WSC – CAM – II A

Quality Control Requirements and Performance Standards for the ***Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

II. Gas Chromatography/Mass Spectrometry (GC/MS) Methods

A. Quality Control Requirements and Performance Standards for WSC-CAM-II A (Volatile Organic Compounds by GC/MS)

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ACRONYM LIST

ASAP	**As soon as possible**
BFB	**Bromofluorobenzene**
BTEX	**Benzene, toluene, ethylbenzene, xylenes**
CAM	**Compendium of Analytical Methods**
CASN	**Chemical Abstracts Service Number**
CCAL	**Continuing calibration**
%D	**Percent difference or percent drift**
DCB	**Dichlorobenzene**
DF	**Dilution factor**
DIPE	**Diisopropyl ether**
EDB	**Ethylene dibromide**
ETBE	**Ethyl tertiary butyl ether**
g	**grams**
GC	**Gas chromatograph**
GC/MS	**Gas chromatography/mass spectrometry**
HCl	**Hydrochloric acid**
ICV	**Initial calibration verification**
IRAs	**Immediate Response Actions**
LCS	**Laboratory control sample**
MassDEP	**Massachusetts Department of Environmental Protection**
MCP	**Massachusetts Contingency Plan**
MD	**Matrix duplicate**
MEK	**Methyl ethyl ketone**
MIBK	**Methyl isobutyl ketone**
mL	**Milliliters**
MNBK	**Methyl n-butyl ketone**
MOHML	**Massachusetts Oil and Hazardous Materials List**
MS	**Matrix spike**
MSD	**Matrix spike duplicate**
MTBE	**Methyl tertiary butyl ether**
NA	**Not applicable**
$NaHSO_4$	**Sodium bisulfate**
OXY	**Oxygenate**
PP	**Poor purging efficiency**
r	**Correlation coefficient**
r^2	**Coefficient of determination**
%R	**Percent recovery**
RPD	**Relative percent difference**
%RSD	**Percent relative standard deviation**
QA	**Quality assurance**
QC	**Quality control**
RAO	**Response Action Outcome**
RCs	**Reportable Concentrations**
RF	**Response factor**
RL	**Reporting limit**
RQs	**Reportable Quantities**
SIM	**Selective ion monitoring**
TAME	**Tertiary amyl methyl ether**
TCE	**Trichloroethene**
THF	**Tetrahydrofuran**
TICs	**Tentatively identified compounds**
TSP	**Trisodium phosphate dodecahydrate**
UCM	**Unresolved complex mixture**
µg/kg	**micrograms per kilogram**
µg/L	**micrograms per liter**
µL	**microliters**
VOCs	**Volatile organic compounds**
VPH	**Volatile petroleum hydrocarbons**

1.0 Quality Control Requirements and Performance Standards for WSC-CAM-II A

1.1 Overview of WSC-CAM-II A

WSC-CAM-II A, *Quality Control Requirements and Performance Standards for the Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) 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-II A, replaces the original Volatile Organic GC/MS CAM document, WSC-CAM-II A (effective date, May 30, 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 8260B, conventional purge-and-trap sample introduction via SW-846 Methods 5030B and 5035A for the analysis of aqueous and solid samples for volatile organic compounds (VOCs) by GC/MS. The QC requirements and performance standards specified in this document in Table II A-1 together with the analytical procedures described in EPA SW-846 Method 8260B, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, constitute the WSC-CAM-II A 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 8260B is a "Presumptive Certainty" requirement of WSC-CAM-II A. Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for VOCs analyzed in support of MCP decision-making are presented in Appendix II A-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 WSC-CAM-II A

The reporting limit (RL) for an individual compound using WSC-CAM-II A is dependent on the concentration of the lowest non-zero standard in the initial calibration, analyzed under identical conditions as the sample, with adjustments made for the sample size, extraction concentration factor, percent solids, dilution factors, etc., as required. Except as provided in the table below, the CAM RLs for WSC-CAM-II A target analytes are:

- 2 µg/L for aqueous samples (surface water, groundwater, and drinking water)
- 5-10 µg/kg (wet weight) for low-level soil/sediment samples (assuming 100% solids), and
- 100-200 µg/kg (wet weight) for high-level soil/sediment samples (assuming 100% solids).

