United States Department of the Interior
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National Water Quality Laboratory
P.O. Box 25585
Denver, CO 80225-0585

NATIONAL WATER QUALITY LABORATORY
TECHNICAL MEMORANDUM 15.02

June 4, 2015

Subject: Changes to National Water Quality Laboratory (NWQL) procedures used to establish and verify laboratory detection and reporting limits

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Author(s): Teresa Williams, Quality Assurance, twilliams@usgs.gov, 303-236-3482
William T. Foreman, Method Research and Development Program, wforeman@usgs.gov, 303-236-3942
Jessica Decess, Quality Assurance, jdecess@usgs.gov, 303-236-3488
Carmen Reed-Parker, Quality Assurance, cgreed@usgs.gov, 303-236-3246
Douglas L. Stevenson, Chief of Quality Assurance, dstevens@usgs.gov, 303-236-3762

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1 PURPOSE

This memorandum describes the implementation by the National Water Quality Laboratory (NWQL) of selected components of ASTM International's Standard Practice D6091-07 (ASTM International, 2007) and supporting DQCALC software (Standard Practice D7510-10; ASTM International, 2010) to determine and verify detection limits (DLs) for selected NWQL methods annually. These ASTM standard practices, referred to as the DQCALC procedure in this memorandum, are being implemented as an alternative to the long-term method detection limit (LT–MDL) procedure previously used for many NWQL water methods (Childress and others, 1999).

Preliminary implementation of the DQCALC procedure was announced in NWQL Rapi-Note 14-09 (USGS access only), *NWQL implements ASTM program DQCALC for establishing laboratory reporting levels*. The expanded use of blank data to determine DLs and reporting limits (RLs) for blank-limited analytes also is addressed in this memorandum. The NWQL's data reporting and coding conventions based on the application of these procedures are described.

Note: the terms "limit" and "level" have been used interchangeably for many of the detection and reporting terms used by the NWQL and by non-USGS scientists. In this memorandum the term "limit" generally is used throughout, including for new terms defined in this document.

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2 BACKGROUND

For any laboratory DL assessment, a primary goal is to ascertain at what concentration the analytical measurement process can reliably differentiate between a measureable signal (peak) that is attributable to the target analyte in a sample from that provided by the laboratory set blanks prepared using a reagent-matrix. This assessment process includes laboratory sample preparation steps, if applied, and the instrumental analysis of the sample or sample extract. It does not include the effects of field sample collection and processing steps. The yearly verification of DLs assures method detection capability, and is a requirement for the NWQL to maintain accreditation by The NELAC Institute (National Environmental Laboratory Accreditation Conference, 2003).

2.1 NWQL use of the method detection limit (MDL) and long-term method detection limit (LT–MDL)

Prior to the changes described in this memorandum, the NWQL typically has used either the method detection limit (MDL) procedure of the U.S. Environmental Protection Agency (EPA) (unchanged since 1986; U.S. Environmental Protection Agency, 2014) or the LT–MDL procedure for the establishment of DLs. As described in Childress and others (1999), the LT–MDL procedure was a minor modification of the MDL procedure that included a greater number of spiked replicate samples (reagent water spiked at one to five times the expected MDL concentration), typically collected for more than 6 months (instead of a few days or weeks), and had been used for annual verification of DLs for many NWQL water methods between 1999 and 2013.

The MDL or LT–MDL is shown in figure 1 and calculated by:

$$MDL \text{ or } LT\text{–}MDL = s \times t \qquad \text{(Eq. 1)}$$

Both the MDL and LT–MDL procedures attempt to simulate the distribution of replicate blank measurements by assuming that the distribution (reflected by the standard deviation) of low-concentration spiked replicate samples used to estimate the MDL or LT–MDL (by Eq. 1) is equivalent to that of blank samples. This simulated blank distribution is further assumed to be centered on the zero concentration and to have a symmetrical and bell-shaped (Student's *t*) distribution. Thus, reporting an analyte as present at the DL concentration is estimated to be a result of blank contamination (a false positive detection) no more than 1 percent of the time (area in red in fig. 1).

Most recently, LT–MDLs were verified annually by the NWQL in coordination with the USGS Branch of Quality System's (BQS) LT–MDL Project. Throughout each year blind spike and/or blind blank samples were submitted by BQS and analyzed by the NWQL. When spiked replicate samples are used, the LT–MDL procedure also provided method performance information at a concentration near the DL.

For many (especially organic) analytes, LT–MDLs were calculated by Eq. 1 using spiked replicate samples. However, the NWQL and BQS recognized that the MDL and LT–MDL procedures attempt to simulate the blank distribution. Thus, BQS blind blank data (see https://bqs.usgs.gov, public access) from inorganic methods were used instead of spike-based data to calculate the DL directly using Eq. 1. BQS also estimated the DL as the 99th percentile concentration or the 2nd highest value when there were less than 100 values of the blank population for BQS blind blank data.

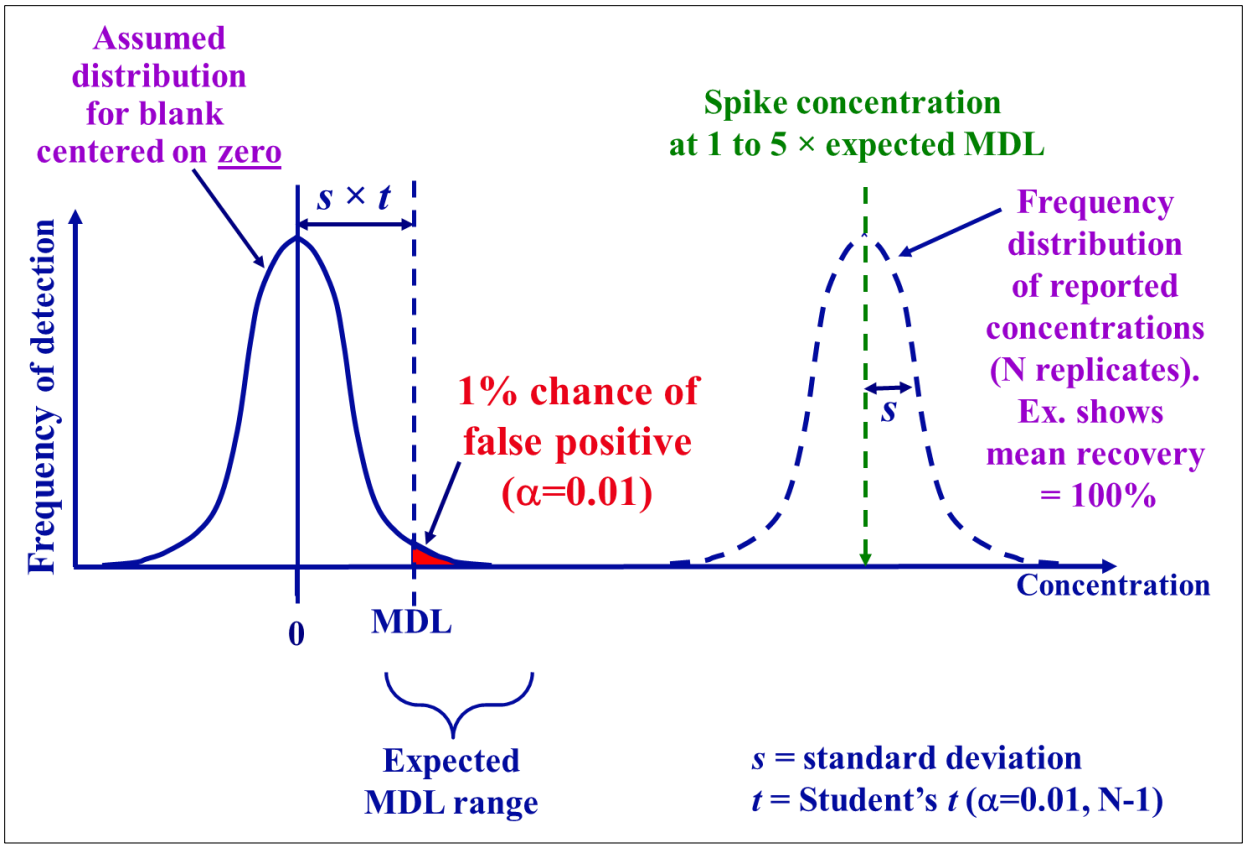

Figure 1. Determination of the method detection limit (MDL) or long-term method detection limit (LT–MDL) using spiked replicate samples.

