WSC – CAM – III C

Quality Control Requirements and Performance Standards for the ***Analysis of Trace Metals by Graphite Furnace Atomic Absorption (GFAA) Spectrometry*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

III. Metals Methods

C. Quality Control Requirements and Performance Standards for WSC-CAM-III C (Metals by GFAA)

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ACRONYM LIST

CAM	Compendium of Analytical Methods
CASN	Chemical Abstracts Service Number
CCB	Continuing calibration blank
CCV	Continuing calibration verification
FLAA	Flame atomic absorption spectrometry
GFAA	Graphite furnace atomic absorption spectrometry
HCl	Hydrochloric acid
HNO_3	Nitric acid
LLCV	Low-level calibration verification
ICB	Initial calibration blank
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	ICP-Mass Spectrometry
ICSA/AB	Interelement interference check samples
ICV	Initial calibration verification
IDL	Instrument detection limit
IDP	Initial demonstration of proficiency
IRAs	Immediate Response Actions
LCS/LCSD	Laboratory control sample / Laboratory control sample duplicate
LLCV	Low-Level Calibration Verification
LR	Linear range
MassDEP	Massachusetts Department of Environmental Protection
MB	Method blank
MCP	Massachusetts Contingency Plan
MD	Matrix duplicate
MDL	Method detection limit
MS	Matrix spike
MOHML	Massachusetts Oil and Hazardous Materials List
%D	Percent difference
%R	Percent recovery
r	Correlation coefficient
RAO	Response Action Outcome
RCs	Reportable Concentrations
RL	Reporting limit
RPD	Relative percent difference
RQs	Reportable Quantities
RSD	Relative standard deviation
QA	Quality assurance
QC	Quality control

<u>UNITS</u>:

g	Gram
mg/L	Milligram per liter
mg/Kg	Milligram per kilogram
mL	Milliliter
µg/L	Microgram per liter
µm	Micrometer
nm	Nanometer
%	Percent

1.0 Quality Control Requirements and Performance Standards for WSC-CAM-III C

1.1 Overview of WSC-CAM-III C

WSC-CAM-III C, *Quality Control Requirements and Performance Standards for the Analysis of Trace Metals by Graphite Furnace Atomic Absorption (GFAA) Spectrometry in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective July 1, 2010, this revised CAM protocol, WSC-CAM-III C, replaces the original Trace Metals CAM document, WSC-CAM-III C (effective date, August 13, 2004). 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 method SW-846 7010, analysis for trace metals in aqueous and solid samples using graphite furnace atomic absorption (GFAA) spectrometry preceded by conventional sample preparation methods via SW-486 Methods, as described in Section 1.3 of this protocol. The QC requirements and performance standards specified in this document in Table III C-1 together with the analytical procedures described in EPA SW-846 Method 7010, *Graphite Furnace Atomic Absorption Spectrophotometry,* constitute the WSC-CAM-III C 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 SW-846 7010 is a "Presumptive Certainty" requirement of WSC-CAM-III C. Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Trace Metals analyzed in support of MCP decision-making are presented in Appendix III C-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 Trace Metals by WSC-CAM-III C

The reporting limit (RL) for an individual analyte using WSC-CAM-III C 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 WSC-CAM-III C target analytes are:

- Aqueous samples (surface water, groundwater, and drinking water)
  - 0.5 - 10 µg/L
- Soil and Sediment samples (assuming 100% solids)
  - 0.1 – 5 mg/Kg

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 WCS-CAM-III C target analytes may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard or LLCV) for each target metal 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-III C

Each laboratory that uses the WSC-CAM-III C 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, the digestion/analysis of laboratory control samples (LCS) and/or matrix spikes (MS) to assess accuracy and LCS duplicates or matrix duplicates (MD) to assess precision.