These values are readily achievable using the techniques specified in CAM, including 5 mL purge volumes, standard quadrupole instrumentation, 1:1 soil/methanol ratio, etc.

There may be exceptions to the above CAM RLs for some target analytes (that is, the CAM RL for some target analytes may not be readily achieved by a laboratory using WSC-CAM-II A). These CAM RL exceptions for the WSC-CAM-II A target analytes are presented in the table below for various matrices. For "Presumptive Certainty" purposes, if the 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.

CAM RL Exceptions for WSC-CAM-II A Target Analytes

Target Analyte	Groundwater/Surface Water (µg/L)	Low-level Soil/Sediment[1] (µg/kg)	High-level Soil/Sediment[1] (µg/kg)
Acetone	10	Not Applicable	Not Applicable
1,4-Dioxane[2]	250 – 500	250 – 500	5,000 – 10,000
2-Butanone (MEK)	10	Not Applicable	Not Applicable
2-Hexanone	10	Not Applicable	Not Applicable
4-Methyl-2-pentanone (MIBK)	10	Not Applicable	Not Applicable

[1]Assuming 100% solids
[2]Refer to Section 1.6 for alternate methods of achieving lower RLs for 1,4-Dioxane.

Reporting limits lower than the above-referenced CAM RLs for WSC-CAM-II A target analytes may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard) for each contaminant of concern 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, such as the use of SIM, an ion trap mass spectrometer, or other instrumentation of improved design to improve sensitivity. All such modifications must be described in the laboratory narrative. Regardless of the instrument that is used, RLs for the WSC-CAM-II A target analytes will be proportionately higher for samples that require dilution or when a reduced sample size is used to avoid detector saturation.

It should be noted that for some analytes of concern, (e.g., 1,2-dichloroethane, cis- and trans-1,3-dichloropropene, 1,1,2,2-tetrachloroethane, etc.), the aforementioned reporting limits associated with high-level soil/sediment analyses (with methanol preservation) may not be adequate to verify regulatory compliance. If a lower reporting limit is required, use of the following options should be considered:

- Low-level soil/sediment method as described in SW-846 Method 5035A; or
- Heated purge-and-trap option (>40ºC) as described in SW-846 Method 8260B, Section 7.1.2.2.

NOTE: Heated purge-and-trap (>40ºC) should only be used as the sample introduction method for oxygenates if the trisodium phosphate dodecahydrate preservative shown in Appendix II A-1 is used. Heated purge-and-trap (>40ºC) should not be used for compounds susceptible to acid hydrolysis.

1.1.2 Initial Demonstration of Proficiency for WSC-CAM-II A

Each laboratory that uses the WSC-CAM-II A 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 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 II A-1 of this protocol and SW-846 Method 8000B. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Method 8000B (Section 8.4) and SW-846 method 8260B (Section 8.3). 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-II A must include the following information:

QC Element	Performance Criteria
BFB Tuning	WSC-CAM-II A, Table II A-1
Initial Calibration	WSC-CAM-II A, Table II A-1
Continuing Calibration	WSC-CAM-II A, Table II A-1
Method Blanks	WSC-CAM-II A, Table II A-1
Average Recovery	SW-846 Method 8000B, Section 8.4
% Relative Standard Deviation	SW-846 Method 8000B, Section 8.4
Surrogate Recovery	WSC-CAM-II A, Table II A-1
Internal Standards	WSC-CAM-II A, Table II A-1

NOTE: Because of the extensive analyte list and number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all non-conforming analytes. All non-conforming analytes along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency documentation.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. Experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices; the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table II A-1 to assess

analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For the WSC-CAM-II A protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table II A-1. It should be noted that the performance standards listed in Table II A-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 GC/MS instrumentation as a quantitative tool and skilled in the interpretation of chromatograms and mass spectra.

1.2 Summary of SW-846 Method 8260B

Volatile compounds are introduced into the gas chromatograph by purge-and-trap. The analytes are then introduced directly to a capillary column by ballistic heating or cryo-focused onto a capillary pre-column before being flash evaporated onto a capillary column for analysis. The GC oven is temperature-programmed to facilitate separation of the analytes of interest which are then detected by a mass spectrometer that is interfaced directly to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing sample electron impact mass spectra with the electron impact mass spectra of standards obtained under identical analytical conditions. Quantitation is accomplished by using the response of a major (quantitation) ion relative to an internal standard and a response factor generated from a minimum five-point calibration curve.