An advantage of the percentile approach is that it makes no assumption about the shape or zero-concentration centering of the blank-data distribution. Use of blank data to estimate the DL has been applied primarily to inorganic analytes for those methods providing uncensored results. The use of blank data also has been applied to several hormone method analytes as described by Foreman and others (2012a). Examples of DLs estimated using spike and blank data approaches are given in Section 11.

2.2 What the method detection limit (MDL) and long-term method detection limit (LT–MDL) concentrations represent

The MDL and LT–MDL concentrations only minimize false positive risk ("type I" error) to ≤ 1 percent, which is represented by the probability (alpha [α]) being set at 0.01. At the MDL or LT–MDL concentration, the false negative risk ("type II" error; beta [β] probability) is ≥ 50 percent (Gibbons, 1995, 1996; attachment C of USGS Office of Water Quality Technical Memorandum 2010.07). As such, both the MDL and LT–MDL are an estimate approximately equal to what others often call the decision or **critical level (L_C)** if α = 0.01 (≤ 1 percent false positive risk), including ASTM D6091-07, the International Union of Pure and Applied Chemistry (Inczédy and others, 1998), and others (for example, Coleman and Vanatta, variously dated).

These organizations and scientists define the "detection limit" (L_D) at a higher concentration that minimizes both the false positive risk (typically $\alpha = 0.01$) and the false negative risk (typically, to ≤ 1 percent or ≤ 5 percent; $\beta = 0.01$ or 0.05, respectively). It is this higher concentration that minimizes both false positive and false negative risks that often has been used by the NWQL as the laboratory reporting level (LRL) or interim reporting level (IRL) concentration. Operationally, these reporting levels have been calculated as two (or more) times the MDL or LT–MDL (Childress and others, 1999) in an attempt to minimize false negative risk to ≤ 1 percent; achieving this low risk rate is dependent in part on the type of data-reporting convention used (see attachment C of USGS Office of Water Quality Technical Memorandum 2010.07).

Since determination of the MDL is required by various federal and state regulatory agencies and laboratory certification organizations, including The NELAC Institute, **the NWQL is continuing to use the term detection limit (denoted by DL) to represent that concentration that minimizes the false positive risk only.** The relation between the DL and L_C as it relates to implementation of the DQCALC procedure is further discussed below.

2.3 Additional limitations of the method detection limit (MDL) and long-term method detection limit (LT–MDL) procedures

The assumptions and limitations of the MDL and LT–MDL procedures, including those noted above, have been discussed by others (for example, Gibbons, 1995, 1996; U.S. Environmental Protection Agency, 2004a, U.S. Army Corps of Engineers, 2013), and one critical assumption is that the measurement variability remains unchanged from the spike concentration down to zero (fig. 1). However, the standard deviation typically is dependent on the spiked concentration, even at low concentrations, and the determined MDL or LT–MDL is strongly dependent on the spiking concentration.

In an attempt to minimize the influence of this dependence, the MDL and LT–MDL procedures rely on the use of analyte spiking concentrations that are within one to five times the expected MDL or LT–MDL, and include optional iterative spiking at successively lower concentrations until the one to five times MDL concentration is achieved (U.S. Environmental Protection Agency, 2014). This approach is especially challenging for those methods having many analytes with widely varying instrumental responses. While the iterative process can provide data at multiple concentrations for some (but typically not all) analytes, the procedure ultimately relies on the use of the standard deviation from a single-concentration for the calculation of the MDL or LT–MDL.

2.4 Multi-concentration procedures to determine the detection and other limits

Various procedures have been proposed, advocated, or used as alternatives to the MDL (see examples in Gibbons, 1995; U.S. Environmental Protection Agency, 2004a), including multi-concentration (calibration-like) approaches, such as the ASTM D6091-07 (DQCALC) procedure (ASTM International, 2007) and the lowest concentration minimum reporting level (LCMRL) procedure (U.S. Environmental Protection Agency, 2004b, 2010; Winslow and others, 2006). Both DQCALC and LCMRL were designed to address some of the limitations of the MDL procedure.

The LCMRL was developed by the EPA Office of Ground Water and Drinking Water and has been applied to analytical methods developed by or for that Office. The LCMRL procedure has been compared with the Federal Advisory Committee on Detection and Quantitation (FACDQ)

Approaches and Uses in Clean Water Act Programs' FACDQ procedure (a single concentration method) developed as a revision of the MDL procedure (U.S. Environmental Protection Agency, 2011). The EPA has not broadly adopted either the LCMRL or FACDQ procedures as official replacements for the MDL procedure.

2.5 NWQL's evaluation of the ASTM DQCALC and EPA's lowest concentration minimum reporting level (LCMRL) procedures

The NWQL evaluated both the DQCALC and the LCMRL procedures/calculators as alternatives to the MDL and LT–MDL procedures. The FACDQ procedure was reviewed, but was not further tested by the NWQL as it is not a multi-concentration, calibration-like procedure. Using multi-concentration approaches for methods with large numbers of analytes is preferred because they can capture the large analyte-specific differences in instrument response.

The DQCALC procedure was used to determine DLs for most analytes in the steroid hormones in water methods as described by Foreman and others (2012a). The LCMRL procedure was first evaluated using the new method for pharmaceuticals by direct aqueous injection liquid chromatography with tandem mass spectrometry (DAI-LC-MS/MS) (Furlong and others, 2014; LCMRL information not included in the method report). A subset of analytes from those methods was compared using both procedures (Foreman and others, 2012b). A similar comparison was conducted for several nutrient analyses and the volatile organic compounds by purge-and-trap gas chromatography-mass spectrometry (GC/MS) methods, from which examples are provided in Section 11.

The DQCALC and LCMRL procedures use spiked replicate samples at multiple concentration levels, preferably using levels in the lower end of the operational range of the method. Although both procedures have minimal replication and level requirements, at least seven replicates at five or more concentration levels are used. When available, additional replicate data provide enhanced statistical power. Both procedures:

- model the change in standard deviation with concentration:
  - DQCALC uses four models—constant (no change), linear, exponential, and hybrid (of linear and exponential).
  - LCMRL uses a modification of the hybrid model only.
- use weighted least-squares regression of expected (true) *versus* determined concentrations, and thus account for method performance,
- estimate L_C ($\approx$ MDL) with false positive risk of ≤ 1 percent ($\alpha = 0.01$) for DQCALC and ≤ 5 percent ($\alpha = 0.05$) for LCMRL,
- estimate L_D (α as for L_C; $\beta = 0.05$ for both); this higher "detection limit" concentration is roughly similar to the NWQL's LRL concentration (typically set at $2 \times$ LT–MDL), and
- estimate one (the LCMRL) or more (by DQCALC) higher reporting/quantitation limits.

