WSC – CAM – VIII B

Quality Control Requirements and Performance Standards for the ***Analysis of Perchlorate by Ion Chromatography (IC) with Electrospray Ionization/Mass Spectrometry (ESI/MS or ESI/MS/MS) or High Performance Liquid Chromatography (HPLC) with ESI-MS or ESI-MS/MS*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

VIII. High Performance Liquid Chromatography (HPLC) and Ion Chromatography (IC) Methods

B. Quality Control Requirements and Performance Standards for WSC-CAM-VIII B (Perchlorate by IC-ESI/MS, IC-ESI/MS/MS, HPLC-ESI/MS, or HPLC-ESI/MS/MS)

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ACRONYM LIST

Amu	**Atomic mass unit**
CAM	**Compendium of Analytical Methods**
CASN	**Chemical Abstracts Service Number**
CCV	**Continuing calibration verification**
ESI/MS	**Electrospray ionization/mass spectrometry**
HPLC	**High performance liquid chromatography**
IC	**Ion chromatography**
ICV	**Initial calibration verification**
IDP	**Initial Demonstration of Proficiency**
IS	**Internal standard**
LC	**Liquid chromatograph**
LCS	**Laboratory control sample**
LCS	**Laboratory control sample duplicate**
LFSSM	**Laboratory fortified synthetic sample matrix**
LLCV	**Low level calibration verification**
LSSM	**Laboratory synthetic sample matrix**
LSSMB	**Laboratory synthetic sample matrix blank**
MassDEP	**Massachusetts Department of Environmental Protection**
MCP	**Massachusetts Contingency Plan**
MD	**Matrix duplicate**
mg/kg	**milligrams per kilogram**
MOHML	**Massachusetts Oil and Hazardous Materials List**
MS	**Matrix spike**
MSD	**Matrix spike duplicate**
m/z	**Mass-to-charge ratio**
NA	**Not applicable**
PTFE	**Polytetrafluoroethylene**
QA	**Quality assurance**
QC	**Quality control**
%R	**Percent recovery**
RAO	**Response Action Outcome**
RCs	**Reportable Concentrations**
RL	**Reporting limit**
RPD	**Relative percent difference**
RQs	**Reportable Quantities**
%RSD	**Percent relative standard deviation**
RT	**Retention time**
SRM	**Standard reference material**
µg/L	**micrograms per liter**

1.0 Quality Control Requirements and Performance Standards for WSC-CAM-VIII B

1.1 Overview of WSC-CAM-VIII B

WSC-CAM-VIII B, *Quality Control Requirements and Performance Standards for the Analysis of Perchlorate by Ion Chromatography (IC) with Electrospray Ionization/Mass Spectrometry (ESI/MS or ESI/MS/MS) or High Performance Liquid Chromatography (HPLC) with ESI/MS or ESI/MS/MS in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Refer to WSC-CAM-I A for an overview of the CAM process. Please note that while this protocol must be followed on and after the effective date of July 1, 2010 for the purpose of "Presumptive Certainty," the revised protocol may be used optionally prior to its effective date upon its publication on April 15, 2010.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with the required analytical methods EPA 331.0, EPA 332.0, SW-846 6850 or SW-846 6860, analysis for Perchlorate in aqueous and solid samples using IC-ESI/MS, IC-ESI/MS/MS, HPLC-ESI/MS, or HPLC-ESI/MS/MS. The QC requirements and performance standards specified in this document in Table VIII B-1, together with the analytical procedures described in the referenced analytical methods, constitute the WSC-CAM-VIII B protocol. All protocols included in the CAM are considered "methods" published by the MassDEP pursuant to the provisions of 310 CMR 40.0017(2). Use of EPA Method 331.0, EPA Method 332.0, SW-846 6850, or SW-846 6860 is a "Presumptive Certainty" requirement of WSC-CAM-VIII B. Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Perchlorate analyzed in support of MCP decision-making are presented in Appendix VIII B-1 of this document and Appendix VII-A of WSC-CAM-VII A *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Data reporting requirements are also provided in WSC-CAM-VII A.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status. For more guidance on data usability, refer to MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.1.1 Reporting Limits for Perchlorate by WSC-CAM-VIII B

The reporting limit (RL) for Perchlorate using WSC-CAM-VIII B is dependent on the concentration of the lowest non-zero standard in the initial calibration or the low-level calibration verification (LLCV), analyzed under identical conditions as the sample, with adjustments made for the sample size, preparation factors, percent solids, dilution factors, etc., as required. The CAM RLs for Perchlorate using the WSC-CAM-VIII B protocol are:

- 0.1 µg/L for aqueous samples (surface water, groundwater, and drinking water); and
- 0.5 µg/Kg for soil/sediment samples (assuming 100% solids).