1.3 Method Interferences

- Refer to SW-846 Method 8260B for a detailed description of chemical contaminants, cross-contamination, and corrective actions which may be taken to eliminate contamination. If a method blank contains a contaminant, 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 concentrations of VOCs. After the analysis of a sample containing high concentrations of VOCs, one or more blanks should be analyzed to check for potential cross-contamination/carryover. Concentrations of VOCs which exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover. In addition, samples containing large amounts of water-soluble materials, suspended solids, or high boiling point compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from high boiling point compounds may not appear until a later sample analysis.

  Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. Refer to Section 3.0

of SW-846 method 8260B for a detailed description of approaches to minimize these interferences, as well as other special precautions associated with the analysis of methylene chloride, the most common laboratory contaminant for this method.

- The use of sodium bisulfate as the low-level preservation method for solid samples with high organic matter or humic material content has been known to result in the formation of acetone and MEK at potentially significant concentrations in samples. Sodium bisulfate preservation must **never** be used when these conditions are either present or suspected. It should be noted that freezing (< -7^{O}C), and not sodium bisulfate addition, is the preferred low-level preservation method for solid samples (see Appendix II A-1).

- Use of methanol in the high-level solid preservation method may also result in the detection of MEK at trace levels in samples due to the presence of MEK as a methanol contaminant.

- Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container's septum during shipment and storage. A trip blank carried through sampling and subsequent storage and handling can serve as a check on such contamination.

1.4 Alternative Sample Introduction Methods

The WSC-CAM-II A protocol is primarily intended to provide QC requirements and performance standards for conventional purge-and-trap sample introduction via SW-846 Methods 5030B and 5035A for aqueous and solid samples, respectively. If other sample introduction methods are required and utilized because of analytical circumstances, the laboratory must provide a full explanation and justification in the laboratory narrative, as well as details and results of the QC samples and calibrations associated with these different sample introduction methods.

1.5 Quality Control Requirements for WSC-CAM-II A

1.5.1 General QC Requirements

Refer to SW-846 Method 8000B for general QC procedures for all chromatographic methods, which includes SW-846 Method 8260B. Instrument QC and method performance requirements for the GC/MS system may be found in SW-846 Method 8260B, Sections 8.0 and 9.0, respectively.

1.5.2 Specific QC Requirements and Performance Standards for WSC-CAM-II A

Specific QC requirements and performance standards for the WSC-CAM-II A protocol are presented in Table II A-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*.

1.6 Special Analytical Considerations for WSC-CAM-II A

The following bullets highlight potential issues that may be encountered with the analysis of VOCs using this protocol.

- Analytes with poor purging efficiency at ambient temperature, designated as "PP" on Table II A-2, may require the heated purge-and-trap option if lower RLs are required.

- Aqueous samples submitted for analysis of oxygenates, designated as "OXY" on Table II A-2, and other compounds susceptible to hydrolysis should not be preserved with acid <u>if heated purge-and-trap</u> (>40ºC) is used as the sample introduction method. See Appendix II A-1 for the preferred preservation technique under this condition.

- Under certain conditions, select VOCs may be potentially reactive (i.e., unstable and susceptible to acid hydrolysis, abiotic degradation and/or loss during storage). At this time MassDEP does not consider any of the compounds on the Analyte List to be "reactive" and requiring special preservation and/or holding times under normal analytical conditions. However, other VOCs that are regulated by MassDEP but not included on the Analyte List may fall into this category (e.g., 2-chloroethyl vinyl ether); refer to Appendix II A-1 for required preservation techniques under this circumstance.

- The recovery of matrix spikes from a soil/sediment sample that has been preserved with methanol cannot be used to directly evaluate matrix-related bias/accuracy in the conventional definition of these terms. QC parameters expressed in terms of these percent recoveries (%R) may be more indicative of the variabilities associated with the analytical system (sample processing, introduction, and/or component separation). This inherent limitation of methanol preservation with respect to the evaluation of matrix spike recoveries is more than compensated for by the marked improvement in

sample integrity and conservation/recoveries of the volatile analytes of concern from soil/sediment matrices by minimizing volatilization losses.