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 III C-1 of this protocol. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Chapter One, Section 9.4 of SW-846 Method 7010 and in the preparation methods (SW-846 Method 3000 series). 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-III C must include the following:

QC Element	Performance Criteria
Initial Calibration	See WSC-CAM-III C, Table III C-1, for Performance Criteria
Continuing Calibration	
Method Blanks	
Percent % Recovery for LCS & MS	
Relative Percent Difference (RPD) for LCS Duplicate or MD	
Other Instrument QC Samples including: Dilution Test (%D); Duplicate Injections (RPD)	

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

For the WSC-CAM-III C protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table III C-1. It should be

noted that the performance standards listed in Table III C-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 who are experienced in using GFAA as a quantitative tool for environmental analyses and knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

1.2 Summary of SW-846 Method 7010

GFAA spectrometry is used to determine trace elements in solution. The method is applicable for all of the analytes listed in Table III C-2 as well as numerous other elements (refer to Table 1, SW-846 Method 7010). All aqueous matrices (except filtered groundwater samples) and solid matrices require digestion prior to analysis. Groundwater samples that have been pre-filtered and acidified do not require acid digestion.

An aliquot of the sample solution (digestate) is deposited into a graphite tube in the furnace, where it is evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated (atomized) in the graphite tube as compared to a flame, the use of smaller sample volumes and detection of lower concentrations of elements is possible with GFAA than with flame AA. Radiation from the "excited" elements passes through a vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. A monochrometer isolates the characteristic radiation from the hallow cathode lamp or electrodeless discharge lamp and a photosensitive device measures the transmitted radiation.

1.3 Sample Digestion/Preparation Methods for WSC-CAM-III C

Samples for analysis by SW-846 Method 7010 must be prepared (digested) to solubilize the sample prior to analysis, except for filtered (dissolved) groundwater samples. Preparation methods for Trace Metals are described in Chapter Three of SW-846 and listed in Appendix III C-4, *Methods for Sample Digestion/Preparation for Trace Metals Analyses*. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

1.4 Method Interferences

Samples submitted to a laboratory for trace metal analysis may become contaminated by numerous routes during both sampling and analysis. Potential sources of contamination may include:

- Metallic or metal-containing containers and sampling equipment,
- Laboratory acids or reagents,
- Improperly cleaned or stored equipment, and
- Atmospheric inputs such as dirt and dust.

Refer to Section 4.0 of SW-846 Method 7010 for further information on method interferences and contamination. Several common interferences and corrective measures are summarized as follows.

- Spectral interferences – causing biased high results due to interelement interferences, matrix interferences with non-target compounds that absorb light at the same wavelength as the target analyte, and other chemical interferences. These interferences can be minimized by using continuum Zeeman background correction (important, for example, in analyzing arsenic in the presence of aluminum and analyzing selenium in the presence of iron), modifying the sample charring and atomization program for the specific matrix, using a graphite platform, and/or using a matrix modifier during char and atomization steps in the graphite furnace.
- Memory interferences – caused by incomplete volatilization of the sample contributing to signals measured in a subsequent sample. These interferences can be minimized by using "blank burns" at regular intervals during the analytical run.
- High salt concentrations (e.g., seawater samples) – cause analyte signal suppression or enhancement, dependent upon the element. Samples with high salt content can cause both physical interference and molecular interferences and may require high dilutions and/or alternate preparation procedures for accurate quantitation. See Section 1.6 of this WSC-CAM-III C protocol for further information.
- Analyte-Specific interferences – interferences specific to antimony, arsenic, barium, beryllium, cadmium, chromium, lead, nickel, selenium, silver, thallium, and vanadium and procedures recommended to minimize these interference effects are detailed in Section 4.15 of SW-846 Method 7010.

1.5 Quality Control Requirements for WSC-CAM-III C

1.5.1 General QC Requirements

For general quality control procedures for all inorganic methods, including SW-846 Method 7010, refer to SW-846 Chapter One. General QC procedures to evaluate the instrument's operation can also be found in SW-846 Chapter One, Section 2.0, and include evaluation of calibrations and performance of sample analyses.

