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Establishing Effective Limits of Detection for Metals in Surface Water

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Abstract

Purpose and Objectives of the investigation: For analysis of metals in environmental samples, the variability of instrument sensitivity over time, coupled with the limitations of the most common approach to determining Method Detection Limits based on the procedures outlined in 40 CFR Part 136 (40 CFR MDL), may lead to data that is qualitatively unreliable, i.e., false positives and false negatives are possible. One means of improving reliability for results near the MDL is to first establish an improved determination for MDL that can be verified over time through the use of results for method blank analysis.

Approach or Experimental Design: This study investigates the use of historical data for laboratory-prepared method blanks to establish detection limits (FAC MDL) that are subsequently verified daily for precision through the analysis of MDL level verification standards.

Results or Findings to Date: False positive results, as determined through the ongoing evaluation of method blanks, were significantly reduced when the Detection Limit was established by the alternate procedure. A false positive result was reported in more than 90 % of the method blanks evaluated for 4 of the analytes of concern when compared to the 40 CFR MDL. When reported using the FAC MDL, less than 10 % of the method blank analyses performed had a reported value above the detection limit. Default precision limits of 70-130 % recovery were met on average for most analytes spiked at the FAC MDL, providing verification for values reported at or near the detection limit in environmental samples. Average recoveries for verification standards spiked at the 40 CFR MDL were outside these acceptance limits for all analytes measured.

Significance and Benefit of Results to Kingston Ash Recovery Program: This approach provides a continuing verification of the precision of data at a minimum detection limit, and provides end users with an increased level of certainty beyond that typically provided by following only the procedures outlined in the 40 CFR MDL requirements. This alternate procedure allows for a more precise evaluation of the risk associated with detection level concentrations of chemicals of concern through the confidence provided by analytically verified data. This alternate procedure also reduces the frequency of positive blank results, providing increased certainty in the results obtained in environmental samples.

Continued or Future Studies: By applying statistically defined acceptance limits for analytical quality control to the recoveries measured in the analyses spiked at the FAC MDL, an established level of certainty can be assigned to results reported at the detection limit. Using this procedure, future studies will measure the effects of changes in instrument and method performance over time to determine how these changes affect the FAC MDL established by this procedure.

Introduction

Method Detection Limits (MDLs) have historically been determined using the procedures outlined in 40 CFR part 136, (40 CFR MDL)(1). As defined by this procedure, the 40 CFR MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. This procedure, however, does not account for bias that may be introduced in the measurement from the blank water used in spiking to calculate the 40 CFR MDL.

An MDL procedure that does not adjust for bias in the blank will underestimate the minimum concentration at which there is 99% confidence that a result from the analysis of a sample can be distinguished from that of a blank. The procedure also assumes that the standard deviation does not change between the calculated 40 CFR MDL and the spike concentration used for determination. Because the standard deviation can not be assumed to be constant over varying concentrations, the calculated 40 CFR MDL may vary based only on the concentration used in spiking the replicates for the determination.

The procedure outlined in 40 CFR part 136 also provides no ongoing measure of the precision associated with the reporting of results at the calculated 40 CFR MDL, and does not account for normal instrument and method variability over time. 40 CFR MDL studies are usually performed once at the initial set up of a new instrument, and then yearly as required by many regulatory agencies. These studies are typically performed on a single day on a freshly cleaned and calibrated instrument, and the values obtained represent an ideal situation not reflective of normal operating conditions.

This study examines an alternate procedure for determining the MDL (FAC MDL) using a statistical evaluation of historical blank data. Through this process, the positive bias associated with methods expected to return non-zero results in blank analyses is accounted for by the inclusion of the average historical blank result in determining the FAC MDL. This evaluation accounts for normal variation over time in both the instrument response and method performance, and is independent of spike level. Once the FAC MDL is calculated using this procedure, ongoing precision can be measured through the analysis of verification standards spiked at a level at or near the calculated FAC MDL and evaluating the recoveries against standard method acceptance criteria. This continuing evaluation of precision allows for greater confidence in the results reported when evaluating against human or environmental risk assessment standards.

