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## **NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1994-12**

July 8, 1994

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NWQL Radiological Advisory Committee  
Chief, Branch of Quality Assurance  
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From: Peter F. Rogerson, Chief  
National Water Quality Laboratory  
Branch of Analytical Services

Subject: Description and guide for interpreting low-level data supplied by the NWQL  
for schedules 2001, 2010, 2050, and 2051

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Revision: None

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### **Introduction**

This memorandum describes National Water Quality Laboratory (NWQL) policy for reporting and interpreting low-level analytical data for recently developed organic pesticide residue schedules

2001, 2010, 2050, and 2051. Until now, there has been no standard procedure for establishing reporting levels and analytical detection limits at NWQL. For new methods, the National Water-Quality Assessment Program (NAWQA) requested statistical techniques be used to (1) estimate method detection limit (MDL), (2) eliminate censoring data below the MDL, and (3) characterize analytical uncertainty at low levels. Analyte detection is described using the concept of analyte identification and quantification in the context of these analytical methods. Additionally, measurement uncertainty and quantification are discussed. Method detection limits are described, based on procedures outlined by the U.S. Environmental Protection-Agency (1992), which have been adopted by most local, State, and Federal agencies working with NAWQA.

### **Discussion of the analytical process for schedules 2001, 2010, 2050, and 2051**

When laboratory personnel analyze an environmental sample, they must first determine which target analytes are present. Detection is evaluated by qualitatively identifying the analyte and quantifying the amount. Detection of an analyte may be reported either correctly or erroneously. Two correct results are as follows: an analyst concludes that an analyte is detected when it is present in the sample, or an analyst concludes that an analyte is not detected when it is not present in the sample. Two erroneous results are as follows: an analyst concludes that an analyte is detected when it is not present in the sample (false positive, or type-I error), or the analyst concludes that an analyte is not detected when it is present in the sample (false negative, or type-II error).

After an analyte is detected, the amount present must be determined. Uncertainty in quantifying the amount of analyte present is influenced by method performance, instrument performance, sample matrix, analyte, and many other factors. The NAWQA schedules contain many analytes, each responding uniquely to the analytical method. Therefore, the uncertainty of determination will vary for each analyte.

Samples for schedules 2001 and 2010 are analyzed by gas chromatography with detection by mass spectrometry (GC/MS). Samples for schedules 2050 and 2051 are analyzed by high-performance liquid chromatography with detection by ultraviolet spectroscopy (HPLC/UV). For these schedules part of the preconcentrated sample extract is passed through a chromatographic column, which causes the sample components to migrate through the column at different rates and results in separation of the analytes. The time at which the analyte exits or elutes from the chromatographic column and produces a signal (or peak) in the detector is called the retention time. This retention time is an indirect identification of the analyte. The size of the peak is directly proportional to the amount of analyte in the sample. A more direct confirmation of analyte identity is provided by the MS or UV detectors in the form of the characteristic mass or UV spectral information unique to the analyte. Thus, an analyst uses the less definitive retention times, coupled with the more definitive MS or UV spectral information, to identify the various analytes in the sample and then uses peak size to quantify the analyte.

### **Measurement uncertainty and quantification**

Measurement uncertainty can be viewed in relation to a two-step decision process: Is the substance present and how much is present? Although these are interrelated questions at low levels, it is useful to consider them separately. The probability of errors in presence/absence decisions is frequently left uncharacterized, because they can occur for several reasons that are difficult to quantify for all samples. False positives can result from random variability in background response, contamination, or misidentification of analyte. False negatives can arise from random variability, lower than

normally expected analyte recovery, or misidentification of analyte. When interpreting trace-level organic data, it is important that the field and laboratory quality-assurance data be compared with the sample data. This is necessary, regardless of concentration value reported for the analyte (including levels less than and greater than the MDL). If the analyte detected in the sample is present in field equipment blanks or laboratory blanks, then the probability of contamination is high and the data should be considered with that in mind.