The DQCALC and LCMRL calculators do not allow flexibility in setting the α (or β). Consequently, with differing α probabilities, these calculators are not expected to provide identical L_C values if the same source data are used (L_C by LCMRL would be lower when compared to L_C by

DQCALC from the hybrid model). Examples of L_C values determined by the DQCALC and LCMRL calculators are compared to MDL values calculated using spike and blank data in Section 11.

The DQCALC calculator was determined to be the preferred implementation tool for determining DLs for the NWQL. The DQCALC calculator from ASTM, a Microsoft® Excel-based program, allows use of many more spiked replicate samples and provides more model options and detection-related information than the LCMRL, including calculated EPA MDL concentrations at each spiking level, which is helpful in meeting NELAC requirements.

3 DQCALC PROCEDURE IMPLEMENTATION

The NWQL decided to implement the DQCALC procedure more broadly for the determination and annual verification of DLs for selected methods/analytes as a replacement for the LT–MDL procedure in August 2013. The LT–MDL and DQCALC procedures are similar in that they are both evaluating data over an extended period of time (a minimum 7-month period) to account for the inherent day-to-day variability exhibited by methods. The DLs determined by both procedures attempt to limit the false positive risk to ≤ 1 percent. Calculations of the LT–MDL were based on either spiked replicate samples or laboratory set blank samples. The DQCALC procedure, however, is based solely on spiked replicate samples, but extends the MDL and LT–MDL procedures by utilizing multiple concentration levels to account for changes in measurement variability at the different concentrations. Although DQCALC does not use blank data in its calculations, the BQS blind blank and/or NWQL set blank data for a given period (≥ 6 months) are also compiled and assessed annually. The DLs estimated by both spiked samples and blank samples are used in the final determination of the detection and reporting limits (see Sections 4 and 7).

3.1 The DQCALC Procedure

The DQCALC calculates L_C to constrain the false positive risk to ≤ 1 percent, and a higher concentration detection estimate that limits the false negative risk to ≤ 5 percent. The detection estimate is roughly comparable to the LRL historically used by the NWQL based on the LT–MDL procedure. The process compares four different models of standard deviation change *versus* spike concentration to calculate both L_C and the detection estimate; the best model is then selected to represent the data. The calculations are described in D6091 (ASTM International, 2007).

The DQCALC procedural steps (some done by the DQCALC calculator) are:

- Determine spiked replicate sample data at multiple concentration levels over time. This is done using instrument/method calibration data when these QC are treated identically to field samples or using spiked replicate samples that are independent of the calibration process when additional laboratory processing or extraction steps are involved.

- Select a random subset of the data if a very large data set exists.

- Model the standard deviation *versus* concentration data (four models noted previously) and select the best model (often the hybrid model), based in part on built-in selection rules.

- Model the expected (true) *versus* determined spike concentration data using weighted least square regression.

- Calculate L_C—**This is what the NWQL is calling the detection limit by the DQCALC procedure [defined as National Water Information System (NWIS) report level type code DLDQC; refer to Section 9]**.

    - L_C by DQCALC is defined as the lowest concentration that with 90 percent confidence will be exceeded no more than 1 percent of the time when a blank sample is measured (≤1 percent false positive risk).

    - Based on theory, L_C should be similar to the NWQL's current DLs, as previously determined either by the LT–MDL or EPA's MDL procedure.

- Calculate the MDL at each concentration level and determine if valid (≥ 7 replicates; spike concentration is between 1 and 5 times the calculated MDL; the calculated MDL is less than the spike concentration).

- Compare the L_C and MDL. By definition, the L_C should nearly equal the MDL concentration calculated using the same data.

- Calculate the ASTM detection estimate ($\alpha = 0.01$; $\beta = 0.05$).

- Compare the detection estimate (the value from same model as selected for L_C) with the NWQL's reporting limit (RL), which is calculated as 2 (or more) × L_C; see Sections 6 and 9.

- Verify that the L_C and RL concentrations are valid by comparing them to the spike data used in the DQCALC calculator or with other instrument calibration or check standards. *This comparison is critical because calculated L_C and RL values sometimes are too low relative to actual instrument/method response capability.* This is especially true for analytes determined by mass spectrometry where qualitative identification of an analyte also requires the presence of at least one secondary qualifier ion whose response signal might be much smaller than that of the primary quantification ion that is used to determine analyte concentrations in L_C and RL calculations and in field samples.

4 EXPANDED USE OF BLANK DATA TO DETERMINE AND VERIFY DETECTION LIMITS (DLs) AND REPORTING LIMITS (RLs)

Even when blank data are not directly incorporated into the calculation of the L_C and RL, data from laboratory blanks factor into the decisions to set these limits. For many analyses data from the BQS Blind Blank Program and/or from NWQL set blank analyses have been and will continue to be evaluated as an independent and internal verification of the NWQL detection and reporting limits. For most analyses extraneous contamination in the laboratory set blanks is not an issue; however, for those analyses for which contamination is commonly detected (some organic analytes), an alternative approach is required. For these analytes blank data can be used as an alternative to spiked replicate sample data to establish or verify the DL and RL, as spike-based procedures, including DQCALC, can substantially underestimate the DL if the goal is to minimize false-positive risk.

The DL can be determined with blank data (**new report level type code DLBLK in NWIS**) by calculating with a dataset of ideally 50 or more blanks using:

- DLBLK = 95^{th} – 99^{th} percentile value of the blank data (Eq. 2)
  - This approach was commonly used by the BQS LT–MDL Project for various inorganic analytes as noted in Section 2.1. It is best applied when there is a large amount of blank data.
  - With a smaller data set (N < 100), the 2^{nd} highest value is used to estimate the 95^{th} – 99^{th} percentile value. The percentile is based on the number of samples, for example, when N = 50, the 2^{nd} highest value is the 98^{th} percentile.
  - With a larger data set (N > 100), the 99^{th} percentile value is used.

- DLBLK = $s \times t$ (Eq. 3)
  where: s = standard deviation of the blank data, in concentration units;
  t = Student's t value at $\alpha = 0.01$ and N – 1 blank samples.
  - This approach was commonly used by the BQS LT–MDL Project for various inorganic analytes as noted in Section 2.1.
  - As with the MDL calculation (Eq. 1), equation 3 assumes a symmetrical blank distribution centered on zero concentration, but more appropriately uses replicate blank data.

- DLBLK = Y + $s \times t$ (Eq. 4)
  where: Y = mean of blank data if a positive value, in concentration units;
  s = standard deviation of the blank data, in concentration units;
  t = Student's t value at $\alpha = 0.01$ and N – 1 blank samples.

  As with the MDL calculation (Eq. 1), Eq. 4 assumes a symmetrical blank distribution, but more appropriately uses replicate laboratory blank data, and includes the positive mean offset of the blank distribution if it is not centered on zero. An example of this approach is described in Foreman and others (2012a).

The Grubb's test for outliers is used to eliminate either high (more typical) or low outlier blank data prior to calculating DLBLK.

5 EPA METHOD DETECTION LIMIT (MDL) PROCEDURE USE FOR DETECTION LIMIT (DL) CALCULATION AND VERIFICATION

Although the DQCALC and/or blank data procedures are being applied to many NWQL methods, annual DL verification for some methods/analytes might be completed using the EPA MDL procedure. Applicable methods might include:

- low-demand methods,

- methods where a regulatory agency (cooperator) or accrediting organization is requiring use of the EPA MDL procedure (the DQCALC procedure also provides MDLs at each spike level if seven or more spiked replicate samples are used), or

- methods that use complicated sample preparation steps where application of DQCALC or blank-data procedures would be unable to provide the required replicate data within an evaluation period.