For "Presumptive Certainty" purposes, if the typical CAM RLs are not achieved, respond "NO" to Question G of the "MassDEP MCP Analytical Protocol Certification Form" and address the CAM RL exceedance in the laboratory narrative.

Reporting limits lower than the above-referenced CAM RLs for Perchlorate may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard or the LLCV) must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, benchmark values, background, etc.). Meeting MCP standards or criteria may require analytical modifications to improve sensitivity. All such modifications must be described in the laboratory narrative.

1.1.2 Initial Demonstration of Proficiency for WSC-CAM-VIII B

Each laboratory that uses the WSC-CAM-VIII B protocol is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the preparation/analysis of laboratory control samples (LCSs) and LCS duplicates to assess analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or matrix duplicates may also be used to evaluate accuracy and precision when such samples are analyzed either at the discretion of the laboratory or at the request of the data user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Table VIII B-1 of this protocol and EPA Method 332.0, regardless of which analytical method is utilized. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in EPA Method 332.0 (Section 9.2 and Table 7), to be modified as indicated in Table VIII B-1 of this protocol. The data associated with the Initial Demonstration of Proficiency must be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for WSC-CAM-VIII B must include the following information:

QC Element	Performance Criteria
Mass Calibration and Instrument Optimization	WSC-CAM-VIII B, Table VIII B-1
Initial Calibration	WSC-CAM-VIII B, Table VIII B-1
Continuing Calibration	WSC-CAM-VIII B, Table VIII B-1
Method Blanks, System Background, Carryover Check	WSC-CAM-VIII B, Table VIII B-1
Average Recovery	% Recovery 80-120% for 7 replicate analyses
% Relative Standard Deviation	%RSD ≤20 for 7 replicate analyses
Internal Standards	WSC-CAM-VIII B, Table VIII B-1
Reporting Limit Confirmation	Section 9.2.4 of EPA Method 331.0 or 332.0

Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table VIII B-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For the WSC-CAM-VIII B protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table VIII B-1. It should be noted that the performance standards listed in Table VIII B-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory.

This protocol is restricted to use by, or under the supervision of, analysts experienced in the use of HPLC, IC, MS and the interpretation of chromatograms and mass spectra.

1.2 Summary of Perchlorate Methods

The following determinative methods may be used for analysis of Perchlorate with WSC-CAM-VIII B:

- EPA Method 331.0 – uses liquid chromatography with electrospray ionization mass spectrometry (LC/ESI/MS) for the determination of Perchlorate in aqueous matrices.
- EPA Method 332.0 - uses ion chromatography with suppressed conductivity and electrospray ionization mass spectrometry (IC-ESI/MS) for the determination of Perchlorate in aqueous matrices.
- SW-846 Method 6850 – uses high performance liquid chromatography (HPLC) coupled with electrospray ionization (ESI) mass spectrometry (MS) or tandem mass spectrometry (MS/MS) for the determination of Perchlorate in aqueous and solid matrices.
- SW-846 Method 6860 – uses ion chromatography (IC) coupled with electrospray ionization (ESI) mass spectrometry (MS) or tandem mass spectrometry (MS/MS) for the determination of Perchlorate in aqueous and solid matrices.

Solids are first extracted prior to analysis using reagent water. Aqueous samples and extracts are filtered, and analyzed via IC/MS or HPLC/MS (with or without fragmentation) or IC/MS/MS or HPLC/MS/MS. The following table summarizes the mass-to-charge (*m/z*) ratios used for the detection of Perchlorate using each method and analytical technique.

