

Sufficiently Sensitive Methods

Determine whether your analytical method if sufficiently sensitive for Regulation 85 nutrient monitoring.

The Water Quality Control Division has discovered that some facilities are not using sufficiently sensitive methods for analysis of nutrient parameters. This is particularly frequent for facilities that 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 sufficiently sensitive methods to ensure required sensitivity for nutrient monitoring.

Definitions¹

MDL (method detection limit): the minimum concentration of an analyte (parameter) 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.

PQL (practical quantitation limit): the minimum concentration of an analyte (parameter) that can be measured with a high degree of confidence that the analyte is present at or above that concentration. This term differs from the ML because ML refers to the capability of the 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.

Sensitivity Requirements

Regulation 85.6(4)(c) details the maximum values for the MDL, as follows:

Nitrate + nitrite (NO) 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 identifies the PQL values that must be achieved by analytical methods as follows:

Ammonia (NH₃) 0.2 mg/L (reported as N) Nitrate (NO₃) 0.1 mg/L (reported as N) Nitrate + nitrite (NO₅) 0.1 mg/L (reported as N) Nitrite (NO₂) 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)

How can I determine if the method I am using is sufficiently sensitive?

An analytical method is sufficiently sensitive if it meets either of the following requirements:

- 1. The method returns a positive, valid result. That is, the analytical result is numeric, and not reported as less than detection limit.
- 2. The method can detect down to the required limit:
 - a. Ambient or in-stream samples must be measured with a method that can detect down to the required MDL for a parameter (see above). Thus, numeric values can be reported down to the MDL. For any



result value reported as less than detection limit, the detection limit must be less than the required MDL.

MDL_{acheived by lab} ≤ MDL_{required}

If the result falls between the ML and the MDL, your lab may choose to qualify this result value as estimated or flag it with a "J" qualifier. For in-stream samples only, this is an acceptable sample result as long as the MDL achieved by the lab meets the above requirement.

b. Effluent samples must be measured with a method that can detect down to the required PQL for a parameter (see above). Thus, numeric values can be reported down to the PQL. For any result value reported as less than detection limit, the ML must be less than the required PQL.

ML_{acheived by lab} ≤ PQL_{required}

Do the analytical methods included on the Regulation 85 approved methods list meet the sensitivity requirements?

To answer this question, we need to know whether your result value is a valid, positive number or is reported as less than detection limit. If the former is the case, then yes, the method is sufficiently sensitive. If the latter is the case, you need to compare the appropriate detection limit (MDL for in-stream or ML for effluent) to the respective required limit (see above).

Often for the analytical test kits, there is a kit for the high range test and another kit for the low range kit. In this case, you should pick the kit that will give you a valid, positive result and/or meets the required limit. For example, let's assume that your effluent total phosphorus (TP) levels typically range from 3-7 mg/L and you can choose a high range kit that measures 2 - 20 mg/L TP or a low range kit that measures 0.02 - 4 mg/L TP. Based on your typical TP levels, you should run your samples using the high range test kit because this is valid for your typical sample. However, if you run a sample that results in < 2 mg/L TP from the high range kit, you will then need to run the sample using the low range kit because the high range kit does not meet the requirements for a sufficiently sensitive method. The ML for the high range kit is 2 mg/L, which is much greater than the 0.05 mg/L PQL required for TP analysis.

When reporting results, please assign the method used to obtain the sufficiently sensitive result.

What about regulatory compliance?

The division recognizes that analytical methods may not have been sufficiently sensitive for data previously collected. Moving forward, the division requests that all facilities employ sufficiently sensitive methods for Regulation 85 nutrient monitoring.

It is important to note that approved methods and sufficiently sensitive reporting requirements for nutrient monitoring 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