Massachusetts Department of Environmental Protection
Division of Environmental Analysis
Senator William X. Wall Experiment Station
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Summary Report of the First Low-Level Perchlorate Proficiency Test Study Conducted by the Massachusetts Department of Environmental Protection

August 10, 2004

1.0 EXECUTIVE SUMMARY

This report summarizes the results of the first single-blind low-level perchlorate proficiency test (PT) study conducted by the Senator William X. Wall Experiment Station (WES) – Massachusetts Department of Environmental Protection (MA DEP) – to assess the analytical performance of the 7 MA DEP-approved laboratories and 10 additional laboratories that are seeking or are interested in seeking MA DEP approval for the analysis of perchlorate in Massachusetts water supplies. An accredited PT provider [under the National Voluntary Laboratory Accreditation Program (NVLAP), National Institute of Standards & Technology (NIST)] was selected by MA DEP to prepare the PT samples, deliver the samples to the participating laboratories, establish study acceptance limits using the bi-weighted statistical procedure specified by the U.S. EPA, and evaluate the resulting analytical data from the participating laboratories. Each laboratory received two whole volume PT samples prepared in a mixed common anion solution at a conductivity typical of, if not higher than, most MA public water supplies (500 μS/cm at 25°C) – one sample was a blank without added perchlorate and the other was spiked with perchlorate at 1.04 μg/L (assigned value). See Appendix A below for additional information provided to participating laboratories regarding this first low-level perchlorate PT study.

All laboratories, except for two that are not MA DEP-approved, successfully analyzed the spiked sample, reporting a perchlorate concentration within ± 2 standard deviations of the study mean (i.e., acceptable perchlorate concentration limits of 0.548 to 1.18 μg/L based on the approved laboratory statistics). The mean perchlorate concentration reported by the approved laboratories for the spiked sample was 0.865 μg/L or 83.2% recovery of the assigned 1.04-μg/L spike (standard deviation of 0.158 μg/L perchlorate or 15.2% recovery of the assigned spike). These results appear to indicate a mean low bias in the analysis of perchlorate at the 1.0-μg/L level for the approved laboratories. All laboratories, except for one MA DEP-approved laboratory, reported no detectable perchlorate in the blank sample down to its method detection limit (i.e., < MDL). One MA DEP-approved laboratory reported 0.417 μg/L perchlorate in the blank or just above its MDL; although a false positive and not acceptable, it was substantially below the MA DEP critical minimum reporting level of 1.0 μg/L (note: this laboratory must now pass two follow-up low-level perchlorate PT studies in a row in order to remain MA DEP-approved for the analysis of perchlorate in Massachusetts water supplies – see below). **These results clearly demonstrate that, in a water matrix with a conductivity typical of most MA drinking water supplies, 15 of the 17 participating laboratories (including all MA DEP-approved laboratories) reliably detected and**

quantitated perchlorate at a concentration of 1 μg/L without incurring false positives at 0.5 μg/L or higher.

Based on this demonstration of proficiency by both Unregulated Contaminant Monitoring Rule (UCMR) and non-UCMR listed laboratories, MA DEP is now extending eligibility for consideration for approval to perform low-level perchlorate analysis in public water supplies to all laboratories that have already expressed interest in being considered for such approval. Laboratories certified by Massachusetts or their resident state for drinking water analysis using an ion chromatography method and that could meet the stringent performance criteria of this program were required to notify the Laboratory Certification Office by February 25, 2004 of their interest in approval as specified in the Department's letter of February 18, 2004 sent to all laboratories certified by the Massachusetts DEP - Wall Experiment Station (http://www.mass.gov/dep/brp/dws/files/perchlor.pdf.) Four of the eligible laboratories have already applied for approval and their applications are currently undergoing review by MA DEP/WES. Four other laboratories that successfully analyzed both samples in this first PT study are now eligible to apply.

MA DEP/WES is planning a new low-level perchlorate laboratory approval round in September 2004 open to all laboratories that can meet the stringent performance criteria of this program. All laboratories that are interested in seeking approval must indicate their intention by FAX (978-688-0352) or by e-mail to John Bardzik at *john.bardzik@state.ma.us* by September 10, 2004. Please include the name and address of your laboratory, the name and telephone number of the contact person, and the target date for your submission of the required documentation to the MA DEP/WES Laboratory Certification Office (LCO). The LCO will acknowledge receipt of all submissions.