1.5.2 Specific QC Requirements and Performance Standards for WSC-CAM-III C

Specific QC requirements and performance standards for the WSC-CAM-III C protocol are presented in Table III C-1. Refer to WSC-CAM-VII A for field QC requirements. ***Note that a project-specific matrix spike (MS) must be performed for target Trace Metals to evaluate accuracy in a solid matrix (soil/sediment) at a frequency of one per 20 samples per matrix***. 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*.

1.6 Special Analytical Considerations for WSC-CAM-III C

- Matrix Spike (MS) Recovery – ***A MS is required for WSC-CAM-III C for solid matrices (soil/sediment) at a frequency of one per 20 samples per matrix***. Consistent with USEPA Region I data validation guidance, MassDEP requires rejection of non-detected metals results with <30% recovery in the MS. If MS recovery is < 30% and non-detected results were found for the affected metal, the laboratory must follow the required corrective actions listed on Table III C-1.
    - Laboratories are not required to monitor whether or not matrix spikes are performed on soil/sediment samples at a frequency of one per 20 samples per matrix. This is the responsibility of the data user.
    - For "Presumptive Certainty" purposes, if the data user does not submit a soil/sediment sample for MS analysis, Question H of the "MassDEP MCP Analytical Protocol Certification Form" must be answered NO and this must be noted in the laboratory narrative.
- RLs, sensitivity and the optimum and linear concentration ranges of the analytes can vary with the atomic absorption spectrophotometer, matrix, and operating conditions. Table 1 of SW-846 Method 7010 lists example quantitation limits (in the ppb range) for numerous elements and Table 2 of Method 7010 shows recommended wavelengths and purge gases for quantitation of numerous elements, including all analytes listed in Table III C-2 of this protocol.
- It is anticipated that a subset of the Table III C-2 Analyte List would be analyzed using this WSC-CAM-III C protocol on a metal-specific basis, based on project data sensitivity (reporting limit) needs. Additionally, Metals other than those listed in Table III C-2 may be analyzed by this protocol if the Initial Demonstration of Proficiency, as described in Section 1.1.2 of this protocol, is demonstrated.
- Matrix interferences, which can affect the accuracy of results for GFAA, can be minimized by optimizing charring (heating) times and temperatures, matrix modifier combinations, and using a stabilization platform in the graphite furnace to stabilize temperature during atomization. Further details are provided in Section 4.0 of SW-846 Method 7010.
- Samples with high dissolved solids, such as seawater samples, will adversely affect instrument performance. Samples should be diluted to minimize the matrix interference effect. Note, however, that this approach (dilution) may raise the sample-specific reporting limit for target analytes above the MCP or data user requirements. Therefore, it is recommended that alternate preparation/extraction methods such as chelation/extraction be used to remove significant salt

interference prior to GFAA analysis. Alternate analytical methods, such as ICP-MS or gaseous-hydride atomic absorption can also be useful in such instances.