Summary of Mass-To-Charge Ratios of Perchlorate Using Each Analytical Method

Analytical Method	Analytical Technique	Perchlorate Ions (*m/z*)	Internal Standard Ions (*m/z*)
EPA Method 332.0	IC-ESI/MS (without fragmentation)	99, 101	107
EPA Method 331.0	LC-ESI/MS (without fragmentation)	99, 101	107
	LC-ESI/MS (with fragmentation)	83, 85	89

Summary of Mass-To-Charge Ratios of Perchlorate Using Each Analytical Method			
Analytical Method	**Analytical Technique**	**Perchlorate Ions (*m/z*)**	**Internal Standard Ions (*m/z*)**
SW-846 Method 6850	HPLC-ESI/MS (without fragmentation)	99, 101	107
	HPLC-ESI/MS or HPLC/ESI/MS/MS (with fragmentation)	83, 85	89
SW-846 Method 6860	IC-ESI/MS (without fragmentation)	99, 101	107
	IC-ESI/MS or IC-ESI/MS/MS (with fragmentation)	83, 85	89

All of the above-referenced methods confirm Perchlorate identification and overcome many of the interference problems encountered when using IC/conductivity suppression analysis for Perchlorate (EPA Method 314.1 or SW-846 Method 9058).

1.3 Method Interferences

- Refer to EPA Method 332.0 (Section 4.0, in particular) for a detailed discussion of contamination and interferences. Sources of interference in this method can be grouped into four broad categories.

  - Contaminated solvents, reagents, or sample processing hardware,
  - Contaminated HPLC carrier gas, parts, column surfaces, or detector surfaces,
  - Non-target compounds simultaneously extracted from the sample matrix which cause a detector response, and
  - Co-elution of target analytes.

  An in-depth discussion of the causes and corrective actions for all of these interferences is beyond the scope of this guidance document. A brief discussion of the more common interferences is presented below.

- Refer to EPA Method 332.0 for a detailed description of chemical contaminants, cross-contamination, and corrective actions that may be taken to eliminate contamination. If a method blank contains Perchlorate, data for samples associated with that blank must **not** undergo "blank correction" (i.e., if an associated sample also contains the contaminant, subtraction of the blank amount from the sample amount is not permitted).

- Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentration of Perchlorate. One or more blanks should be analyzed to check for potential cross-contamination/carryover following samples with Perchlorate concentrations that exceed the upper limit of calibration.

- Coelution of a contaminant may cause a low bias in Perchlorate results due to ionization suppression or may cause a high bias in Perchlorate results if the coeluting contaminant has the same m/z as Perchlorate. Coelution problems may be resolved by modifying the IC eluent strength or modifying the IC eluent with organic solvents, using MS/MS, or selective removal of the interference with sample pretreatment. Dilution is only beneficial if the coelution is a result of column overloading.

- Sulfate is the most problematic interference because it elutes before Perchlorate but elutes broadly, tailing into the retention time of Perchlorate. However, it should be noted that sulfate does not interfere with the detection of Perchlorate when analysis is performed with fragmentation and the ions of interest are m/z 83/85. High concentrations of sulfate can result in an inability to detect m/z 99 or an area count ratio of m/z 99/101 that does not meet the acceptance criteria. If either of these effects is observed, the background counts of m/z 99 must be evaluated in the half minute before Perchlorate elutes. If the background counts are 10-20 times higher than the background counts in the first continuing calibration verification (CCV) of the batch, sample dilution or pretreatment with barium cartridges must be performed to reduce or remove the sulfate. If pretreatment is performed, the method blank must also undergo pretreatment. Column age may also increase the effect of sulfate on the detection of Perchlorate.

- Water samples high in organic carbon or dissolved solids (i.e. salts of chloride, sulfate, carbonate/bicarbonate, etc.) can cause ionization suppression when high levels of dissolved salts are introduced into the mass spectrometer, resulting in a reduction in the Perchlorate analyte peak and a low bias in the results.

