



Introduction and Definitions

What is the Minimum Reporting Level (MRL)?

Minimum Reporting Level (MRL) defines the smallest measured concentration of a particular compound that can be reliably reported using a given analytical method.¹ MRLs are determined from statistical data gathered from analyses over time. The MRL is derived from Method Detection Limit data, as discussed in 4.

What is the Method Detection Limit (MDL)?

Method Detection Limit (MDL) is the minimum concentration of a particular compound that can be measured at a 99% statistical confidence that the concentration is greater than zero.⁷ The U.S. EPA defines the MDL by measurement of at least seven aliquots of a prepared solution with a concentration of 1 to 5 times the expected concentration.^{1,2,3} Low concentration measurements are indicative of variability due to instrument noise, analytical technique, etc. The MDL is calculated from Equation 1, where s is the standard deviation of n sample measurements, and $t_{n-1, \alpha=0.01}$ is the Student's t value at the 99% confidence level.

$$MDL = s \times t_{n-1, \alpha=0.01} \quad (\text{Equation 1})$$

What is the Long-Term Method Detection Limit (LT-MDL)?

Long-Term Method Detection Limit (LT-MDL) assesses the variability of data over time. LT-MDLs are calculated from Equation 2, where s_{LT} is the standard deviation of n low-concentration samples measured over a 1 year period of time.

$$LT-MDL = s_{LT} \times t_{n-1, \alpha=0.01} \quad (\text{Equation 2})$$

How can the MRL be calculated?

It is proposed to set the MRL at twice the LT-MDL, which statistically balances the chances of false positives and negatives at 1%.

Data Analysis Methodology at the Central Analytical Laboratory (CAL)

FR10 Concentrations 2000 - 2001 (mg/L)

Ion	2000	2001
Cl ⁻	0.052	0.053
NO ₃ ⁻	0.190	0.193
SO ₄ ²⁻	0.250	0.260
NH ₄ ⁺	0.032	0.025
Ca ²⁺	0.031	0.031
Mg ²⁺	0.007	0.007
Na ⁺	0.020	0.020
K ⁺	0.005	0.005

Determination of MDL

Since 2000, the MDL has been determined from a sample matrix approximating the 10th percentile of historical wet deposition measurements (FR10). FR10 concentrations are shown in the table. MDLs are determined from unfiltered solutions. FR10 data is not available before 2000.

Proposed Changes to Data Reporting Limits for the NTN & AIRMoN

Determination of MRL

The NADP has traditionally set MRLs at approximately the MDL values. If MDL values did not vary significantly from year-to-year, MRLs were not changed, maintaining data uniformity. It is proposed to set the MRL at twice the LT-MDL.

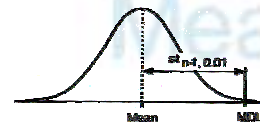
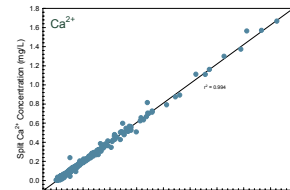
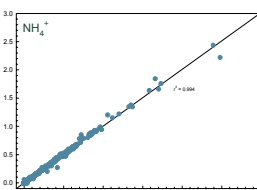
Determination of LT-MDL

It is proposed to calculate LT-MDL values from filtered blind FR10 sample data over a period of one to two years.