- Though analysis for dissolved (filtered and acidified) metals does not require sample preparation, digestion may be beneficial to reduce potential matrix effects.
- It is recommended that all GFAA analyses be carried out using an appropriate matrix modifier, such as a palladium modifier solution, to reduce potential matrix interferences. Analysts should consult instrument manufacturer's directions and also see Sections 4.12 and 7.7 of SW-846 Method 7010 for further details.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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 (IDP)	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must contain all target analytes. (4) Must follow procedures in Section 9.4 of SW-846 7010 and the applicable preparation method (SW-846 3000 series).	No	NA	Refer to Section 9.4 of SW-846 7010, the applicable preparation method requirements in SW-846 3000 series methods, and Section 1.1.2 of this protocol.	NA
Preparation of Samples	Accuracy and Representativeness	(1) All aqueous (except dissolved/filtered groundwaters) and solid samples must be prepared (digested) prior to analysis. See Appendix III C-4 for preparation method references.	No	NA	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Frequency: Daily prior to sample analysis. (2) Minimum calibration blank plus 3 calibration standards (multi-point) which may include the RL (LLCV) standard; if LLCV standard is not included in calibration curve, then LLCV QC sample is required (see below). High level standard in calibration defines the upper end of the linear calibration range. (3) Linear regression with correlation coefficient r $\geq$0.995.	No	NA	Perform instrument maintenance as necessary; re-optimize instrument; re-calibrate as required by SW-846 7010.	Suspend all analyses until initial calibration meets criteria.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	(1) Frequency: Immediately after each initial calibration. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve. (4) Must contain all target analytes. (5) Percent recoveries must be between 90-110% for each target analyte.	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.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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 Calibration Blank (ICB)	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency: Immediately after ICV. (2) Prepared using same concentration of acids as calibration standards. (3) Target analytes must be <RL.	No	NA	(1) Reanalyze ICB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV & ICB.	Suspend all analyses until ICB meets criteria.
Low-Level Calibration Verification (LLCV)	Laboratory Analytical Sensitivity (verify low-end of calibration range / verify RL)	(1) Frequency: Daily prior to sample analysis if initial calibration did not contain a low-level standard at the RL. If initial calibration includes the RL as the low-level standard in the initial calibration curve, then LLCV is not required. (2) Prepared using same source as initial calibration standards. (3) Concentration level must be at the level of the RL for all target analytes. (4) Percent recoveries must be 70-130% for all target analytes.	No	NA	(1) Reanalyze LLCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and associated analytes are ≤10x RL in associated field samples, recalibrate and reanalyze LLCV and associated samples. (3) If associated analytes 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 the affected target analytes are >10x RL in the associated field samples.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	(1) Frequency: Every 10 samples and at the end of the analytical run. (2) Prepared using same source as initial calibration standards. (3) Concentration level near midpoint of curve. (4) Must contain all target analytes. (5) Percent recoveries must be 90-110% for each target analyte.	No	NA	(1) Reanalyze CCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCV – unless (3) applies. (3) If recovery is high (>110%) and all associated sample results are non-detected, no corrective action required	If (3) applies, include explanation in laboratory narrative.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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
Continuing Calibration Blank (CCB)	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency: Every 10 samples following CCV and at the end of the analytical run. (2) Prepared using same concentration of acids as calibration standards. (3) Target analytes must be <RL.	No	NA	(1) Reanalyze CCB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCB – unless (3) applies. (3) If concentration of contaminant in CCB is >RL but all associated sample results are either non-detected or >10x concentration of contaminant in CCB; no corrective action required.	If (3) applies, include explanation in laboratory narrative.