6 SETTING THE NWQL'S REPORTING LIMITS

Analyte reporting levels (LRL or IRL), derived from the MDL or LT–MDL procedures or using blank data, historically have been set at two (or more for some analytes) times the calculated DL (Childress and others, 1999). Although DQCALC calculates a higher concentration (the detection estimate) that could be used as the reporting limit, the ratio between L_C and the detection estimate is not a constant value across all analytes. By continuing to set RLs at least two times the DL, the false negative risk is estimated to be ≤ 1 percent, which is lower than the ≤ 5 false negative risk probability used by the DQCALC calculator for the detection estimate.

Thus, for many analytes:

$$RL = 2 \times DL \qquad \text{(Eq. 5)}$$

For other analytes the RL will be set to a concentration that is greater than 2 × DL for one or more of the following reasons:

- Spike recovery performance of the analyte requires a greater RL; see attachment C of USGS Office of Water Quality Technical Memorandum 2010.07.

- The analyte cannot be routinely qualitatively identified at 2 × DL. This is primarily a limitation for mass spectrometry or dual-column gas chromatography methods (see Section 3.1).

- Instrumental detection and quantification at 2 × DL is not routinely achieved.

- For blank-limited analytes, a higher RL may be used:
  - because there are insufficient blank data available for determining the DL and establishing the RL (interim values are used);

  - in specific cases to account for specific method-blank or field-blank contamination bias issues that warrant setting a more conservative, higher RL; see example in setting the RL for bisphenol A in Foreman and others (2012a).

For most NWQL organic methods/analytes, the RL concentration calculated as described above will be reported as the "less than" value to NWIS when a compound either is not detected or is detected at a concentration below the DL (or below an even lower threshold concentration for mass spectrometry methods); see also Section 10.

For most NWQL inorganic methods/analytes, the DL concentration calculated as described above will be reported as the "less than" value to NWIS when an analyte either is not detected

or is detected at a concentration below the DL based on the reporting convention changes given in USGS Office of Water Quality Technical Memorandum 2010.07.

Reporting convention examples are presented in Section 10.

7 UPDATES TO DETECTION LIMITS (DL) AND REPORTING LIMITS (RL)

Updates to DL and/or RL are made, as needed, based on the annual DL/RL verifications with updates typically implemented at the beginning of a fiscal year (FY) on October 1. Updates also might occur at other times, as required, based on method performance considerations.

Annual updates to DL/RL concentrations are only made when the NWQL determines that there is a significant change relative to the current value. The DLs are generally evaluated against a 95 percent confidence interval of the chi-square distribution of the current value to determine if a change might be necessary. Other method-limiting factors such as the qualitative identification of an analyte also are considered in this decision (see Section 3.1).

Current and historical DL and RL information are available at http://nwql.cr.usgs.gov/usgs/limits/limits.cfm (USGS access only).

8 STATUS OF DQCALC IMPLEMENTATION

Verification of DLs using the DQCALC procedure was and continues to be applied first to those NWQL methods where the calibration standards and field samples are treated identically prior to instrumental analysis (no separate laboratory preparation steps are required for field samples). This includes many inorganic water methods and selected organic water methods, including those for volatile organic compounds by GC/MS, and pharmaceuticals and pesticides by DAI-LC-MS/MS. A staged implementation will occur over the next 1–2 years for those methods having sample preparation steps to accommodate the time needed to acquire the required data.

Beginning on October 1, 2013 (FY14), DL and RL updates based on use of the DQCALC procedure were made for some volatile organic compounds by GC/MS and selected nutrients. This initial phase of implementation was targeted to selected analytes previously evaluated by the BQS LT–MDL Project and that had calibration data readily available for use in the DQCALC calculator. Initial implementation of DQCALC for establishing laboratory DLs was announced in Rapi-Note 14-09 (USGS access only).

During the annual DL verification cycle for FY15 (data collected in FY14), the DQCALC procedure was applied to methods/analytes that determine volatile organic compounds by GC/MS, carbon (DOC and TOC), metals by inductively coupled plasma with optical emission spectroscopy (ICP–OES) or mass spectrometry (ICP–MS), nutrients (Kjeldahl, discrete analyses, low-level phosphorous, and alkaline persulfate methods), silica, and major ions by ion chromatography. Beginning October 1, 2014 (FY15), DLs and RLs were updated as needed.

Note, however, that even though the determination process changed, the DL and RL values used by the NWQL and shown in the NWQL services catalog (USGS access only) and NWIS might not have required an update (Section 7). A list of methods and updated DLs and RLs is available at: http://wwwnwql.cr.usgs.gov/qas.shtml?ReportingLimitsCurrent (USGS access only).

9 NEW NWQL AND NWIS REPORT LEVEL TYPE CODES

New NWQL and NWIS report level type codes shown in table 1 have been created to identify whether the DL and RL were calculated and/or evaluated and verified by the NWQL using the DQCALC or blank data procedures (see all NWIS DL/RL codes in table 12 at http://nwis.usgs.gov/nwisdocs5_2/qw/QW-AppxA.pdf).

Table 1. New NWIS report level type codes (result level).

[NWIS, National Water Information System; DLDQC, detection limit by the DQCALC procedure; DQCALC, ASTM International's program to establish laboratory reporting levels; ≤, less than or equal to; =, equal; L_C, critical level in Section 2.2; ≈, approximately equal; MDL, method detection limit; DLBLK, detection limit by blank data; RLDQC, reporting limit by the DQCALC procedure; RL, reporting limit; RLBLK, reporting limit by blank data]

Report level [type]* code	Definition	Description
DLDQC	detection limit by DQCALC	Lowest concentration that with 90 percent confidence will be exceeded no more than 1 percent of the time when a blank sample is measured (≤ 1 percent false positive risk). DLDQC = critical level "L_C" by ASTM D6091 ≈ MDL.
DLBLK	detection limit by blank data	Lowest concentration that will be exceeded no more than 1 percent of the time when a blank sample is measured (≤ 1 percent false positive risk) as determined using replicate blank data.
RLDQC	reporting limit by DQCALC	Equal to (or greater than) two times DLDQC. The probability of falsely reporting a non-detection for a sample that contains an analyte at the RLDQC concentration is predicted to be ≤ 1 percent.
RLBLK	reporting limit by blank data	Equal to (or greater than) two times DLBLK. The probability of falsely reporting a non-detection for a sample that contains an analyte at the RLBLK concentration is predicted to be ≤ 1 percent.

*In Appendix A, "Codes used in water-quality processing system," table 12 , "Report level type codes (result level)," the column header refers to the report level type codes as "report level codes."

For analytes with DLs being established or verified by the DQCALC procedure during the annual evaluation of the DLs, the report level type codes DLDQC or RLDQC, as well as the associated value, will be displayed in NWIS with the field sample result. For analytes with DLs and RLs being established or verified using blank data, the report level type codes DLBLK, RLBLK, or MRL (minimum reporting level) will be displayed in NWIS.

The NWQL applies the MRL as a censoring limit concentration below which no results may be reported. Application of the various code types to data reported in NWIS are discussed in Section 10.

The report level type coding changes will be applied retroactively for all data reported in FY15 for those methods/analytes that were evaluated using the DQCALC procedure. Completion of these updates is expected by October 2015 with notification by the NWQL.

No report level type coding changes are being applied to data in NWIS prior to FY15.

10 NWQL REPORTING CONVENTIONS FOR NEW NWIS REPORT LEVEL TYPE CODES

As outlined in USGS Office of Water Quality Technical Memorandum 2010.07 and continued with the new NWIS report level type codes (table 1), results reported to NWIS are based on the conventions outlined below. The reporting conventions are unchanged from those used by the NWQL since October 2010. The applied reporting convention is identified by the report level type code that is associated with the reported sample result in NWIS. This code also identifies the procedure used to establish or verify the DL and RL.