1.4 Quality Control Requirements for WSC-CAM-VIII B

Specific QC requirements and performance standards for the WSC-CAM-VIII B protocol are presented in Table VIII B-1. Refer to WSC-CAM-VII A for field QC requirements. Strict compliance with the QC requirements and performance standards, as well as satisfying the CAM's other analytical and reporting requirements will provide a data user with "Presumptive Certainty" in support of Response Actions under the MCP. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty" for analytical data, parties must:

(a) Use the analytical method specified for the selected CAM protocol;
(b) Incorporate **all** required analytical QC elements specified for the selected CAM protocol;
(c) Implement, as necessary, required corrective actions and analytical response actions for **all** non-conforming analytical performance standards;

(d) Evaluate and narrate, as necessary, **all** identified CAM protocol non-compliances; and
(e) Comply with **all** the reporting requirements specified in WSC-CAM-VII A, including retention of reported and unreported analytical data and information for a period of ten (10) years.

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data; and

- ✓ May be used in a data usability and representativeness assessment, as required in 310 CMR 40.1056(2)(k) for Response Action Outcome (RAO) submittals, consistent with the guidance described in MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.5 Special Analytical Considerations for WSC-CAM-VIII B

- Matrix Spike (MS) Recovery – Consistent with USEPA Region I data validation guidance, MassDEP requires rejection of non-detected Perchlorate results with <30% recovery in the MS.

- During the Initial Demonstration of Proficiency, it must be demonstrated that the internal standard does not contain unlabeled Perchlorate at a concentration greater than the RL.

1.6 Analyte List for WSC-CAM-VIII B

The MCP analyte list for WSC-CAM-VIII B consists of Perchlorate (ClO_4^-), CASN 14797-73-0.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL for the target analyte. Sources of various MassDEP standards and criteria are as follows:

- Reportable Quantities (RQs) and Concentrations (RCs) as described in 310 CMR 40.1600, The Massachusetts Oil and Hazardous Materials List (MOHML), in Subpart P of the MCP may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more. An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL: https://www.mass.gov/service-details/oil-hazardous-material-list.
- An updated list of MCP Method 1 Standards may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.

Perchlorate has promulgated MCP Method 1 groundwater/soil standards.

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
Initial Demonstration of Proficiency	Laboratory Analytical Accuracy, Precision, & Sensitivity	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must follow procedure in Section 9.2 and Table 7 of EPA Method 332.0, modified that Perchlorate must be <RL for carryover check and demonstration of system background.	No	NA	Refer to Section 9.2 and Table 7 of EPA Method 332.0 and Section 1.1.2 of this protocol.	NA
Quarterly Instrument Performance Check	Laboratory Analytical Accuracy	(1) Frequency: quarterly. (2) Analyze LSSMB (Laboratory Synthetic Sample Matrix Blank) and LFSSM (Laboratory Fortified Synthetic Sample Matrix) at mid-range of calibration curve; both solutions must be from same stock of LSSM. (3) LSSMB: Perchlorate <RL. (4) LFSSM: Perchlorate 80-120%.	No	NA	If outside of the acceptance criteria, perform instrument maintenance.	Suspend all analyses until quarterly instrument performance check meets criteria.
Mass Calibration & Instrument Optimization	Laboratory Analytical Accuracy	(1) Mass calibration must be performed prior to using method on samples or when major instrument maintenance is performed. (2) MS resolution must be 1 amu or better. (3) If performing IC/MS or HPLC/MS without fragmentation: after mass calibration, verify that Perchlorate peaks are symmetric about m/z 99, 101, & 107. Follow directions in Section 10.2 of EPA Method 332.0.	No	NA	Perform new mass calibration of mass spectrometer or perform other instrument maintenance.	Suspend all analyses until mass calibration and instrument optimization meet all criteria.
Initial Calibration	Laboratory Analytical Accuracy	(1) Must be analyzed at least once prior to analyzing samples, when initial calibration verification or continuing calibration verification does not meet the performance standards, and when major instrument maintenance is performed. (2) Minimum of 5 standards (or 6 if non-linear	No	NA	Recalibrate as required by method and/or try a different regression model.	Suspend all analyses until initial calibration meets criteria.