Method Blank (MB)	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency: One per digestion batch of ≤20 field samples. (2) Must be digested with the samples using the same preparation method as the samples. (3) Target analytes must be <RL.	Yes	NA	(1) Reanalyze MB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, redigest and reanalyze MB and all associated field samples in batch – unless (3) applies. (3) If concentration of contaminant in MB is >RL but all associated sample results are either non-detected or >10x concentration in MB; no corrective action required.	If (3) applies, include explanation in laboratory narrative.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) Frequency: One per digestion batch of ≤20 field samples. (2) Must be matrix-matched by digesting 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 the analytes of interest at known concentrations and with 95% confidence limits. (3) Concentration levels for aqueous LCS near midpoint of curve. (4) Must contain all target analytes. (5) Percent recoveries for all target analytes must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS.	Yes	Aqueous LCS: Recovery <50%: affected analytes 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 same analyte; no corrective action required. (3) If LCS and LCSD are both outside of criteria, redigest and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery exceedances in laboratory narrative.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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
LCS Duplicate (LCSD)	Laboratory Analytical Accuracy & Precision	(1) Frequency: One per digestion batch of ≤20 field samples ONLY if not performing project-specific MD. (2) Must be matrix-matched by digesting with the samples using the same preparation method. CAM requires a solid SRM be prepared and analyzed with solid field samples as the "solid LCSD." An SRM is a soil or sediment matrix that contains the analytes of interest at known concentrations and with 95% confidence limits. (3) Concentration levels must be same as LCS. (4) Must contain all target analytes; analyze immediately following LCS. (5) Percent recoveries for all target analytes must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. (6) RPDs must be ≤20 for aqueous LCS/LCSD and ≤30 for solid LCS/LCSD.	Yes ONLY if no MD	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 and LCS is in-control for same analyte, no corrective action required. (3) If LCSD and LCS are both outside of recovery criteria, redigest and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery and RPD exceedances in laboratory narrative.
Matrix Spike (MS) Project-Specific	Method Accuracy in Sample Matrix	(1) Solid Samples (Soil/Sediment) Frequency: One per 20 field samples per matrix; designated by data user on COC or at project set-up. Aqueous Samples Frequency: One per digestion batch of ≤20 field samples per matrix strongly recommended (designated by data user on COC or at project set-up). (2) Concentration levels near midpoint of curve. (3) Must contain all target analytes. (4) Percent recoveries for all target analytes must be 75-125%.	Yes ONLY when requested by the data user	Recovery <30%: affects non-detects for affected metal in all associated samples.	(1) Reanalyze MS; if acceptable, no further action required. (2) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in-control, no corrective action is required. (3) If MS recovery is <30% and associated with non-detected results, redigest (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.	Report MS exceedances in laboratory narrative. If redigested due to recoveries <30%, report both sets of sample/MS data.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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 Duplicate (MD) Project-Specific	Method Precision in Sample Matrix	(1) Frequency: One per digestion batch of ≤20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up). (2) Prepare by digesting and analyzing an additional aliquot of the same field sample used for MS. (3) RPD for each target analyte must be ≤20 for aqueous and ≤35 for solids.	Yes ONLY when requested by the data user	NA	Narrate.	Report exceedances in laboratory narrative.
Dilution Test	Accuracy in Sample Matrix	(1) Frequency: One per ≤20 field samples per matrix; only if project-specific MS requested and analyte concentration is >50x RL. (2) Perform 5x serial dilution on same sample used for MS/MD. (3) %D of the Sample & Dilution results for target analytes at levels >50x RL must be ±10% for all matrices.	Yes ONLY if project-specific MS requested by data user	NA	Narrate.	Report exceedances in laboratory narrative.
Duplicate Injections	Method Precision	(1) Frequency: Each calibration standard, QC sample, and field sample must be analyzed (injected) twice. (2) RPD must be ≤10 for calibration standards and ≤20 for all other detected results. (3) Report the average result of duplicate injections for all target metals.	No	NA	(1) Reanalyze; if duplicate injection RPD meets criteria, no further action required. (2) If RPD still outside of criteria, dilute sample and re-analyze diluted sample with duplicate injections. (3) If RPD still outside of criteria on dilution, narrate.	Report Duplicate Injection RPD exceedances in laboratory narrative – potential sample matrix interference.