For analytes reported by NWQL with NWIS report level type code "DLDQC:"

- The DLDQC code is used primarily for NWQL inorganic methods/analytes.
- The detection limit (DL = the critical level, L_C) was calculated or verified by the DQCALC procedure.
- The value shown under the "reporting level (RL)" field and displayed with the sample result in NWIS (and in the NWQL services catalog) will be the DLDQC concentration.
- Measured sample concentrations that are less than the detection limit (DLDQC) will be reported as "less than" the DL concentration (< DLDQC).
- Results in the concentration range: DLDQC ≤ result < RLDQC will include an "n" result-level qualifier code in NWIS, where RLDQC typically is set at 2 × DLDQC. Having a "reporting limit" concentration (RLDQC) that is higher than the DL concentration, and qualifying reported concentrations between DLDQC and RLDQC with the "n" code, are requirements of accreditation by The NELAC Institute (National Environmental Laboratory Accreditation Conference, 2003). However, this higher RL value is not used as the "less than" concentration for analytes shown with the DLDQC code in NWIS.
- Results that are less than the lowest calibration standard will have a "b" result-level value qualifier code in NWIS, indicating that the result was extrapolated below the lowest calibration standard.

For analytes reported by NWQL with NWIS report level type code "DLBLK:"

- The DLBLK code is used primarily for NWQL inorganic methods/analytes.
- The detection limit (DLBLK) was calculated or verified using replicate blank data (see Section 4).
- All other reporting features are the same as for report level type code DLDQC except that DLBLK and RLBLK are substituted for DLDQC and RLDQC, respectively.

For analytes reported by NWQL with NWIS report level type code "RLDQC:"

- The RLDQC code is used primarily for NWQL organic methods/analytes.

- The evaluated detection limit (DLDQC = L_C) was calculated or verified by the DQCALC procedure.

- The reporting limit (RLDQC) will generally be set at 2 × DLDQC. For some analytes, a factor greater than 2 (but less than or equal to 10) will be used (see Section 6).

- Non-detections or measured sample concentrations that are less than the detection limit (DLDQC) will be reported as "less than" the reporting limit concentration (< RLDQC); see data reporting exception for mass spectrometry methods below.

- The value shown under the "reporting level (RL)" field and displayed with the sample result in NWIS (and in the NWQL services catalog) will be the RLDQC concentration.

- Results in the concentration range: DLDQC ≤ result < RLDQC will have an "n" result-level qualifier code in NWIS.

- Results that are less than the lowest calibration standard will have a "b" result-level value qualifier code in NWIS, indicating that the result was extrapolated below the lowest calibration standard.

- Measured sample concentrations that are less than the DLDQC (down to a lower limit typically set at 10 percent of the DLDQC) will have a "t" result-level qualifier code in NWIS. Only mass spectrometry methods, which are classified as being "information rich," report results in this range (Childress and others, 1999). Concentrations reported below the DL are for those analytes that first meet required mass spectral qualification criteria.

  Mass spectrometry methods are classified as "information rich" because they rely on analyte identification using multiple pieces of information (characteristic chromatographic retention time plus high-fit mass spectral matching with a library spectra, or plus presence of the quantitation ion and one or more qualifying ions and ion ratios that meet acceptance criteria; see, for example, Foreman and others, 2012a; Furlong and others, 2014).

  Note: A sample result below the DL will have an increasing risk of being a false positive as the concentration decreases, and thus must be carefully evaluated for use by the data user relative to the associated laboratory and field blank data.

For analytes reported by NWQL with NWIS report level type code "RLBLK:"

- The RLBLK code is used primarily for NWQL organic methods/analytes.

- The detection limit (DLBLK) was calculated or verified using replicate blank data (see Section 4).

- All other reporting features are the same as for report code type RLDQC except that DLBLK and RLBLK are substituted for DLDQC and RLDQC, respectively.

Reminder regarding analytes reported by NWQL with NWIS report level type code "MRL:"

- The MRL code is defined as the minimum reporting level (see table 12 at http://nwis.usgs.gov/nwisdocs5_2/qw/QW-AppxA.pdf)

- The MRL might be used for NWQL organic or inorganic methods/analytes.

- The DL for MRL analytes might be unknown, or be estimated or calculated by various methods.

- Some blank-limited (primarily organic) analytes with determined DLBLK concentrations (Section 4) might be reported using the MRL code.

- Concentrations below the MRL are reported as < MRL. The MRL is a censoring limit concentration below which the NWQL does not report final (censored) results to NWIS.

- The reporting limit value displayed with the sample result in NWIS (and in the NWQL services catalog) will be the MRL concentration.

- Results that are less than the lowest calibration standard but above the MRL will have a "b" result-level value qualifier code in NWIS, indicating that the result was extrapolated below the lowest calibration standard.

11 RESULTS/SELECTED PLOTS OF DETECTION LIMIT (DL) DETERMINATIONS

Below are selected plots of the DLs determined by the various procedures outlined in this memorandum (table 2) for a selection of analytes used as part of the initial determination or continuing verification of DLs by the DQCALC procedure (figs. 2–8). These plots include all calculations of the DL that are available for the analyte for FY10 through FY15, with the data used to determine the DLs collected in the preceding FY. Plotted values include an extra, insignificant digit to help reduce symbol overlap. Graphs of additional analytes are available http://wwwnwql.cr.usgs.gov/qas.shtml?ReportingLimitsCurrent (USGS access only).

Also shown on the plots are the applied DL concentrations used by the NWQL for the given FY (blue line). A shift in this blue line at 10/1/2009 indicates a DL change occurred from FY09 to FY10. In FY11, USGS Office of Water Quality Technical Memorandum 2010.07 went into effect, changing the reporting convention and data qualification approach at the NWQL for inorganic analytes only, as indicated by "**" on the plots.

These selected plots show that DLs vary (a) with time, (b) within a given time period based on the applied procedure, and (c) regardless of whether blank or spiked sample data are used. The DLs calculated for a given fiscal year by the various procedures described in this memorandum might agree well (for example, see fig. 2, chromium, 10/1/2014) or show greater differences (such as fig. 3, zinc, 10/1/2014; fig. 4, mercury, 10/1/2013; and fig. 5, ammonia + organic N, 10/1/2013). Clearly, the DL is not a static value and should not be considered as such. These examples also show the benefit of using multiple approaches to estimate the DL "range," and help provide greater confidence when selecting the DL concentration to apply relative to data reporting. While spike-based methods (ASTM L_C or EPA MDL) can provide a good estimate of the DL, they may sometimes substantially underestimate the DL calculated based on actual blank data (see fig. 4, 10/1/2014 for mercury or fig. 6, ortho-PO_4, 10/1/2014).

The DL value used by the NWQL (blue line) typically is updated only when there is a statistically significant difference in this value relative to the calculated DL(s) (see Section 7). For these example plots, the applied DL (blue line) falls within or is just above the calculated DLs. An exception example is benzene by purge-and-trap GC/MS (fig. 7), which has a substantially higher applied DL because its quantification ion (used to calculate the DL) is substantially more responsive than its secondary qualifying ions (see Section 3.1, last paragraph). The calculated DL for benzene does not match the reality of the actual instrumental detection capability when multi-dimensional information (presence of multiple ions having differing responses) is required to identify the analyte. For other organic analytes, the quantification ion can more accurately calculate the applied DL (for example, fig. 8, acetone).

Table 2. Legend description for plots of detection limits (DL).