Table 1 Comparison of Calculated MDL values using 40 CFR Procedures with Average Method Blank Results

Analyte	40 CFR MDL (ug/L)	Average Blank Concentration (ug/L)	Standard Deviation of Blank Concentration	FAC MDL (ug/L)
Aluminum	10.2	4.7	5.2	20.4
Antimony	0.02	0.11	0.09	0.37
Arsenic	0.02	0.03	0.10	0.32
Beryllium	0.06	0.01	0.03	0.11
Cadmium	0.02	0.01	0.02	0.07
Chromium	0.25	0.14	0.28	0.97
Cobalt	0.11	0.01	0.03	0.08
Copper	0.25	0.10	0.20	0.69
Lead	0.08	0.01	0.02	0.09
Manganese	0.11	0.19	0.44	1.51
Molybdenum	0.05	0.37	0.51	1.91
Nickel	0.08	0.02	0.03	0.12
Selenium	0.04	0.005	0.03	0.09
Silver	0.10	0.01	0.03	0.11
Thallium	0.02	0.01	0.03	0.10
Vanadium	0.13	0.31	0.19	0.89
Zinc	0.61	1.3	2.0	7.3

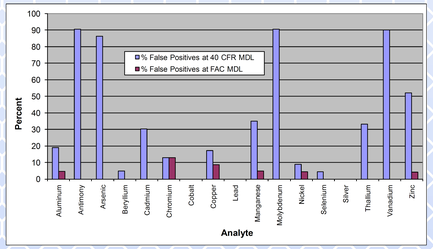
Research Design

Analysis of surface waters from the Kingston Fly Ash Recovery Project for metals requires the lowest limits of detection that can be analytically verified for evaluation against established risk assessment criteria. Data used for risk evaluation should provide a level of certainty that the values obtained are distinguishable from method blank results, and the precision associated with the values should be analytically determined through the use of Detection Level verification standards. 40 CFR MDL values do not account for variations in instrument and method performance over time, and method blank analyses for metals are often positive for the target analytes at levels greater than the 40 CFR MDL, making it difficult to ascertain whether the results obtained on surface water samples can be distinguished from Laboratory blank levels.

This study evaluated the use of an MDL procedure outlined by the EPA Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Programs (2). This procedure uses historical method blank data generated over time to estimate the limit at which there is a 99 % certainty that the result is distinguishable from normal blank levels. Analyses were conducted using the procedures defined by EPA Method 200.8, and were performed on a single Agilent 7500ce ICP-MS instrument. In the alternate MDL procedure, a minimum of 7 blank analyses, prepared and analyzed on different days, are required to determine an average blank level inherent in the procedure. The FAC MDL is defined as the mean of the measured blank concentrations + 3 SD, providing the desired 99% confidence level that the result obtained is distinguishable from blank levels. This process accounts for the normal variations that occur in laboratory instrumentation over time, and larger populations of blanks should be used when available.

In this study, 21 method blanks analyzed on different days were used to calculate the FAC MDL. A comparison of the average blank levels present in this population against both the 40 CFR MDL and FAC MDL values is presented in Table 1. To provide an estimate of the level of precision associated with FAC MDL-level positive results, verification standards were analyzed on a daily basis, with general method acceptance criteria applied to increase the level of certainty in the results obtained for surface water samples. When attempting to analyze verification standards spiked at the 40 CFR MDL level, the normal distribution of expected results around that detection limit would yield wide recovery ranges that are outside the acceptance criteria necessary to provide an acceptable level of precision, with a 50 % probability that the result obtained would be less than the 40 CFR MDL. This study also evaluated the variance in 40 CFR MDL values based only on the concentration used for spiking the replicate measurements. 40 CFR MDL studies were performed at 5 spike concentrations to compare the differences in detection limits obtained at each spiking level.

Figure 1 Percent of False Positive Results for Method Blank Analyses



Results and Findings

The results of method blanks analyzed for Metals were evaluated over time and compared to the 40 CFR MDL. As shown in Figure 1, several elements analyzed in the study routinely returned positive results in method blanks at levels greater than the 40 CFR MDL, and five elements of concern for the Kingston Fly Ash Recovery Project had a false positive result (blank value greater than the MDL used for reporting) using the 40 CFR MDL in more than 50 % of the total method blank analyses evaluated (n=21). Defined as the detection of an analyte at a level above the MDL value used for reporting, false positive results for Antimony, Arsenic, Molybdenum, and Vanadium were reported in 90% or more of the method blanks analyzed. When the method blank results are compared to the FAC MDL, the incidence of false positive results was less that 10 % for all but one of the metals evaluated in the study (chromium). The frequency of positive blank results compared to the 40 CFR MDL make it improbable to state with analytical certainty that similar results obtained in the surface water samples analyzed are actual detections suitable for risk evaluation. To determine if the concentrations detected in the digested method blank samples were due only to contamination in the digestion process or were consistent with variations in instrument performance, the results of the digested method blanks were compared to non-digested instrument blanks analyzed during the same time period (Figure 2). The data suggest that there are isolated cases of contamination from the procedure in digested method blanks, the concentrations measured in both the digested method blanks and the instrument blanks show a similar trend.