Table III C-1: Specific QC Requirements and Performance Standards for Metals (SW-846 7010) Using WSC-CAM-III C

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
General Reporting Issues	NA	(1) Non-detected values must be reported with the sample-specific RL for each target analyte using all preparation/dilution factors. (2) The laboratory must only report values ≥ the sample-specific RL. (3) Sample concentrations that exceed the highest calibration standard must be diluted and reanalyzed to fall within the linear calibration range. (4) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (5) 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] (6) Refer to Appendix III C-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times.	NA	NA	NA	(1) The performance of dilutions must be documented in the laboratory narrative or on the report form. Unless due to elevated concentrations of target analytes, reasons for dilutions must be explained in the laboratory narrative. (2) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (3) If samples are digested and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative. (4) Narrate any additional method non-compliance or sample-specific anomaly.

[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 detected 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.

1.7 Analyte List for WSC-CAM-III C

The MCP analyte list for WSC-CAM-III C includes 13 target Metals as listed in Table III C-2. These include: antimony, arsenic, barium, beryllium, cadmium, chromium, lead, nickel, selenium, silver, thallium, vanadium, and zinc.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL for the target analytes. 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.

The target Trace Metals listed on Table III C-2 have promulgated MCP Method 1 groundwater/soil standards.

1.7.1 Analyte List Reporting Requirements for WSC-CAM-III C

While it is not necessary to request and report all the WSC-CAM-III C analytes listed in Table III C-2 to obtain "Presumptive Certainty" status, it is necessary to document use and reporting of a reduced analyte list, for site characterization and data representativeness considerations. MassDEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In some cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- ✓ Sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or

- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

Note: a data user who avoids the detection and quantitation of a contaminant that is present or likely present at a site above background levels by limiting an analyte list could be found in criminal violation of MGL c. 21E or any regulations or orders adopted or issued thereunder.

In cases where a reduced list of analytes is requested, laboratories must still employ the specified QC requirements and performance standards in WSC-CAM-III C to obtain “Presumptive Certainty” status.

Table III C-2: Analyte List for WSC-CAM-III C (SW-846 7010)

Analyte	CASN
Antimony	7440360
Arsenic	7440382
Barium	7440393
Beryllium	7440417
Cadmium	7440439
Chromium (Total)	7440473
Lead	7439921
Nickel	7440020
Selenium	7782492
Silver	7440224
Thallium	7440280
Vanadium	7440622
Zinc	7440666

CASN – Chemical Abstracts Service Numbers

NOTE: Other Trace Metals may also be analyzed using the WSC-CAM-III C protocol but are not considered part of the CAM target analyte list.

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-III C

3.1 General Reporting Requirements for WSC-CAM-III C

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-III C

Specific QC requirements and performance standards for WSC-CAM-III C are presented in Table III C-1. Specific reporting requirements for WSC-CAM-III C are summarized below in Table III C-3 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 III C-3 Routine Reporting Requirements for WSC-CAM-III C (SW-846 7010)

Parameter	Required Analytical Deliverable
Initial Calibration	***NO***
Initial Calibration Verification (ICV)	***NO***
Initial Calibration Blank (ICB)	***NO***
Low-Level Calibration Verification (LLCV)	***NO***
Continuing Calibration Verification (CCV)	***NO***
Continuing Calibration Blank (CCB)	***NO***
Method Blank	***YES***
Laboratory Control Sample (LCS)	***YES***
LCS Duplicate	***YES***
Matrix Spike (MS)	***YES*** *(if requested by data user)*
Matrix Duplicate (MD)	***YES*** *(if requested by data user)*
Dilution Test	***YES*** *(if MS requested by data user)*
Duplicate Injections	***NO***
Identification and Quantitation	***NO***
General Reporting Issues	***YES***

3.2.1 Sample Dilution

Under circumstances that sample dilution is required because the concentration of one or more of the target or non-target metals exceeds the concentration of the respective highest calibration standard, the RL for the affected metal must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL for the diluted sample, RL_d:

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

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. Such increases in RLs are the unavoidable but acceptable consequence of sample dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the laboratory narrative.

Appendix III C-1

Sample Collection, Preservation, and Handling Procedures for Trace Metals Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Trace Metals 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)*. Additional guidance may be found in SW-846, Chapter Three.

Matrix	Container[1]	Preservation[5]	Holding Time[2]
Aqueous Total Metals	500 mL Polyethylene Bottle	HNO_3 to pH <2	180 days
Aqueous Dissolved Metals (Filtered)	500 mL Polyethylene Bottle	Filter (0.45 µm) on site or at the laboratory ***(prior to acid preservation)*** within 24 hours of collection; then preserve with HNO_3 to pH <2	180 days
Soil and Sediments	4-ounce glass jar with teflon-lined cap	Cool to ≤ 6°C[3]	180 days[4]
Concentrated Waste	125 mL wide mouth glass or plastic	Cool to ≤ 6°C[3]	180 days

[1]The collection of multiple sample containers per sample location may be required to collect enough sample for matrix QC.

[2]Holding time begins from time of sample collection. 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, data users should consider non-detect results as unusable and detected results as estimated (low bias). Note: The holding time is for the target Trace Metals CAM list of 13 metals, not including mercury (mercury holding time is 28 days; analyze by alternate method.

[3]SW-846 does not require preservation for total metals (other than mercury) in solid samples; however, as a practical consideration since one sample container is generally collected for solid samples for all total metals analyses, preservation (cooling ≤6°C) for this CAM protocol has been defined.