[BQS, Branch of Quality Systems; NWQL, National Water Quality Laboratory; ASTM L_c, ASTM International's critical level in Section 2.2; DQCALC, ASTM International's program to establish laboratory reporting levels; α, alpha; EPA, U.S. Environmental Protection Agency; MDL, method detection limit; s × t, standard deviation of blank data in concentration units multiplied by the Student's *t* value at α = 0.01 and N – 1 blank samples; LT–MDL, long-term method detection limit; LCMRL, EPA's lowest concentration minimum reporting level procedure; Y, mean of blank data if a positive value in concentration units]

Symbol	Legend descriptor	Equation used (this memo) or description	DL procedure or BQS Project	Sample type used
—	NWQL detection limit	detection limit value used by NWQL	–	–
●	ASTM L_C	Critical level from DQCALC (α = 0.01; see Section 3.1)	DQCALC	Calibration (spike) samples[1]
○	EPA MDL	1	DQCALC	Calibration (spike) samples[2]
▲	BQS blank, s × t	3	BQS LT–MDL	BQS blind blanks
■	BQS blank, 99 percent	2	BQS LT–MDL	BQS blind blanks
□	BQS spike, s × t	1	BQS LT–MDL	BQS spike samples
◆	LCMRL, L_C[3]	Critical level from LCMRL (α = 0.05; limited assessment; see Section 2.5)	LCMRL	Calibration (spike) samples
×	Set blank, s × t	3	Blank	NWQL set blanks
+	Set blank, 99 percent	2	Blank	NWQL set blanks
✱	Set blank, Y + s × t	4	Blank	NWQL set blanks

[1]ASTM L_C and LCMRL L_C in these plots were calculated using multi-concentration calibration standard samples processed comparably to environmental samples for the method and, as such, represent method spike data.

[2]EPA MDLs in these plots were calculated by the ASTM DQCALC software using a single concentration of the same calibration standard data as used for calculating ASTM L_C using multiple concentration levels.

[3]LCMRL L_C only evaluated for FY14 (10/1/2013) for selected methods/analytes.

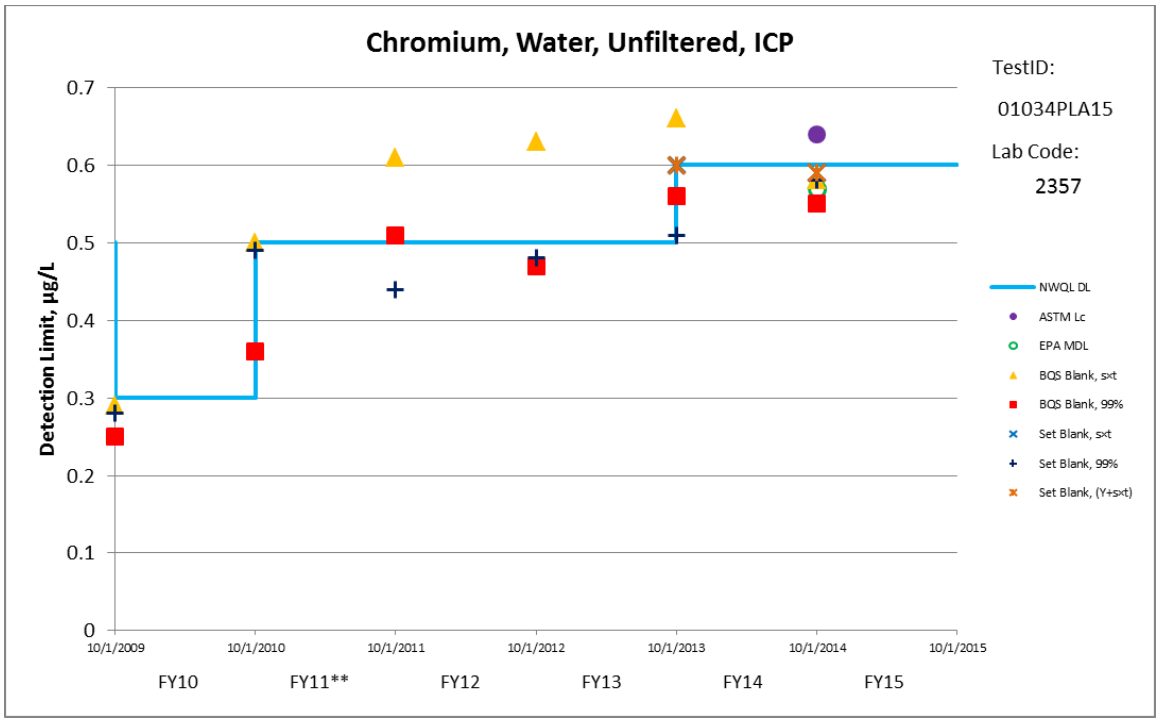

Figure 2. Plot of the detection limits (DLs) calculated by the various DL procedures for unfiltered chromium by ICP.

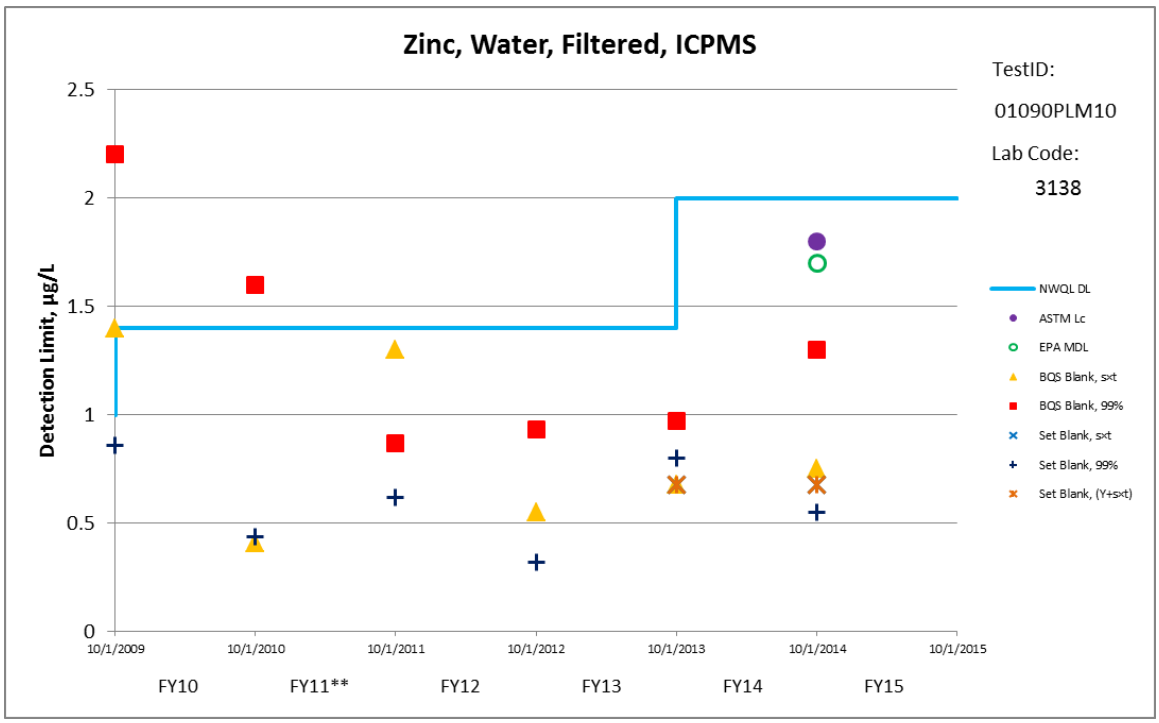

Figure 3. Plot of the detection limits (DLs) calculated by the various DL procedures for zinc, water, filtered, ICPMS.

