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Water Quality Reporting Limits, Method Detection Limits, and Censored Values: What Does It All Mean?

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The Arkansas Water Resources Center (AWRC) maintains a fee-based water-quality lab that is certified by the Arkansas Department of Environmental Quality (ADEQ). The AWRC Water Quality Lab analyzes water samples for a variety of constituents, using standard methods for the analysis of water samples (APHA 2012). The lab generates a report on the analysis, which is provided to clientele, and reports the concentrations or values as measured.

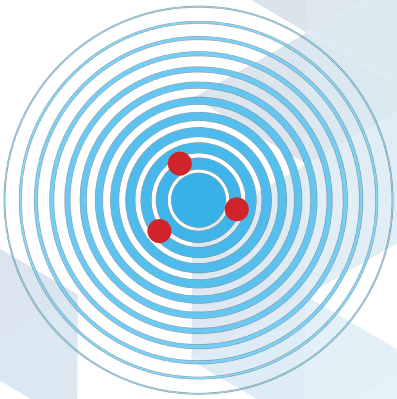
Often times the concentrations or values might be very small, even zero as reported by the lab – what does this mean? How should we use this information? This document is intended to help our clientele understand the analytical report, the values, and how one might interpret information near the lower analytical limits.

Every client wants the analysis of their water sample(s) to be accurate and precise, but what do we really mean when we say those two words? These words are often used synonymously or thought of as being the same, but the two words mean two different things. Both are equally important when analyzing water samples for constituent concentrations.

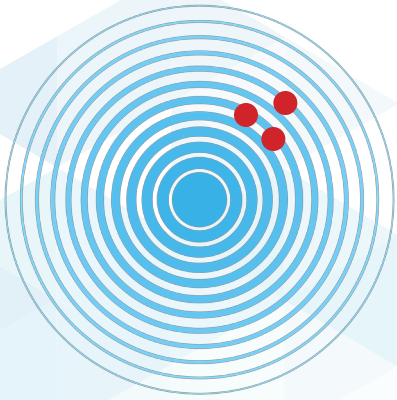
So, What Is The Difference Between Accuracy and Precision?

Accuracy of an analysis describes how close the measured values are to the true values (Table 1).

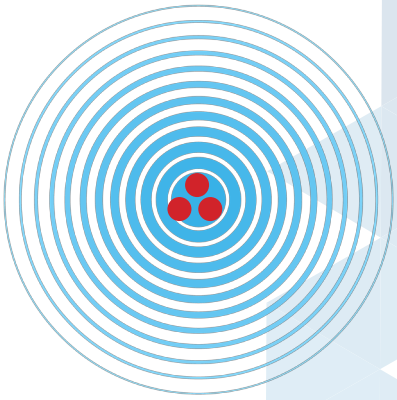
Precision of an analysis describes how similar measured values are to each other, regardless of how accurate or inaccurate the analysis may be (Table 1).



High Accuracy
Low Precision



Low Accuracy
High Precision



High Accuracy
High Precision

Table 1: Glossary of Terms

Term	Definition
Accuracy	Describes how close a measured value is to the true value.
Precision	Degree of similarity between measured values among duplicates or replicates of a sample, independent of the accuracy of the values.
Significant Digits	The number of digits within a measured value that carry meaning.
Reporting Limit (RL)	The lowest quantified level within an analytical methods operational range.
Method Detection Limit (MDL)	Minimum concentration measured with 99% confidence that the true value is greater than zero.
Censored Data	Reported value that provides some information about the measured value but limits the accuracy of the values by grouping data into specific categories (i.e., below MDL, between MDL and RL etc.).

Both accuracy and precision are equally important when analyzing water samples.

What Are Significant Digits?

Significant digits are the number of digits within a value that carry meaning and are determined by the level of accuracy and precision that can be attained for each specific method and constituent (Table 1). So, the number of significant digits or places beyond the decimal will vary between constituents, as well as with the accuracy and precision of the actual measurements. The significant digits are also tied to the lower limits of quantification, or how small of a concentration we can actually measure.

The goal of water quality analysis (and all analyses) is to have high accuracy and precision. However, every analytical method has a lower limit related to the physical properties of the instrumentation and human error in chemical preparation. As the lower limits of a method are reached, accuracy and precision of reported values decrease. The AWRC Water Quality Lab derives reporting limits (RLs) and method detection limits (MDLs) for each of the constituents analyzed at the lab to aid in the understanding of what the reported values in your water quality analysis report mean.

Every analytical method has a lower limit related to the physical properties of the instrumentation and human error in chemical preparation.

