

March 29, 2004

Dr. Alan Newman
Managing Editor
Environmental Science and Technology
1155 16th St. N.W.
Washington, DC 20036

Dear Dr. Newman:

We were disappointed to hear that ES&T has rejected Richard Burrows' paper on Detection Limits in Environmental Analysis, apparently on the basis of negative comments from one reviewer. ACIL and its numerous ACS ES&T subscribers who represent the vast majority of the commercial testing industry support the discussion of detection limits presented in Dr. Burrows' manuscript.

This issue is of great importance to the laboratory and environmental measurement community as well as the regulated community. The current EPA MDL procedure is widely used, but there is broad scientific consensus that the procedure is seriously flawed. In this paper we have pointed out that the proposed procedure, implemented according to EPA instructions, will in some cases produce MDL values that are far below the instrument background, resulting in positive results for all measurements regardless of whether the analyte is present. In other cases the procedure results in MDL values where the qualitative identification criteria for the compounds cannot be met. The regulated community is routinely being required to report all measurements down to the MDL and as a result we are seeing (1) false positive results that produce apparent but spurious violations, and (2) presumed false negative results in cases where analytes can not be qualitatively identified at the MDL. This issue affects the reliability of environmental measurements nationwide as well as decisions being made to protect human health and the environment.

EPA is also in the process of deciding what to promulgate for a new MDL procedure and their draft proposal, in reality, has few changes from the existing procedure. This paper is timely and important. The time for a serious scientific discussion on detection levels is now, and this paper exposes the serious weaknesses in the proposed EPA approach. Whether this is published as a research paper, a topic review, or a feature article, the topic should be addressed in ES&T. We feel ES&T as a preeminent journal for the environmental industry, has a responsibility to ensure that this discussion is presented.

We are proposing that the following persons be added as authors, and have attached a detailed response to the reviewer comments.

Author list:

Dr. Richard Burrows (Primary author)
Gary Ward, Columbia Analytical Services
Ross Ostenberg, Continental Analytical Services, ACIL Environmental Sciences Section Vice Chair
Dr. Charles Carter, Severn Trent Laboratories
Robert Wyeth, Severn Trent Laboratories, ACIL Environmental Sciences Section Chair
Dr. Doug Later, Dionex Corporation
Robert DiRienzo, Data Chem Laboratories
Jerry Parr, Catalyst Information Resources

Sincerely,



Joan Walsh Cassedy, CAE
Executive Director
Attachment

Response to Comments.

1. The reviewer suggests that the title should be changed to “Regulatory Aspects of Analyte Detection”

We would not object to this change, although better would be “Regulatory Aspects of Analyte Detection in Environmental Analysis” The main reason for a detailed analysis of the performance of the current MDL procedure is that in most cases environmental testing laboratories are required to use it (by regulation or statute).

2. The reviewer states that “First you must establish the detection limit as a performance criterion of an analytical method and then take issue with the regulatory uses of the concept”.

We agree with this statement. Since the MDL is widely required by regulation, it is appropriate (indeed vital) that the reliability of detection limits determined using the MDL procedure be examined. This examination comprises the first part of the paper.

3. The reviewer states that “The argument concerning “positive bias” of the MDL as portrayed in Table 1 and accompanying text is without merit”.

This section is included to illustrate the fact that if the analytical method has a positive bias, then the detection limit that is calculated through application of the MDL procedure is likely to be unreasonably low, i.e., below the level at which there is 99% confidence in distinguishing a true detection from a blank. We agree with the reviewer that the bias can be laid upon the analytical methodology itself. The point that we are trying to make is that the MDL procedure does not consider the possibility of this bias, and will subsequently result in an incorrect estimate of the detection limit anytime there is a bias in the method.

4. The reviewer comments that “there are no control experiments that establish critical mean and recovery data.”

The data that we quote and appropriately cite is drawn from work performed for the EPA by a contractor, and which forms the primary support for the EPA’s discussion of the MDL in their Technical Support Document. We assume that EPA ensured that the work was performed within the control requirements of the EPA methods that are quoted. The experimental design used by EPA in this study required replicate analysis of samples spiked at ranges from 0.10 to 100 times the initial detection limit estimate.

5. The reviewer states that the manuscript is “not ... an objective scientific review”
While we believe that we have been objective, we also recognize that this is a controversial topic and would have no objection to the journal inviting manuscripts from authors with other views. In fact, we would be happy to propose some other authors.