[4]Alternatively, soil and sediment samples for Metals analyses may be held for up to one (1) year if frozen within 24 hours of collection at <-10°C. Sampling container should only be filled to 2/3 of capacity to avoid breakage caused by expansion during freezing. Preparation must commence within 24 hours of thawing. Temperature must never be allowed to go below -20°C to avoid damage to container seals and breakage.

[5]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 III C-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-III C (Trace Metals by GFAA: SW-846 7010)	
Laboratory Narrative	Must comply with the required laboratory narrative contents as described in WSC-CAM-VII A
Sample Handling Information	Chain-of-custody (external and internal), sample receipt logs (cooler temperatures and sample pH), correspondences
Miscellaneous Logs	Dry weight logs; Analytical logs; Freezer logs
Initial Calibration Data	Raw instrument data for initial calibration, including calculation of linear or non-linear regression and correlation coefficient values; Concentrations of calibration standards used
Initial Calibration Verification and Initial Calibration Blank Data	Percent recoveries for all ICVs; ICV source & true value; Results and raw instrument data for ICV and ICB
Low-Level Calibration Verification, Continuing Calibration Verification, and Continuing Calibration Blank Data	Percent recoveries for all LLCV and CCV; LLCV and CCV source & true value; Results and raw instrument data for LLCV, CCV, and CCB
Sample Results including results of Duplicate Injections	Sample result forms with dilution factors, units, reporting limits, method reference, date of preparation, date of analysis; Raw instrument data including Duplicate Injection results and RPD; Percent solids results; Sample preparation logs (initial and final weights/volumes; preparation method reference)
Method Blank Results	Method Blank results, units, reporting limits; Raw instrument data; Preparation logs
LCS/LCS Duplicate Results and/or SRM results	Summary of results, including concentrations detected, concentrations spiked or known (vendor limits) if SRM, percent recoveries and RPDs; Raw instrument data; Preparation logs
MS Results – if analyzed Dilution Test Results – required if MS performed and failed criteria MD Results – if analyzed	Summary of results, project-specific sample ID, unspiked sample concentration, concentration detected, concentration spiked, percent recoveries for MS, %D for Dilution Test Results, RPD for MD; Raw instrument data; Preparation logs

Appendix III C-3

Analysis Sequence for Trace Metals by WSC-CAM-III C

Typical analytical sequence for Trace Metals by GFAA using WSC-CAM-III C:

- Initial Calibration
- ICV
- ICB
- LLCV – only required if initial calibration curve does not have a low-level standard at the level of the RL
- MB
- LCS
- LCSD – only required if not performing a project-specific MD
- 7 samples – include the project-specific MS and/or MD if applicable, plus Dilution test sample, if applicable
- CCV
- CCB
- 10 samples
- CCV
- CCB
- Etc. (continue 10 samples and CCV/CCB pairs)
- CCV – ending
- CCB – ending

Appendix III C-4

Methods for Sample Digestion/Preparation for Trace Metals Analyses

Methods for Sample Digestion/Preparation for Trace Metals Analyses		
SW-846 Digestion/ Preparation Method	**Matrix**	**Title/Description**
3015A	Aqueous: Drinking Water/ Surface Water/ Groundwater/ Mobility-procedure extracts/ aqueous waste	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts
3020	Aqueous: Surface Water/ Groundwater/ Mobility-procedure extracts/ aqueous waste	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy
3031	Solid: Oily Waste/Tar/ Wax/Paint/ Petroleum Product	Acid Digestion of Oils for Metals Analysis by Atomic Absorption or ICP Spectrometry
3040A	Solid: Oil/Grease/Wax	Dissolution Procedure for Oils, Greases, or Waxes
3050B	Solid: Soil/Sediment/ Sludges	Acid Digestion of Sediments, Sludges, and Soils
3051A	Solid: Soil/Sediment/ Sludge/Oil	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils
3052	Solid: Biological Tissue/Oil/Ash Soil/Sediment/ Sludge	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices