluted 1:5 and there is now a 10 ug/L nitrate solution.
        ii. Place 0.5 mL of the 10 ug/L nitrate solution into a vial and add 4.5 mL of reagent water. Thus, the solution has been diluted 1:10 and there is now a 1 ug/L nitrate solution to use as the "near-blank."
    c. A simple Google search of "serial dilution" will provide more information on this process.
3. Repeat above process to create **seven** "near-blank" vials and then measure and record the concentration of each one (yes, seven, not eight, not six)
4. Calculate the standard deviation of the seven "near-blank" measurements (see 1.b above).
5. Multiply the standard deviation of your "near-blank" measurements by 3.143. The product is your MDL.

What about regulation compliance?

The division recognizes that detection limits may not have been reported properly (for 2013 or 2014 data), and is working on ways to deal with this matter. Moving forward into 2015, the Division requests that all facilities properly determine and report their detection limits.

It is important to note that reporting requirements for nutrient monitoring data may differ from those for DMR and other permit-related data. Please contact the division's permits section for more information about DMR and other permit-related reporting by phone at 303-692-3517 or by locating your appropriate contact on the permitting contacts website.

Contacts

For questions/concerns about nutrient monitoring detection limit reporting, please email the division's nutrient monitoring team at cdphe_nutrients@state.co.us, or contact one of the staff listed below:

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References

1 - WQCD Policy CW6