The second low-level perchlorate PT study was just completed; the PT provider sent the final study results to the participating laboratories and to MA DEP on August 6, 2004 (see Appendix B below for additional information about the second PT study). The LCO is currently reviewing the results of this second perchlorate PT study, including all raw perchlorate analytical data from the participating laboratories, and plans to publish a summary report of this study on the DEP web site in the very near future.

2.0 STUDY DESIGN AND RESULTS

A laboratory seeking approval to test drinking water for low-level perchlorate in support of the MA DEP Drinking Water Program's emergency perchlorate regulations must demonstrate to the Department that it can achieve the stringent performance requirements of 310 CMR 22.06D(4). This demonstration includes successful performance in two out of a total of three proficiency test (PT) studies.

The principal objective of the MA DEP low-level perchlorate PT study was to evaluate the ability of laboratories to reliably detect and quantitate perchlorate at or above a concentration of 1.0 ug/L in a typical MA drinking water matrix without incurring false positives at or above this concentration. The MA DEP emergency perchlorate monitoring program is intended to identify and provide public notification for public water supplies that have perchlorate concentrations at or above 1.0 ug/L.

The first PT study was completed on May 24, 2004. A total of seventeen laboratories participated in the study: seven laboratories previously approved by MA DEP/WES based on their having met other criteria set by the Department; four laboratories that have filed applications for approval; and six laboratories that had expressed interest in seeking approval but that were not eligible for consideration for approval at the time of the study because they were not approved by the U.S. EPA for monitoring perchlorate under the UCMR.

Because of the small number of laboratories eligible to participate in this study, only one PT provider was used. After a review of proposals from several NVLAP-accredited PT providers, the Department selected Wibby Environmental of Golden, Colorado to conduct the study. On May 10, PT study samples were shipped to the laboratories that had until May 18 to report their results to the PT provider. On May 24, reports of the evaluation of each laboratory's performance were sent to the participating laboratories and to MA DEP.

The PT study consisted of two whole volume water samples prepared in a mixed common anion solution containing chloride, sulfate and carbonate, per U.S. EPA Method 314.0 (USEPA, 1999), adjusted to a conductivity of 500 µS/cm at 25°C. Public water supply wells in all 27 Massachusetts water-resources basins have 75th-percentile conductivities ranging from 114 to 350 µS/cm at 25°C and a mean maximum conductivity of 641 (standard deviation = 317) µS/cm at 25°C (Trombley, 1992). Fresh surface waters in MA and most of New England have conductivities under 300 µS/cm at 25°C (Flanagan *et al.*, 1999). Therefore, the matrix conductivity of 500 µS/cm at 25°C selected for the samples in this PT study is typical of, if not higher than, most MA drinking water supplies. The PT study consisted of two samples – one sample was a blank without added perchlorate and the other was spiked with perchlorate at 1.04 µg/L (assigned value).

The PT provider established the acceptance criteria for the study in two ways using the bi-weighted statistical procedure specified by the U.S. EPA: one using the data from only the approved laboratories, the other using the data from all laboratories participating in the study.

All MA DEP-approved perchlorate laboratories and laboratories whose application for approval is undergoing review were required to report to WES all the raw perchlorate analytical data for the two PT samples, including chromatograms and all supporting quality control documentation. Laboratories that, at the time, were ineligible to be considered for approval were not required to submit (but many did submit) data packages to WES for these PT samples but were required to keep the documentation available in the event that eligibility for approval were to be extended to non-UCMR laboratories, as has now occurred.

The study report and supporting raw data of some laboratories required further evaluation by the Department before a determination could be made concerning the acceptability of their performance when analyzing Sample # 1 of the PT study (note: the evaluation of laboratory performance for the analysis of Sample # 2 did not require further review by the Department). When reporting the result of the analysis of Sample # 1, five laboratories did not follow the perchlorate sample reporting protocol that requires the laboratory to report < MDL (method detection limit) when no perchlorate is detected. Four of these laboratories reported the results of Sample # 1 as < MRL (minimum reporting level). The fifth laboratory used a reporting protocol accepted by other agencies. A review of the raw data from these laboratories confirmed that the laboratories had determined that no perchlorate was present in Sample # 1 down to the laboratory's MDL; therefore, the Department evaluated their performance as acceptable.