The uncertainty associated with the quantification of an analyte determined to be present is generally proportional to the concentration of the analyte down to some low concentration where it levels out. The relation of measurement uncertainty to concentration for prometon is shown in figure 1. An increase in prometon concentration results in a corresponding increase in the magnitude of the measurement uncertainty as given by standard deviation. As the concentration determined approaches zero, however, the standard deviation does not change as much. Therefore, the standard deviation becomes proportionally larger relative to the concentration as the measured concentration decreases. This effect is shown in figure 1 by the relative standard deviation (RSD) in percent (standard deviation  $\times$  100/concentration) in relation to prometon concentration. Prometon concentrations less than 0.1  $\mu\text{g/L}$  have greater RSD, while prometon concentrations greater than 0.1  $\mu\text{g/L}$  have small and slowly decreasing RSD. The standard deviation is relatively unchanging for prometon concentrations between 0.1 and 0.04  $\mu\text{g/L}$ , but the RSD increases from 7 to 33 percent.

Adequacy of quantification is subjective, according to the level of uncertainty in the information that a data user is willing to accept for interpretation. A data user may define adequate quantification so that each individual determination has a 10 percent measurement uncertainty or less. For example, for prometon, in such a case, the data user should censor the data at about 0.1  $\mu\text{g/L}$ . Quantification requirements of this sort are often important when the emphasis on data interpretation is legal or regulatory. Otherwise, much larger quantification error in individual measurements can be tolerated for scientific interpretation, and thus other data users may define adequacy by much less stringent criteria. In particular, many water-quality studies are best served by using the best available determination for an analyte that is detected, even if measurements have large RSD (50-100 percent).

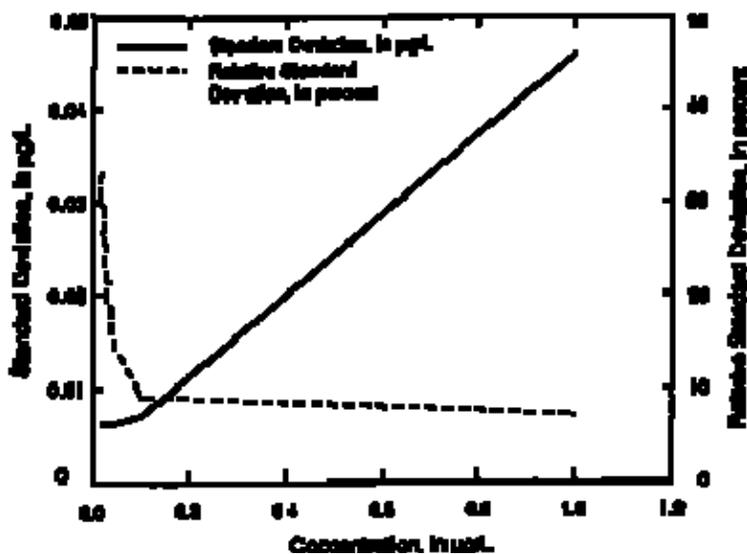


Figure 1.--Measurement uncertainty in standard deviation and relative standard deviation in relation to prometon concentration.

## Method detection limit

Method detection limits (MDL) are concentration levels for a particular analytical process and matrix combination which yield a determination that, considering only quantification uncertainty, has a specified high probability that the analyte concentration is greater than zero.

The U. S. Environmental Protection Agency (USEPA) defines MDL as follows:

The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

The U.S. Geological Survey (USGS) definition for the limit of detection (LOD) found in Wershaw and others (1987), and Fishman and Friedman (1989) is nearly identical to the USEPA definition, except the word "identified" is included because qualitatively identifying the substance is a critical part of the definition.

The minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing [the] analyte.

The definitions specify a confidence level for detection by controlling the risk of false positives, owing to quantification uncertainty, thus suggesting that the definition is statistically based.

The USEPA procedure for determining MDL uses statistical techniques to arrive at the 99 percent confidence level. Determining the MDL requires analysis of replicate samples (at least 7) of a relatively clean environmental matrix or laboratory matrix with analyte concentrations, either natural or spiked, at 1 to no more than 5 times the estimated MDL. The samples should be analyzed over several days to account for between-calibration (batch-to-batch) method variation. The samples must be processed through all steps involved in the method, including preparation steps.

The MDL is calculated from the following equation:

$$MDL = t_{(n-1, 1-\alpha=0.99)} (S)$$

where

**MDL** = method detection limit,

**$t_{(n-1, 1-\alpha=0.99)}$**  = the one-sided Student's *t*-value appropriate for a 99 percent confidence level and a standard deviation estimate for *n-1* degrees of freedom (*n*, number of replicates analyzed), and

***S*** = standard deviation of the replicate sample analyses.

The MDL must be iteratively determined by repeating the above described procedure at least twice at different concentration levels to ensure that the concentration of analyte in the MDL test samples are in the range where the standard deviation is relatively unchanging. Using prometon as an example (figure 1), the analyte concentrations where the standard deviation is relatively unchanging are less than 0.1 µg/L. Thus, the MDL test sample must have less than or equal to 0.1 µg/L prometon. From the data shown in figure 1, the estimated MDL for prometon is 0.018 µg/L.