In order to provide a level of precision around the results measured at or near the MDL value used for comparison, MDL level verification standards were also analyzed with each analytical batch over the same time period used for the method blank population. The laboratory chose general acceptance limits of 70 - 130% recovery for use in evaluating the precision of these measurements. When verification standards were analyzed at the 40 CFR MDL, the positive bias expected from the method blank evaluation was noted, with average recoveries for all analytes of interest greater than the 130% upper acceptance limit, and five of the nine analytes measured had average verification standard recoveries > 150% (Figure 3). The results for verification standards analyzed at the FAC MDL determined from the method blank population show an average recovery for all but two analytes of interest within the 70 - 130% acceptance criteria. Average recoveries for Nickel and Vanadium exceeded the acceptance criteria for the population evaluated, but recoveries for these two analytes were less than 150%.

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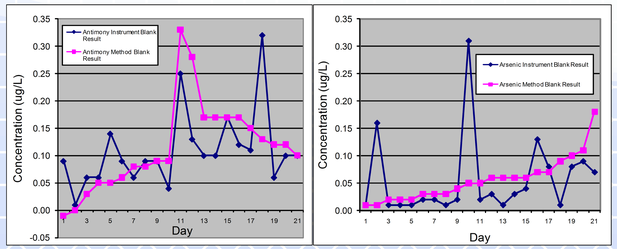
Figure 2 Comparison of Method Blank Results to Instrument Blank Results



Results and Findings (continued)

In generating 40 CFR MDL values for this study, the differences in acceptable results obtained at varying spiking levels were also evaluated. In order to be considered an acceptable result, the 40 CFR MDL obtained statistically through this procedure was required to meet general laboratory evaluation criteria required for acceptance. 40 CFR MDL studies were conducted at five different spiking levels, all less than or equal to the standard reporting limit used in the analysis. Four analytes included in this study met the laboratory general acceptance criteria at all 5 levels analyzed (Figure 4). As the spiking concentration increased, the calculated 40 CFR MDL also increased, with a 2.5 to 10 fold increase in the calculated value obtained at the highest spiking level evaluated (2.0 ug/L). The assumption of the 40 CFR procedure that the standard deviation of a measurement for an analyte does not change between the 40 CFR MDL and the spike level of the samples used to determine that limit is not supported by this data. This means that because the standard deviation of analytical measurements may vary with concentration, the 40 CFR MDL may also vary depending only on the initial spike level chosen for the measurements.

Figure 4 Variance in Calculated MDL using the 40 CFR Procedure at Increasing Spike Levels

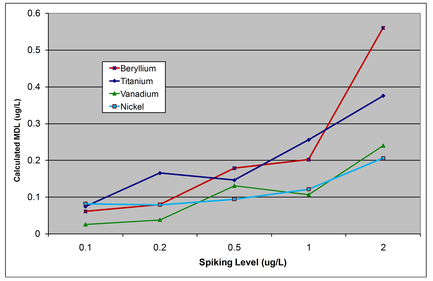
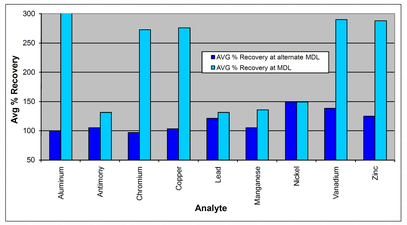


Figure 3 Average Percent Recovery of MDL Level Verification Standards



Conclusion

Traditional procedures used in determining the 40 CFR MDL for reporting of metals fail to account for potential bias associated with positive blank sample results or instrument performance variation over time. Recoveries for verification standards analyzed at the 40 CFR MDL level generally fall outside standard acceptance criteria, resulting in a significant level of uncertainty for similar results obtained for environmental samples. Using the alternate procedure proposed by the EPA Federal Advisory Committee for determining an FAC MDL based on historical blank data, provides a limit of detection with reduced blank interference and verifiable precision for comparison to established risk assessment criteria, increasing the level of confidence in the results for the end data user.

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