A sixth laboratory reported a result for perchlorate in Sample # 1 that was above its MDL but well below the MRL of 1.0 µg/L. A review of the laboratory's data indicated that the laboratory was aware of the presence of an interfering peak but failed to evaluate it correctly when reporting data for Sample # 1, therefore the Department evaluated the laboratory's performance as not acceptable for Sample # 1. Even though this laboratory reported a detection of perchlorate in the blank sample, the Department is not removing the laboratory's approval at this time because the amount reported is substantially below the critical minimum reporting level of 1.0 µg/L. This laboratory will be required to take the appropriate corrective action, and participate in and pass two consecutive follow-up low-level perchlorate PT studies.

The results of this first low-level perchlorate PT study clearly demonstrate that, in a water matrix with a conductivity typical of most MA drinking water supplies, 15 of the 17 participating

laboratories (including all MA DEP-approved laboratories) reliably detected and quantitated perchlorate at a concentration of 1 μg/L without incurring false positives at 0.5 μg/L or higher.

Table 1. Summary of First Low-Level Perchlorate PT Study Results

MA DEP Laboratory Approval Status for Low-Level Perchlorate Analysis	Sample 1 Perchlorate Result Reported by the Lab (μg/L)	Sample 1 Evaluation	Sample 2 Perchlorate Result Reported by the Lab (μg/L)	Sample 2 Evaluation (Approved Lab Statistics)	Sample 2 Evaluation (All Lab Statistics)
				Mean ± 2 SD (0.548 – 1.18 μg/L perchlorate)	Mean ± 2 SD (0.463 – 1.22 μg/L perchlorate)
Approved[a]	< 0.20	Acceptable	0.76	Acceptable	Acceptable
Approved[a]	< 0.217[b]	Acceptable[c]	0.9	Acceptable	Acceptable
Non-UCMR listed	< 0.5	Acceptable	0.559	Acceptable	Acceptable
Approved[a]	< 0.300	Acceptable	0.912	Acceptable	Acceptable
Approved[a]	0.417	Not Acceptable[c]	1.04	Acceptable	Acceptable
Non-UCMR listed	< 0.4[b]	Acceptable[c]	< 1.00	Not Acceptable	Not Acceptable
Applied—UCMR listed	< 0.50	Acceptable	0.8	Acceptable	Acceptable
Applied—UCMR listed	< 0.13[b]	Acceptable[c]	0.888	Acceptable	Acceptable
Approved[a]	< 0.17[b]	Acceptable[c]	0.646	Acceptable	Acceptable
Non-UCMR listed	< 0.5	Acceptable	0.76	Acceptable	Acceptable
Non-UCMR listed	< 0.367	Acceptable	0.724	Acceptable	Acceptable
Non-UCMR listed	< 0.31	Acceptable	0.614	Acceptable	Acceptable
Non-UCMR listed	< 0.40	Acceptable	1.28	Not Acceptable	Not Acceptable
Approved[a]	< 0.5	Acceptable	0.99	Acceptable	Acceptable
Applied—UCMR listed	< 0.1[b]	Acceptable[c]	0.965	Acceptable	Acceptable
Approved[a]	< 0.180	Acceptable	0.783	Acceptable	Acceptable
Applied—UCMR listed	< 0.40	Acceptable	0.974	Acceptable	Acceptable

Sample 1 = Blank (assigned value = < MDL perchlorate) prepared in a mixed common anion solution at a conductivity of 500 μS/cm at 25°C

Sample 2 = Perchlorate-spiked sample (assigned value = 1.04 μg/L perchlorate) prepared in a mixed common anion solution at a conductivity of 500 μS/cm at 25°C

Mean (for approved labs) = 0.865 µg/L perchlorate, 83.2% of assigned spike
Standard deviation (SD) (for approved labs) = 0.158 µg/L perchlorate, 15.2%
Mean (for all labs) = 0.840 µg/L perchlorate, 80.2% of assigned spike
SD (for all labs) = 0.189 µg/L perchlorate, 18.2%

[a] Approved laboratories are listed at: http://www.mass.gov/dep/brp/dws/files/perclab.pdf

[b] Result confirmed by MA DEP/WES from review of the raw data for the PT study submitted by the laboratory prior to the release of the study results.