Reporting Limit

The reporting limit, commonly known as the RL, is the lowest concentration of a constituent that can be reliably measured with accuracy and precision (Table 1). In many cases, a calibration curve is used to measure the concentration of a constituent in a sample. The AWRC Water Quality Lab reports the RL as the lowest non-zero standard that's used in the calibration for a given analysis. RLs can change over time, and generally do so to meet the needs for determining MDLs for each constituent as described below.

Method Detection Limit

The method detection limit, commonly known as an MDL, should be viewed as the lower concentration limit of a constituent that the analytical equipment and technician is capable of detecting (Table 1). Concentrations or values below this lower limit should be interpreted cautiously because the concentration or reported value is lower than what can be measured with sufficient accuracy. The MDL is based on statistics, and the AWRC Water Quality Lab calculates MDLs every year for each constituent.

What is The MDL?

- The MDL for a specific constituent is the minimum concentration that can be measured with 99% confidence that the constituent concentration is greater than zero (U.S. EPA, 1997; Oblinger Childress et al., 1999).
- The MDL is a statistically derived value and, as indicated in the name, is specific to the method used; additionally it is specific to the laboratory conducting the analysis.

Measured values at or below the MDL should be interpreted cautiously because the true value is lower than what can be measured with sufficient accuracy.

MDLs can change over time for various reasons, including new or aging equipment, chemical reagents, concentration evaluated, etc. However, these variations should be relatively small in magnitude – but, still it is very common and required for certification to calculate MDLs every year and that's what the AWRC Water Quality Lab does.

How is The MDL Calculated?

Similar to the U.S. Geological Survey, the AWRC Water Quality Lab follows methods set by the U.S. Environmental Protection Agency (U.S. EPA) to determine the MDLs for almost all constituents analyzed in the Lab.

1 The lab technician adds the constituent to seven blanks (water that does not have the constituent in it at measurable concentrations); the constituent is added at a set concentration equivalent to the lowest calibration standard or RL.

2 Following the analysis of the seven water samples where the constituent was added, the MDL is calculated as the standard deviation across the samples multiplied by the Students' t-value (i.e., 3.14 for n=7) for the 99% confidence interval (U.S. EPA, 1997; Oblinger Childress et al., 1999).

The MDL must be less than the RL but greater than 1/10 of that concentration. For example if the concentration for the RL for soluble reactive phosphorus (SRP) is 0.010 mg/L, the MDL should be less than 0.010 mg/L but greater than 0.001 mg/L (i.e., 1/10 RL < MDL < RL).

If the MDL is greater than the RL, the procedure must be repeated using a higher concentration for the RL. Similarly, if the MDL is lower than 1/10 of the RL, the procedure must be repeated using a lower concentration for the RL (Rosecrance, 2000).

The MDL must be less than the RL but greater than 1/10 of the RL

$$1/10\ RL < MDL < RL$$

How Should You Interpret Values Less Than the MDL and/or RL? Why are These Considered Estimated Values?

The AWRC Water Quality Lab reports the concentrations as measured – we do not censor data that is greater than zero and above the reported level of significant digits for a constituent (i.e., show the values as less than (<) the MDL or RL). Therefore, the analytical reports provided to clientele might have reported values which are less than the MDL and or RL. The lab reports the concentration data like this to allow clientele to determine how concentrations less than the lower limits of detection will be interpreted. It is important to remember that values below the MDL may be difficult to distinguish between an actual measured value and background noise of the analytical equipment.

Interpreting Values Less than the MDL and RL Con.