The MDL determined is dependent on the method, instrument performance, materials, skill of the analyst, and other operational sources of variation. The MDL is not an absolute and invariant

number; it is subject to random variation caused by day-to-day changes in calibration solutions and instrument sensitivity. Each time the MDL is determined for a particular method, slightly different estimates for MDL will be calculated. The USEPA procedure accounts for this variability in MDL estimates by calculating the 95 percent confidence interval for multiple determinations of MDL. The 95 percent confidence interval is calculated according to the following equations derived from the ratio of chi square distribution to the degrees of freedom distribution ( $X^2/df$ ):

$$LCL = \sqrt{(n-1) \frac{s^2}{Z_{(0.025, n-1)}^2}} \quad MDL$$

$$UCL = \sqrt{(n-1) \frac{s^2}{Z_{(0.975, n-1)}^2}} \quad MDL$$

where,  $Z_{(0.025, n-1)}^2$  and  $Z_{(0.975, n-1)}^2$  are, respectively, the upper and lower chi square critical values for n-1 degrees of freedom  
**LCL = the lower 95 percent confidence limit; and**  
**UCL = the upper 95 percent confidence limit.**

Periodically, MDL estimates should be checked because of inherent variation in analytical processes. The USEPA recommends every 3 to 6 months or whenever an existing analytical procedure is significantly altered. New MDLs must be determined for all new analytical procedures.

The MDL does not account for matrix interferences. With clean environmental samples, analysts are able to detect analyte in concentrations less than the MDL; while conversely, with complex samples, analysts may be unable to detect analyte in concentrations greater than the MDL.

The MDL is an arbitrary position on the uncertainty continuum. Various measures of uncertainty, probability of false positives, and probability of false negatives (if values were censored at the MDL) because of random variability for a series of prometon concentrations are listed in table 1. The MDL is useful for characterizing a method under specified operating conditions and for comparing methods for project planning. The MDL also can be used to monitor the ongoing method performance throughout a study.

Table 1.-- Standard deviation, relative standard deviation, and probability of false positive and negative for various prometon concentrations.

Prometon concentration measurement (µg/L)	Standard deviation (µg/L)	Relative standard deviation (%)	Probability that true value is zero (false positive) (%)	Probability that true value is greater than MDL (%)
0.005	0.006	120	20	1.5 *
0.006	0.006	100	16	2 *
0.008	0.006	75	9	5 *
0.01	0.006	60	5	9 *
MDL = 0.018	0.006	33	1	50 *
0.04	0.006	15	<1	>99
0.1	0.007	7	<<1	>>99
1.0	0.046	5	<<1	>>99

\* False negatives if data are censored at MDL.

The USGS definition and USEPA procedure achieve low probability of false positive or type-I statistical error if data are censored at the MDL. The MDL concept does not provide a low probability of false negative or type-II statistical error, however. The statistical probability of making a false negative decision because of quantification uncertainty (not identification uncertainty) is about 50 percent for measured concentrations near the MDL if data are censored at the MDL.

Use of the terms method detection limit, limit of detection, and statistically determined detection limit all refer to the USGS definition and USEPA procedure previously cited. To simplify, the NWQL will only use the term method detection limit (MDL) in reference to NWQL analytical methods used for schedules 2001, 2010, 2050, and 2051. By following the USGS definition and USEPA procedure, there will be consistent understanding of the meaning and procedure for determining the MDL if data are censored at the MDL.

The previous discussion of the analytical process, measurement uncertainty and quantification, and the definition for MDL sets the framework for describing the NWQL policy for identifying and quantifying analytes for the NAWQA schedules.

### **NWQL policy for reporting data for schedules 2001, 2010, 2050, and 2051**

The NWQL policy for reporting measured values for all target analytes identified in a sample for schedules 2001, 2010, 2050, and 2051 uses the MDL as a standard to characterize method capabilities and remark codes for analytical results in general categories of reliability.