[c] Evaluation decision made by MA DEP/WES following review of the raw data for the PT study submitted by the laboratory prior to the release of the study results.

3.0 REFERENCES

Flanagan, S.M., M.G. Nielsen, K.W. Robinson, and J.F. Coles. 1999. *Water-Quality Assessment of the New England Coastal Basins in Maine, Massachusetts, New Hampshire, and Rhode Island: Environmental Settings and Implications for Water Quality and Aquatic Biota.* Water-Resources Investigations Report 98-4249. National Water-Quality Assessment Program, U.S. Geological Survey, New Hampshire/Vermont District, U.S. Department of the Interior, Pembroke, NH.

Trombley, T.J. 1992. *Quality of Water from Public-Supply Wells in Massachusetts, 1975-86.* Water-Resources Investigations Report 91-4129. Water Resources Division, U.S. Geological Survey, U.S. Department of the Interior, Boston, MA.

U.S. Environmental Protection Agency (USEPA). 1999. Method 314.0 – Determination of Perchlorate in Drinking Water Using Ion Chromatography, Revision 1.0. National Exposure Research Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio.

APPENDIX A – ANNOUNCEMENT OF THE FIRST LOW-LEVEL PERCHLORATE PT STUDY

The following e-mail was sent to the laboratory directors of the participating laboratories prior to the commencement of the first low-level perchlorate PT study.

Dear Laboratory Director:

This e-mail announces a proficiency test study for low-level perchlorate analysis of drinking water.

As stated in our letter of February 18, 2004, passing a proficiency test (PT) for the analysis of low-level perchlorate in potable water is a requirement for approval from the Massachusetts Department of Environmental Protection (MADEP) to analyze drinking water samples in support of emergency regulations at 310 CMR 22.06D.

Because of the small number of laboratories involved in this study, only one PT provider will be used. After a review of proposals from several PT providers, we have selected Wibby Environmental of Golden, Colorado. Samples are scheduled for shipment on May 10, 2004 to all participating laboratories. May

18, 2004 is the study closing date and final reports of study results will be sent out to the laboratories and to MADEP on May 24, 2004.

Laboratories will participate in two PT studies about 30 days apart. A laboratory that fails one of these two studies must participate in a third study and pass in order to demonstrate acceptable performance in two out of three PT studies. A laboratory that fails a study will have its approval suspended until satisfactory performance in the next PT study is achieved.

Each PT study will consist of two whole volume samples containing low levels of perchlorate. Samples from PT studies are to be analyzed in exactly the same manner and using all required quality control procedures (listed in the February 18, 2004 letter from MADEP) as actual drinking water samples:

1) Samples must be analyzed by EPA Method 314.0, Revision 1, November 1999, *Determination of Perchlorate in Drinking Water Using Ion Chromatography* as modified to achieve the performance requirement of a minimum reporting level for perchlorate of 1.0 µg/L.

2) Samples determined to have perchlorate present at concentrations between 0.8 µg/L and 2.0 µg/L must be retested with and without a perchlorate spike approximately equal to the native perchlorate concentration.

3) MADEP-approved perchlorate laboratories and laboratories whose application for approval is currently under review must report the conductivity and perchlorate concentration of samples, duplicates, and spiked samples to MADEP. Submittals must include chromatograms and all supporting quality control documentation. Send the information via e-mail to John Bardzik at john.bardzik@state.ma.us. (Laboratories that are currently ineligible to be considered for approval are not required to submit data packages to MADEP but must keep the documentation available in the event that eligibility for approval is extended to non-UCMR laboratories).

4) Only the perchlorate concentration of the PT samples must be reported to the PT provider on forms provided by the PT provider.