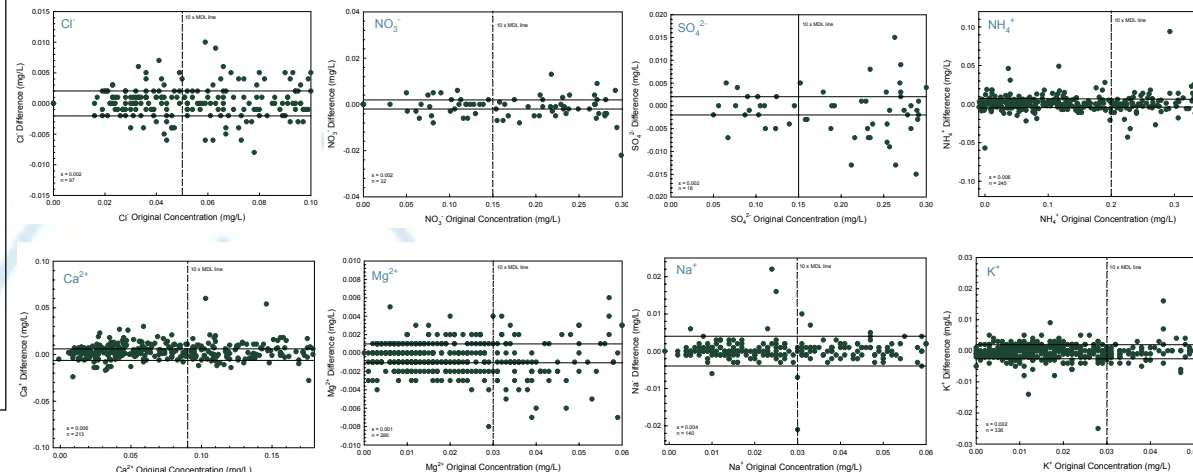
Determination of LT-MDL for Data Before 2000

Sample "split" data is available since 1978. Low-level sample split data may provide a surrogate means of determining the LT-MDL to determine MRLs before 2000.

NTN Split Data, 2000 - 2001



NTN Split Data Difference, 2000 - 2001



F - Test (F99%) Results Comparing Split, FR10 Unfiltered, and FR10 Filtered Samples 2000 - 2001

Ion	FR10 Filtered vs. FR10 Unfiltered	Split vs. FR10 Unfiltered	Split vs. FR10 Filtered
	Cl ⁻	different	same
NO ₃ ⁻	same	different	different
SO ₄ ²⁻	same	different	different
NH ₄ ⁺	same	same	same
Ca ²⁺	same	same	same
Mg ²⁺	same	same	same
Na ⁺	same	different	different
K ⁺	same	same	same

MDLs & MRLs for 2000 - 2001

Ion	EPA-Method MDLs [mg/L]		LT-MDL [mg/L] 2000-2001	Proposed MRL [mg/L]	Current CAL MRL [mg/L]
	2000	2001			
Cl ⁻	0.0052	0.0050	0.009	0.019	0.005
NO ₃ ⁻	0.0066	0.0079	0.009	0.018	0.015
SO ₄ ²⁻	0.0127	0.0147	0.012	0.024	0.015
NH ₄ ⁺	0.0138	0.0099	0.01	0.03	0.02
Ca ²⁺	0.0082	0.0142	0.014	0.028	0.009
Mg ²⁺	0.0014	0.0024	0.003	0.006	0.003
Na ⁺	0.0031	0.0038	0.005	0.010	0.003
K ⁺	0.0031	0.0021	0.005	0.009	0.003

Conclusions

- Proposed MRLs would be between 1.2 and 3.7 times current MRLs
- LT-MDLs for 2000 - 2001 are between 0.8 and 2.4 times the 2001 EPA-method MDL
- FR10 filtered and unfiltered data have the same variability, except for Cl⁻
- Split and FR10 data have the same variability for NH₄⁺, Ca²⁺, Mg²⁺, and K⁺; others are statistically different.
- It is inconclusive whether split data can be used to calculate MRLs for data before 2000.

References

- Childress, C.J.O., et al., "New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory," U.S. Geological Survey, 1999.
- 40 Code of Federal Regulations Part 136, Vol. 49, No. 209, *Federal Register*, Rules and Regulations, Appendix B, pp. 198-199. Oct 1984.
- Berthouex, P.M., and Linfield, C.B., *Statistics for Environmental Engineers*, Second Edition, Boca Raton: Lewis, 2002.

Acknowledgements

The authors gratefully acknowledge the graphics support of Pam Biedent in preparing this poster. The background graphic is adapted from