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
		regression used) (3) Low standard must be ≤RL. (4) Perform regression (linear or other). Verify all standards (including the RL) by recalculating concentrations using the final calibration curve; recoveries must be 80-120% for standards ≥RL and 50-150% for standards <RL.				
Blank Carryover Check	Laboratory Analytical Accuracy and Sensitivity	(1) Frequency: Immediately following the high calibration point in the initial calibration. (2) Perchlorate must be <RL in the Blank Carryover Check.	No	NA	(1) Determine source of contamination. (2) Reanalyze high calibration point followed by blank carryover check.	Suspend all analyses until Blank Carryover Check meets criteria.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	(1) Frequency: immediately following the Blank Carryover Check at the end of the initial calibration. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve. (4) Percent recovery must be 85-115%.	No	NA	(1) Reanalyze ICV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV.	Suspend all analyses until ICV meets criteria.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	(1) Frequency: Daily prior to sample analysis, every 10 field samples and at the end of the analytical run. (2) Concentration level near midpoint of curve. (3) Percent recovery must be 85-115%. (4) Area counts (response) of internal standards (IS) in CCV must be between 50-150% of the average IS area counts in the standards from the associated ICAL.	No	NA	(1) Reanalyze CCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and/or perform instrument maintenance and reanalyze all associated samples since last compliant CCV – unless (3) applies. (3) If CCV is high (>115%) and all associated sample	If (3) applies, include explanation in laboratory narrative.

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
					results are non-detected, no corrective action required.	
Low-Level Calibration Verification (LLCV)	Laboratory Analytical Accuracy & Sensitivity (verify low-end of calibration range / verify RL)	(1) Frequency: Daily prior to sample analysis following CCV. (2) Prepared using same source as initial calibration standards. (3) Concentration level must be at or below the level of the RL. (4) Percent recovery must be 70-130%.	No	NA	(1) Reanalyze LLCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and concentrations of perchlorate are ≤10x RL in associated field samples, perform instrument maintenance, recalibrate and reanalyze LLCV and associated samples. (3) If concentrations of Perchlorate are >10x RL in associated field samples, include explanation in laboratory narrative; no further action required.	Suspend all analyses until LLCV meets criteria unless the concentrations of Perchlorate are >10x the RL in the associated field samples.
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency - One per preparation batch of ≤20 field samples. (2) Must be prepared using the same syringe filter device used for sample collection. (3) Perchlorate must be <RL.	Yes	NA	(1) Reanalyze method blank; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, reprepare and reanalyze method blank and all associated field samples in batch unless (3) applies. (3) If concentration of Perchlorate in method blank is >RL but all associated sample results are either non-detected or >10x concentration in method blank, no	If (3) applies, include explanation in laboratory narrative.

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
					corrective action required.	
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) Frequency – One per preparation batch of ≤20 field samples. (2) Must be matrix-matched by preparing with the samples using the same preparation method. CAM requires a solid Standard Reference Material (SRM) be prepared and analyzed with solid field samples as the "solid LCS." An SRM is a soil or sediment matrix that contains perchlorate at a known concentration and with 95% confidence limits. (3) Concentration level for aqueous LCS near midpoint of curve. (4) Must be prepared using the same syringe filter device used for sample collection. (5) Percent recovery must be 80-120% for aqueous LCS and within vendor supplied control limits (95% confidence limits) for solid LCS.	Yes	Aqueous LCS: Recovery <50%: Perchlorate results in associated samples may be rejected.	(1) Reanalyze LCS; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and LCSD is in-control for Perchlorate, no further corrective action required. (3) If LCS and/or LCSD are above the acceptance criteria and all Perchlorate results are non-detected, no corrective action required. (4) If LCS and LCSD are both outside of criteria, re-prepare and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery exceedances in laboratory narrative.
LCS Duplicate (LCSD)	Laboratory Analytical Accuracy & Precision	(1) Frequency: one per preparation batch of ≤20 field samples ONLY if not performing project-specific MD. (2) Must be matrix-matched by preparing with the samples using the same preparation method. CAM requires a solid SRM be prepared and analyzed with solid field samples as the "solid LCS." An SRM is a soil or sediment matrix that contains perchlorate at a known concentration and with 95% confidence limits. (3) Concentration level for aqueous LCS near	Yes	Same as above for LCS for recovery evaluation	(1) Reanalyze LCSD; if acceptable, no further action required. (2) If reanalysis is still outside of recovery criteria for Perchlorate, and LCS is in-control, no corrective action required. (3) If LCS and/or LCSD are above the recovery criteria and all Perchlorate results are non-detected, no corrective action	Report recovery and RPD exceedances in laboratory narrative.