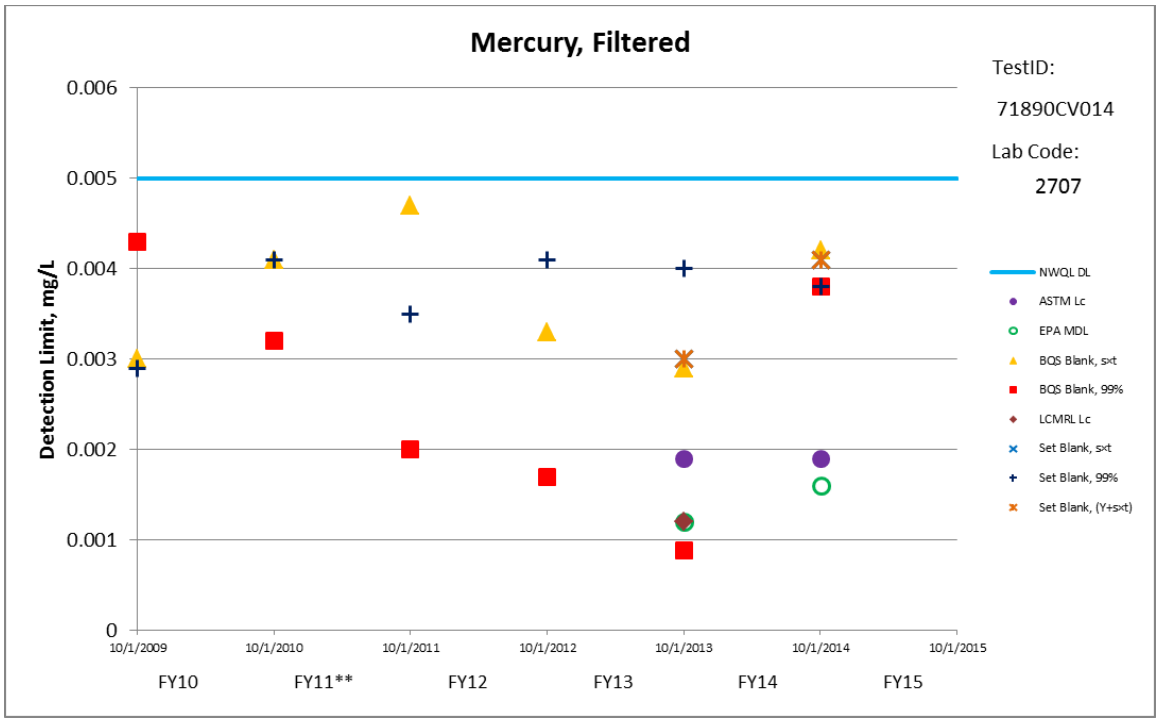

Figure 4. Plot of the detection limits (DLs) calculated by the various DL procedures for filtered mercury.

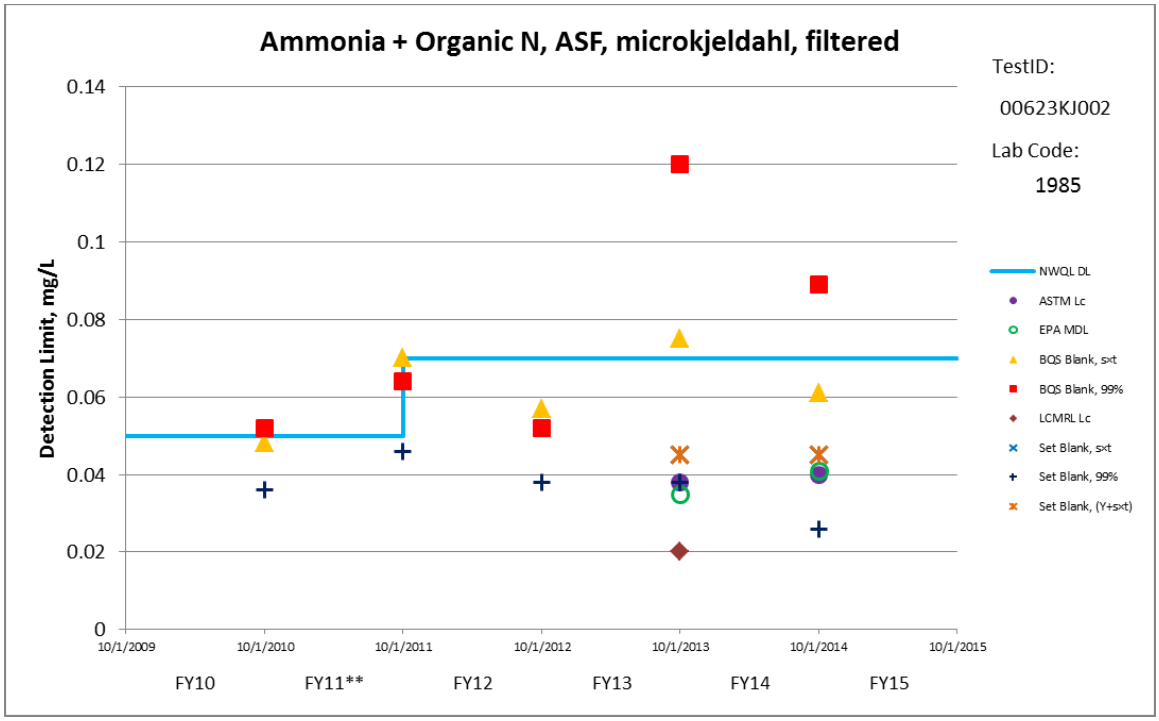

Figure 5. Plot of the detection limits (DLs) calculated by the various DL procedures for ammonia + organic N, ASF, microkjeldahl, filtered.

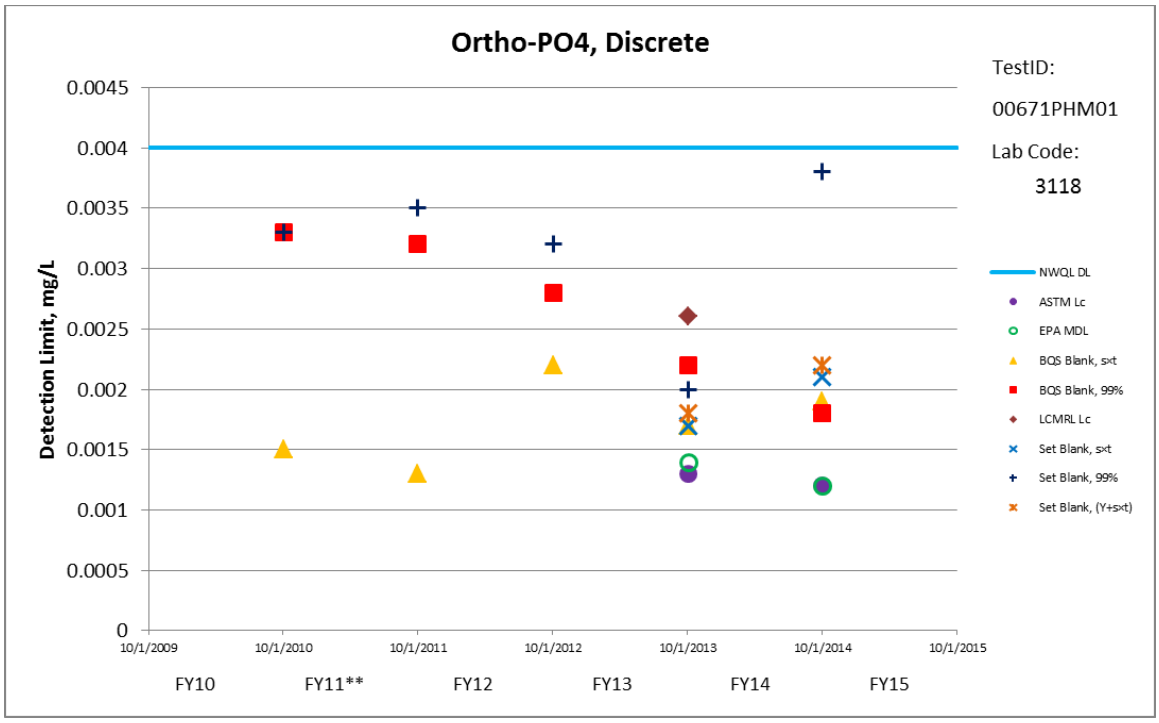

Figure 6. Plot of the detection limits (DLs) calculated by the various DL procedures for ortho-PO4, discrete.