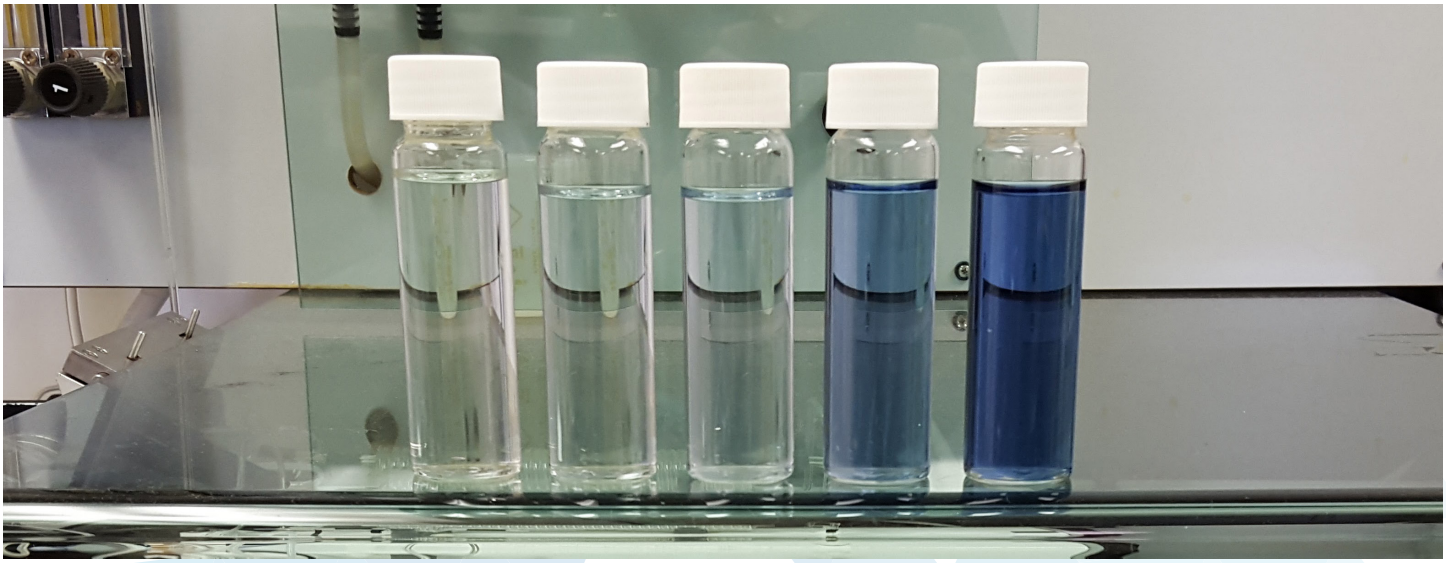
- For example, if you get your water quality analysis report back and the reported value of a water sample for SRP is 0.001 mg/L but the MDL is 0.002 mg/L, you cannot say for certain that the actual concentration is different from zero.

Reported values that fall between the RL and MDL should also be considered as estimated values, but we would generally have more confidence in the accuracy of these measures – that is, these values are probably good estimates of the actual concentrations. However, measured values falling within this range are approaching the analytical limits of the lab's equipment and methods and our clientele should be aware that these values are less than the RL.

- Keeping with the same example, if your reported SRP value is 0.004 mg/L and the RL is 0.005 mg/L, it is certain that the actual concentration is greater than zero but we cannot be certain of the accuracy of the reported value.
- However, if the reported value is 0.006 mg/L, as this value is greater than the RL we should have high confidence in the accuracy of the reported value.

With this understanding in mind, all values below the MDL and RL are estimated and denoted with an "E" to the left of the value in each analytical report. These values should be analyzed and reported with caution, realizing that the values reported may not be true to what is actually present in the sample. The AWRC Water Quality Lab allows its clientele to determine the best way to handle these values.

With few exceptions the AWRC reports values as they are measured to allow our clientele the ability to determine the best way to analyze and report their own data.



What Are Censored Data, and Why Can These Values Be Problematic?

Censored data relate to values that fall below specific detection limits for a particular constituent (Table 1). If a concentration falls below the applicable MDL, instead of reporting that measured value, water-quality labs might report the MDL with a less than sign next to the value.

- Returning to the first example where the measured SRP value fell below the MDL, some labs may report < 0.002 mg/L, instead of 0.001 mg/L.

Additionally, some labs may report only the MDL for any measured value that falls between the MDL and RL.

- In the example where the measured SRP value was 0.004 mg/L, between the RL and MDL, some water-quality labs might report 0.002 mg/L (the MDL) instead of 0.004 mg/L.

While this provides more information about the true value of the constituent for the sample than just reporting 0, data about the true value of the constituent is lost. The AWRC water quality lab reports values as they are measured even when these are less than the MDL and RL, instead of reporting the MDL. This allows researchers or clientele to control how they prefer to analyze and report data.

The AWRC Water Quality Lab only reports censored data when the measured value is negative and or below the reported level of significant digits for a constituent. In the event of a negative value measured for a constituent, zero is reported. Similarly, a zero is reported when the measured value for a constituent is lower than the reported level of significant digits. For example, the measured value for SRP in a sample is 0.0002 mg/L; however, since the number of significant digits reported for this constituent is 3, when the measured value is rounded to three significant digits the reported value will be 0.000 mg/L. So, it is not necessarily that there is no SRP in the water sample – it is that there is no measureable concentration of SRP in the water sample at the lab's level of accuracy, precision, and significant decimal places.

Values below the MDL may be difficult to distinguish between an actual measured value and background noise of the analytical equipment.

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