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
		midpoint of curve. (4) LCS must be prepared using the same syringe filter device used for sample collection. (5) Percent recovery must be 80-120% for aqueous LCS and within vendor supplied control limits (95% confidence limits) for solid LCS. (6) Analyze immediately after LCS in analytical sequence. (7) RPD must be ≤15 for aqueous and solids LCSs.			required. (4) If LCSD and LCS are both outside of recovery criteria, re-prepare and reanalyze LCS/LCSD and all associated field samples in batch.	
Internal Standards (IS)	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) One IS required for Perchlorate (oxygen-18 [^{18}O] enriched ClO_4^-). (2) Area counts in samples must be between 50-150% of the area counts in the associated CCV. (3) Retention time (RT) of IS must be within ±30 seconds of RT in the associated CCV.	Yes	IS Recovery <10%: affects nondetect results in affected samples.	(1) If the IS is outside of acceptance limits, reanalyze sample. (2) If the IS is still outside of acceptance limits, analyze sample at a dilution or perform pre-treatment to remove interferences. See Section 1.3 for further details.	(1) Report nonconformances in laboratory narrative. Include actual recovery of IS. (2) If reanalysis yields similar IS non-conformance, the laboratory must report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable IS recovery, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of the holding time and yields acceptable IS recovery, the laboratory must report results of both analyses.

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
Matrix Spike (MS) Project-Specific	Method Accuracy in Sample Matrix	(1) Frequency: One per preparation batch of ≤20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up). (2) Concentration level near midpoint of curve. (3) Percent recovery must be 80-120% for aqueous MS and 70-130% for solid MS.	Yes ONLY when requested by the data user	Recovery <30%: affects non-detects for Perchlorate in all associated samples.	(1) Reanalyze MS; if acceptable, no further action required. (2) After reanalysis, if MS recovery is outside of acceptance limits but ≥30% and LCS was in control, no corrective action is required. (3) If MS recovery is <30% and associated with non-detected results, re-prepare (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.	Report MS exceedances in laboratory narrative.
Matrix Duplicate* (MD) * An MSD sample may be substituted for an MD if Perchlorate is expected to be non-detected.	Method Precision in Sample Matrix	(1) Frequency: One per preparation batch of ≤20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up). (2) Prepare and analyze an additional aliquot of the same field sample used for MS. (3) RPD must be ≤15 for aqueous and ≤30 for solids.	Yes ONLY when requested by the data user	NA	Narrate.	Report exceedances in laboratory narrative.
Identification	NA	(1) The calculated *m/z* 99/101 or 83/85 area count ratios in all standards, field samples, and QC samples must be within ±25% (2.31 - 3.85) (2) Retention time ratio of *m/z* 99/107 and *m/z* 101/107 or *m/z* 83/89 and *m/z* 85/89 for all standards, field samples and QC samples must be within 0.98 - 1.02.	NA	NA	(1) If area count ratio is outside of limits in field samples, reanalyze. (2) If area count ratio is still outside of limits, analyze at a dilution or perform pre-treatment to remove interferences. See Section 1.3 for further	NA

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
		(refer to Sections 9.3.5 and 9.3.6 in EPA Method 332.0 for further details)			details.	
Quantitation	NA	(1) Quantitation must be based on internal standard calibration. (2) The laboratory must use the regression curve generated from the associated initial calibration for quantitation of Perchlorate. (3) Results must be reported with 2 or more "significant figures" if ≥ RL. If reporting values below the RL, report with 1 or more "significant figures".[2]	NA	NA	NA	NA
General Reporting Issues	NA	(1) The laboratory must only report values ≥ the sample-specific RL. Optionally, values below the sample-specific RL can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: Sample concentrations that exceed the calibration range must be diluted to fall within the calibration range when re-analyzed. If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range. The associated QC (e.g., method blanks, LCS, etc.) for the reported dilution must be reported. (3) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (4) Refer to Appendix VIII B-1 for chain-of-	NA	NA	NA	(1) Qualification of the data is required if reporting values below the sample-specific reporting limit. (2) The performance of dilutions must be documented in the laboratory narrative or on the report form. Unless due to Perchlorate concentrations that exceed the calibration range, reasons for dilutions must be explained in the laboratory narrative. (3) If samples are not properly collected (i.e., not filtered for aqueous samples, no headspace in sample container) or are not received with an

Table VIII B-1: Specific QC Requirements and Performance Standards for Perchlorate Using WSC-CAM-VIII-B

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
		custody requirements regarding preservation, cooler temperature, and holding times.				acceptable cooler temperature, note the non-conformances in the laboratory narrative. (4) If samples are prepared and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative.

[1]As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if these results are observed, data users should consider nondetect results as unusable and positive results as estimated with a significant low bias.

[2]Reporting protocol for "significant figures" is a policy decision included for standardization and consistency for reporting of results and is not a definition of "significant" in the scientific or mathematical sense.

2.0 Data Usability Assessment

Specific guidance applicable to all Class A, B or C RAO Statements, including partial RAOs, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) of the MCP is provided in *MCP Representativeness Evaluations and Data Usability Assessments* (Policy #WSC-07-350). This document provides general information regarding the purpose and content of these required evaluations as a component of and in support of an RAO submittal. The most current version of this document may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data objectives using MassDEP Policy #WSC-07-350, regardless of "Presumptive Certainty" status.

3.0 Reporting Requirements for WSC-CAM-VIII B

3.1 General Reporting Requirements for WSC-CAM-VIII B

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VII A, Section 2.4. This guidance document provides limited recommendations for field QC, as well as the required content of the laboratory report, which includes:

- Laboratory identification information,
- Analytical results and supporting information,
- Sample- and batch-specific QC information,
- Laboratory Report Certification Statement,
- Copy of the Analytical Protocol Certification Form,
- Laboratory narrative contents, and
- Chain-of-custody form requirements.

3.2 Specific Reporting Requirements for WSC-CAM-VIII B

Specific QC requirements and performance standards for WSC-CAM-VIII B are presented in Table VIII B-1. Specific reporting requirements for WSC-CAM-VIII B are summarized below in Table VIII B-2 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements must always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data must be available for review during an audit and may also be requested on a client-specific basis.

Soil and sediment results must be reported on a dry-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

Table VIII B-2 Routine Reporting Requirements for WSC-CAM-VIII B (Perchlorate)

Parameter	Required Analytical Deliverable
Quarterly Instrument Performance Check	***NO***
Mass Calibration and Instrument Optimization	***NO***
Initial Calibration	***NO***
Initial Calibration Verification	***NO***
Blank Carryover Check	***NO***
Low-Level Calibration Verification (LLCV)	***NO***
Continuing Calibration Verification (CCV)	***NO***
Method Blank	***YES***
Laboratory Control Sample (LCS)	***YES***
LCS Duplicate	***YES***
Matrix Spike (MS)	***YES (if requested by data user)***
Matrix Spike Duplicate (MSD)	***YES (if requested by data user)***
Matrix Duplicate (MD)	***YES (if requested by data user)***
Internal Standards	***YES***
Identification and Quantitation	***NO***
General Reporting Issues	***YES***

3.2.2 Sample Dilution

Under circumstances that sample dilution is required because the concentration of Perchlorate exceeds the concentration of the highest calibration standard or due to matrix interference, the RL for Perchlorate must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL for the diluted sample, RL_d:

$$RL_d = DF \times \text{Lowest Calibration Standard for Perchlorate}$$

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy MCP standards/criteria in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. All dilutions must be fully documented in the laboratory narrative.

Appendix VIII B-1

Sample Collection, Preservation, and Handling Procedures for Perchlorate Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Perchlorate analyzed in support of MCP decision-making are summarized below and presented in Appendix VII A-1 of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*.

Matrix	Container[1]	Preservation[4]	Holding Time[2,3]
Aqueous Samples	(1) 125-mL polyethylene bottle	Filter with 0.2 µm PTFE or sterile cellulose acetate filter in the field; Cool to ≤ 6°C but not frozen; Store with headspace	28 days to extraction and analysis
Soil/Sediment Samples	(1) 8-oz. amber glass jar w/ a Teflon-lined screw cap	Cool to ≤ 6°C but not frozen; Store with headspace.	28 days to extraction and analysis

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]Holding time begins from time of sample collection.

[3]As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if the holding time is exceeded by >2x the allowable holding time, data users should consider nondetect results as unusable and positive results as estimated with a significantly low bias.

[4]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6ºC are acceptable.

Appendix VIII B-2

Data Deliverable Requirements for Data Audits

If requested by MassDEP, submission of the information listed below may be required to perform a data audit to verify compliance with the analytical methods and to evaluate accuracy and reliability of the reported results. These deliverables represent a "full data package" including all sample documentation from receipt through preparation, analysis, and data reporting. The laboratory must ensure that these deliverables are available, in the event a data audit is performed. The laboratory is required to retain these deliverables for a period of 10 years from the date generated.

DELIVERABLE REQUIREMENTS FOR DATA AUDITS **WSC-CAM-VIII B (Perchlorate by IC-ESI/MS, IC-ESI/MS/MS, HPLC-ESI/MS, or HPLC-ESI/MS/MS)**	
Laboratory Narrative	Must comply with the required laboratory narrative contents as described in WSC-CAM-VII A
Sample Handling Information	Chains-of-custody (external and internal), sample receipt logs (cooler temperatures and sample pH), correspondences
Miscellaneous Logs	Dry weight logs Injection logs Soil/sediment sample weight logs Sample preparation/cleanup logs[1]
Initial Calibration Data	Summary of regression curve and recoveries of Perchlorate in each standard calculated using the curve Chromatograms for all standards used in initial calibration Quantitation reports for all standards used in initial calibration Concentrations of standards used must be clearly presented
Initial Calibration Verification Data	Percent recovery of Perchlorate Chromatograms for all ICVs Quantitation reports for all ICVs
Blank Carryover Check Data	Chromatograms for all blank carryover checks Quantitation reports for all blank carryover checks Mass spectra of reported positive results Summary of results, including reporting limits
Continuing Calibration Verification Data	Summary of percent recoveries of Perchlorate Chromatograms for all continuing calibration standards Quantitation reports for all continuing calibration standards Concentrations of standards used must be clearly presented

DELIVERABLE REQUIREMENTS FOR DATA AUDITS **WSC-CAM-VIII B (Perchlorate by IC-ESI/MS, IC-ESI/MS/MS, HPLC-ESI/MS, or HPLC-ESI/MS/MS)**	
Sample Results	Chromatograms for all sample analyses, reanalyses, and dilutions Quantitation reports for all sample analyses, reanalyses, and dilutions Mass spectra of reported positive results Percent solids results Summary of results, including reporting limits for each sample Date of analysis
Method Blank Results	Chromatograms for all method blanks Quantitation reports for all method blanks Summary of results, including reporting limits Mass spectra of reported positive results Summary of how method blank was prepared in solid and aqueous matrices, as appropriate
LCS/LCS Duplicate Results	Chromatograms for all LCS and LCS Duplicates Quantitation reports for all LCS and LCS Duplicates Summary of results, including concentrations detected, concentrations spiked, percent recoveries and RPDs Summary of how LCS/LCS Duplicates were prepared in solid and aqueous matrices, as appropriate
MS/MSD or MD Results (if performed)	Chromatograms for all MS/MSDs and MDs Quantitation reports for all MS/MSDs and MDs Summary of results, including unspiked sample concentrations, concentrations detected, concentrations spiked, percent recoveries and RPDs Summary of how MS/MSDs were prepared in solid and aqueous matrices, as appropriate
Mass Calibration and Instrument Optimization Data	Raw data showing MS resolution and Perchlorate peak symmetry
QC Summaries	Internal standard performance
Other Information	Demonstration that ICV prepared from second source standard
Quantitation reports must exhibit area counts of Perchlorate and the internal standards. [1]Must clearly indicate sample weights or volumes, final extract volumes, extraction method used, extraction times where appropriate for the method, etc.	