This PT study is required of all laboratories currently approved by MADEP and those laboratories whose application for approval is currently under review. The PT study is voluntary for those laboratories interested in MADEP approval but that are not UCMR laboratories and therefore not eligible at this time for approval. The performance of approved laboratories will be evaluated separately from that of laboratories not having Massachusetts approval and then the performance of all laboratories will be evaluated.

Laboratories are responsible for contacting the PT provider themselves to arrange their participation in the study. As with other PT studies, the cost of the study must be borne by the laboratory. Wibby Environmental stated to us that the cost to each participating laboratory per study including shipping and the final report is $95.00.

To participate in the PT study, contact Chuck Wibby of Wibby Environmental at cwibby@wibby.com.

If you have any questions regarding the Massachusetts low-level perchlorate laboratory approval program, please contact John Bardzik.

Ann Marie Allen
Director, Laboratory Certification Office
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APPENDIX B – ANNOUNCEMENT OF THE 2nd LOW-LEVEL PERCHLORATE PT STUDY

The following e-mail was sent to the laboratory directors of the participating laboratories prior to the commencement of the second low-level perchlorate PT study.

Dear Laboratory Director:

This e-mail announces the second proficiency test study for low-level perchlorate analysis of drinking water.

As stated in our letter of February 18, 2004, passing a proficiency test (PT) for the analysis of low-level perchlorate in potable water is a requirement for approval from the Massachusetts Department of Environmental Protection (MADEP) to analyze drinking water samples in support of emergency regulations at 310 CMR 22.06D.

Wibby Environmental of Golden, Colorado is scheduled to ship the samples on **July 12, 2004** to all participating laboratories. July 23, 2004 is the study closing date and final reports of study results will be sent out to the laboratories and to MADEP by August 6, 2004.

The PT study will consist of two whole volume samples containing low levels of perchlorate. Samples from PT studies are to be analyzed in exactly the same manner and using all required quality control procedures (listed in the February 18, 2004 letter from MADEP) as actual drinking water samples:

1) Samples must be analyzed by EPA Method 314.0, Revision 1, November 1999, *Determination of Perchlorate in Drinking Water Using Ion Chromatography* as modified to achieve the performance requirement of a minimum reporting level for perchlorate of 1.0 μg/L.

2) Samples determined to have perchlorate present at concentrations between 0.8 μg/L and 2.0 μg/L must be retested with and without a perchlorate spike approximately equal to the native perchlorate concentration.

3) MADEP-approved perchlorate laboratories and laboratories whose application for approval is currently under review must report the conductivity and perchlorate concentration of samples, duplicates, and spiked samples to MADEP. Submittals must include chromatograms and all supporting quality control documentation. Send the information via e-mail to John Bardzik at john.bardzik@state.ma.us.

4) Only the perchlorate concentration of the PT samples must be reported to the PT provider on forms provided by the PT provider. **Please remember to follow the Massachusetts perchlorate sample reporting protocol that requires the laboratory to report < MDL when no perchlorate is detected.**

This PT study is required of all laboratories currently approved by MADEP and those laboratories whose application for approval is currently under review. The PT study is voluntary for those laboratories interested in MADEP approval but that have not yet applied for approval. The performance of approved laboratories will be evaluated separately from that of laboratories not having Massachusetts approval and then the performance of all laboratories will be evaluated.

Based on the competence demonstrated by laboratories that participated in the first PT study, the Department is extending eligibility for consideration for approval to perform low-level perchlorate analysis to all laboratories that have already expressed their interest in being considered for such approval. Laboratories certified by Massachusetts or their resident state for drinking water analysis using an ion chromatography method and that could meet the stringent performance criteria of this program were required to notify the Laboratory Certification Office of their interest in approval by February 25, 2004 as specified in the Department's letter of February 18, 2004 sent to all Massachusetts-certified laboratories.

Laboratories are responsible for contacting the PT provider themselves to arrange their participation in the study. As with other PT studies, the cost of the study must be borne by the laboratory. To participate in the PT study, contact Chuck Wibby of Wibby Environmental at cwibby@wibby.com.

If you have any questions regarding the Massachusetts low-level perchlorate laboratory approval program, please contact John Bardzik.

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