6. The reviewer states that “Regulatory decisions are based on assessments of adverse health or ecological effects (risk), and not on analytical detection limits.”

We agree with the reviewer’s statement. However, in many cases the risk levels are close to or below the detection limits of the methods in use. In these cases it is vital that the detection limit estimate generated by the laboratory is good, otherwise false positives or false negatives will occur, resulting in incorrect assessments of the risk level. The USEPA in several guidance documents for their permit writers have indicated that detection levels are sometimes used to establish compliance limits when risk levels are not achievable by analytical methods.

7. The reviewer discusses our use of the terms false positive and false negative and states that our use of the terms is incorrect or misleading.

We agree with the reviewer’s statements that a false positive is an incorrectly identified analyte and a false negative is a missed analyte due to a method failure. There are a number of method failures that can result in false negatives or false positives, but one of the most common is a claimed detection limit that is lower than can actually be achieved. For example, considering a method with considerably qualitative identification criteria, if the lowest level that an analyte can be definitively identified is a true concentration of

5ppb, but a detection limit of 1ppb is claimed then a sample with a true concentration of 2ppb would result in what we are calling a false negative. Good examples of this type of failure are found in the EPA Episode 6000 data set for method 524.2. Most of the analytes in this data set exhibit consistent non-detections for spike levels that are above the detection limits calculated using the MDL procedure.

For other methods the true detection limit is controlled by noise, method bias or contamination. In these cases if the calculated detection limit is too low, then positive detections will be obtained even if the true concentration in the sample is zero. These are what we refer to as false positives. Good examples can be found in the EPA data set for ICP/MS analysis. We believe that this usage is commonly understood in the industry.

8. The reviewer states that the last sentence of the first paragraph is and should be stated as an opinion.

While we believe that the data presented in our paper goes a long way towards proving the assertion, we agree with the reviewer that the statement should be presented as an opinion.

9. The reviewer states that the critical level as defined by Currie and determined from the standard deviation of blank results is no longer viable, because the variability of a signal from a blank is essentially non-existent.

We disagree with the reviewer on this issue. As illustration we would point to the detection limits calculated from long term blank results for ICP-OES analysis (discussed in the paper) which in almost all cases were greater than the detection limits calculated following the EPA MDL procedure. We also note that many EPA methods (for example, 200.7) call for determination of instrument detection limits by means of measuring the standard deviation of replicate blank results.

10. The reviewer states that our statement that the MDL just determines the critical level is simply untrue.

We referred here to statements in the EPA's technical support document on the MDL, section 2.2:

"The MDL functions as a practical, general purpose version of Currie's Critical value"

And also to the Federal Register notice proposing EPA's modifications to the MDL procedure, section 1.0 of the MDL procedure defining the MDL:

The MDL is calculated from replicate analyses of a matrix containing the analyte and is functionally analogous to the "critical value" described by Currie...

11. The reviewer points out that a number of issues can impact the determination of chromium by ICP/MS, including interference from ArO and ArC.

We completely agree with the reviewer on this point. Since this work was performed for EPA under contract we cannot determine what caused the positive bias in this method – it could be the interferences that the reviewer mentions or even something as simple as a calibration curve with a significant deviation from the 0,0 intercept. Our point is that the EPA used these results to calculate a detection limit that is unsupportable, illustrating that the MDL is not rugged enough with relation to calibration bias, blank contamination, interferences and other issues that adversely impact the true detection limit of the method.

12. The reviewer mentions that the results cited in table 5 may represent a small fraction of the total data available.

The data in table 5 are indeed a small fraction of the data available. (The full data set is available from EPA). However there are problems throughout the data. For example, as noted in our paper, 72 of 81 analytes determined by method 524.2 have every replicate at the lowest spike level above the MDL returning results of not detected.

13. The reviewer states that the first statement in the first paragraph on page 5 is not true.

The statement referred to is: "The MDL procedure also makes the assumption that there will be no threshold at which ability to detect and identify an analyte is lost."

We agree that this could be better stated as: "The MDL procedure includes no process to demonstrate the ability to qualitatively identify the analyte when present at the calculated detection limit."

This is well illustrated by the 524.2 data in EPA's episode 6000 data set – the ability to qualitatively identify the analyte at the calculated detection limit was indeed lost for most analytes.

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