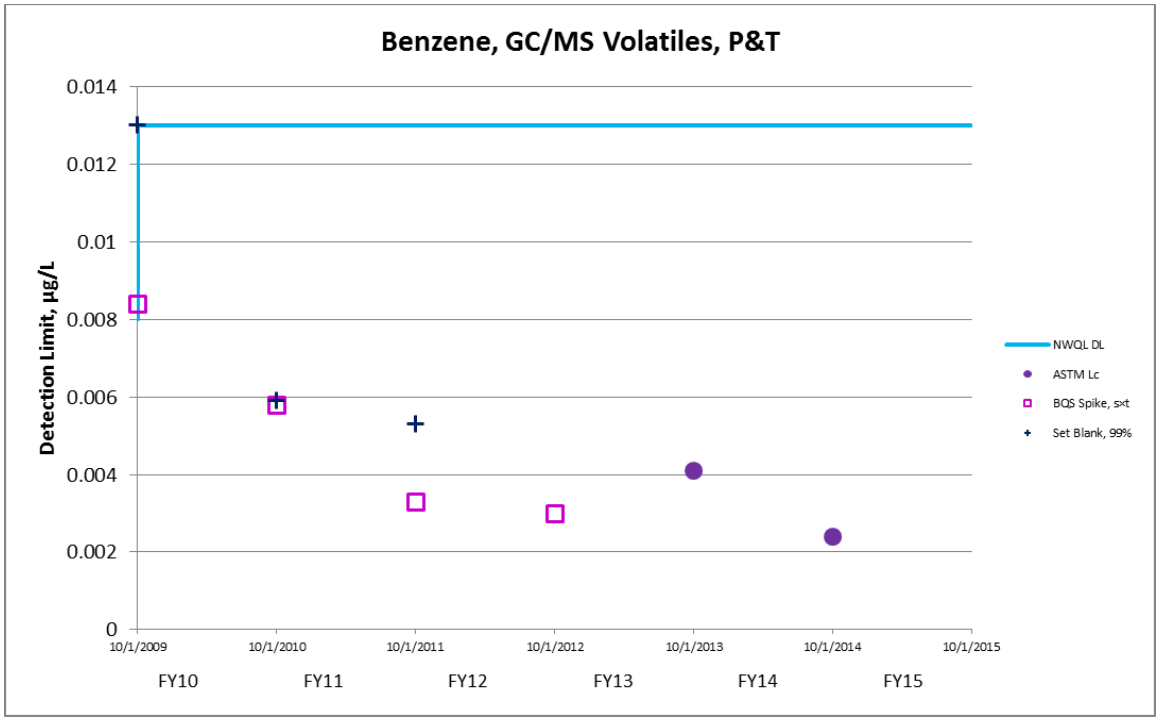

Figure 7. Plot of the detection limits (DLs) calculated by the various DL procedures for benzene, GC/MS volatiles, P&T.

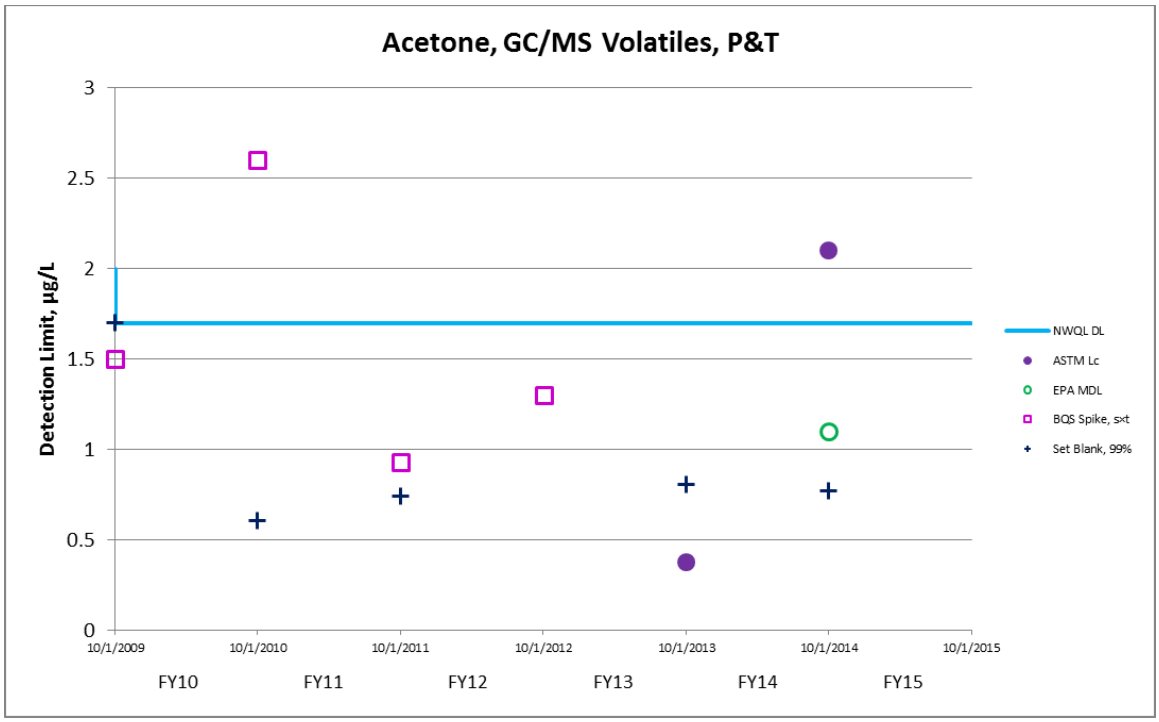

Figure 8. Plot of the detection limits (DLs) calculated by the various DL procedures for acetone, GC/MS volatiles, P&T.

12 SUMMARY

Even though the methodology/calculators used to determine and verify detection limits (DLs) at the NWQL are evolving, there are basic principles that remain the same. Determination of the DL concentration for any analyte is dependent on the capabilities of the instrument, the potential background/blank detections, the sample preparation steps involved, and the reproducibility of results. Applied DLs that are set too low based on actual DLs result in increased false positive risk, whereas applied DLs set too high result in unnecessary data censoring.

Complications also arise simply due to changes in DLs and reporting limits (RLs) in either direction as Water Science Centers track historical trends for their sites. Balancing these considerations is part of the assessment performed by the NWQL. Understanding and interpreting sample results relative to DLs and RLs and associated quality-control and method performance information by the data user are critical components in the assessment of the usability of data reported by the NWQL.

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/signed/
Dave Reppert, Assistant Chief
National Water Quality Laboratory
Branch of Analytical Services

Supersedes: N/A

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