#### **Case A -- Reporting detections with values greater than the MDL and less than the highest calibration standard**

Measured concentrations are usually reported without remark codes when: (1) an analyte elutes at the characteristic retention time, (2) the analyte is identified from the spectral information, and (3) the quantification steps indicate the analyte concentration is greater than the MDL and less than the highest quantification standard from the instrument calibration.

Occasionally, situations occur in the analytical data interpretation for a few analytes where the retention times are correct and analytes are properly identified, yet the quantitative determination is substantially more uncertain than for other analytes. For such analytes, the NWQL will identify results with an E remark code even though the measurement is greater than the MDL and less than the highest calibration standard. The E remark code in this case indicates that the value reported is estimated and should be used with caution. The NWQL will be releasing technical memoranda and Open-File Reports in the future describing the method performance of various analytical schedules. Within these documents more specific information will be available that describes reporting estimated values for various analytes.

#### **Case B -- Reporting detections with values less than the MDL**

A numerical value will be reported for measurements less than the MDL if a peak is observed at the correct retention time and the qualifying information from the spectra conclusively identifies the analyte. The NWQL will indicate results less than the MDL with an E remark code.

NOTE: Because of the limitations of the current National Water Information System (NWIS) data, the E remark code has multiple definitions in the context of the usage defined here. In the future,

with the more capable NWIS-II data system, indicators with unique definitions will be used to remark each of the situations described.

### **Case C -- Reporting nondetections**

Nondetections result from four different situations:

1. No peak (signal) is observed at the characteristic retention time. Since no peak is observed, there is no subsequent qualifying information from the spectra to identify the analyte. A blank sample is an example. The result will be reported with a less than sign (<) and the MDL.
2. A small peak (corresponding to a value less than the MDL) is observed at the characteristic retention time, but the analyte is not conclusively identified from the spectrum. This occurs when an unidentifiable interfering substance elutes from the chromatographic column at the characteristic time for the analyte. The analyte can be present yet be masked by the interfering substance; but because the analyte cannot be conclusively identified by characteristic spectrum-pattern matching, the result will be reported with a 'less than' sign (<) and the MDL.
3. In cases where an interference caused by the matrix may mask an analyte at concentrations greater than the MDL, the laboratory will report either a raised reporting limit based on analyst's judgement of the data or a DU deletion code (unable to determine analyte because of interference).
4. In cases where a full liter of sample is not available or used and an analyte is not detected, a higher than MDL reporting limit with a less than sign (<) will be reported in proportion to the sample analyzed. The MDL is inversely proportional to the amount of sample used. Note that the higher reporting limit is not an MDL because MDL has not been determined for the different sample amount.

### **Case D -- Reporting results above highest calibration standard**

Another situation in which a censored value will be reported by the NWQL for these schedules occurs when a target analyte is detected and identified, but the quantification is not completed because the resulting value is greater than the highest calibration standard for the method. The result will be reported as greater than (>) the highest calibration standard for the method, although estimated values can be reported on a custom basis. For example, if the 1948 highest calibration standard for a target analyte is 20 µg/L and the target analyte exceeds 20 µg/L in a sample, then the laboratory will report >20 µg/L for the result. Schedules 2001, 2010, 2050, and 2051 were designed as low-cost reliable methods for reporting low-level data. Consequently, sample extracts will not be diluted and reanalyzed, unless specifically arranged at additional cost. The NWQL provides other methods specifically for higher level samples.

### **Summary**

This memorandum has described NWQL policy for reporting low-level data for schedules 2001, 2010, 2050, and 2051. When an analyte is identified and the value reported is less than the MDL, an E remark code will be associated with the result. In addition, the E remark code represents an estimated value for analytes which present larger than expected uncertainty within the analytical range for the method. Only in two situations (Case C, number 3 and 4) will a data user see a censoring value greater than the MDL. A data user needs to define adequate quantification for interpretation because of measurement uncertainty. The data user may apply an appropriate censoring limit, applicable to the needs of the project, for quantifying analytes from schedules 2001,

2010, 2050, and 2051. The USEPA procedure and USGS definition for MDL were described to put the NWQL data reporting policies in perspective. The MDL is arbitrarily defined as the 99 percent confidence level that the analyte concentration is greater than zero. The MDL is best suited to compare methods for the purpose of project planning and to monitor the ongoing method performance throughout the study.

**Supersedes:** none

**Effect on Existing Data Base:** none

**Key Words:** Method detection limits, Reporting limits, Quantification

**Distribution:** See above plus the continua USGS.labnews and .water.quality

## **References**

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