- 1,4-Dioxane is included on the analyte list of WSC-CAM-II A. The analytical sensitivity (i.e., RL) for this compound (200 – 500 µg/L in water) is not adequate to evaluate compliance with some MCP regulatory limits if conventional (ambient temperature) purge-and-trap sample introduction is utilized. If 1,4-Dioxane is not a contaminant of concern for the site, conventional purge-and-trap sample introduction (ambient temperature) may be used for sample analysis.

  If 1,4-dioxane is a contaminant of concern for the site, special analytical techniques, as listed below, must be utilized in order to evaluate compliance with MCP cleanup standards.

  - Heated ($80\pm5^{o}C$) purge-and-trap with SIM analysis by SW-846 Method 8260B is an acceptable approach for aqueous and solid samples. However, if elevated concentrations of other chlorinated VOCs are present in the sample, this approach may not be preferable due to the likely contamination/saturation of the trap during the analysis.
  - Extraction using SW-846 methods 3510C or 3535A followed by isotope dilution analysis using SW-846 method 8270D, as outlined in Appendix II B-4 of WSC-CAM-II B, is an acceptable approach for aqueous samples.

- A linear or non-linear calibration model must not be used to compensate for detector saturation or to avoid proper instrument maintenance. As such, linear or non-linear regression must not be employed for initial calibration calculations that typically meet percent relative standard deviation (%RSD) requirements specified in Table II A-1.

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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	(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 procedure in Section 8.4 of SW-846 8000B.	No	NA	Refer to Section 8.4 of SW-846 8000B and Section 1.1.2 of this protocol.	NA
GC/MS Tunes with BFB	Inter-laboratory Consistency & Comparability	(1) Criteria listed in Table 4 of SW-846 8260B (the same criteria must be used for all analyses). (2) Every 12 hours prior to sample analysis.	No	NA	Perform instrument maintenance as necessary; retune instrument.	Suspend all analyses until tuning non-compliance is rectified.
Initial Calibration	Laboratory Analytical Accuracy	(1) Must be analyzed at least once prior to analyzing samples, when initial calibration verification or continuing calibration does not meet the performance standards, and when major instrument maintenance is performed. (2) Minimum of 5 standards (or 6 if non-linear regression used). (3) Low standard must be ≤RL. (4) %RSD ≤20, r ≥0.99 (linear regression), or r^2 ≥0.99 (non-linear regression) for each target analyte. (5) If %RSD >20, linear or non-linear regression must be used. (6) Minimum RFs as per Table 4 of SW-846 8260C for lowest concentration standard and for average RF. (7) Must contain all target analytes. (8) Calibration must be performed under the same conditions as the samples (e.g., heated purge). (9) If autosampler used to spike surrogates in calibration standards, one-point	No	RF <0.05; affects nondetect results for affected analyte in all samples analyzed under this initial calibration.	(1) Recalibrate if >10% of target analytes exceed %RSD, "r", or "r^2" criteria. (2) If ≤10% of compounds exceed criteria, recalibration is not required as long as %RSD <40, r >0.98, or r^2 >0.98. (3) If recalculated concentrations from the lowest calibration standard are outside of 70-130% recovery range, either: * The RL must be reported as an estimated value[2], or * The RL must be raised to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration curve.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds (%RSD >20, r <0.99, r^2 <0.99 or minimum RF not met) in laboratory narrative. If non-linear regression (i.e., quadratic equation) is used for calibration, this must be noted in the laboratory narrative along with the compounds affected.

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
		calibration with 5 standards acceptable for surrogates. (10) If linear or non-linear regression used, verify the RL by recalculating concentrations in lowest calibration standard using the final calibration curve; recoveries must be 70-130%. (11) SIM: Laboratory must monitor a minimum of two ions per analyte (the primary ion or quantitation ion and a minimum of one confirmation ion); this is required for all target analytes, surrogates and internal standards.				
Initial Calibration Verification	Laboratory Analytical Accuracy	(1) Immediately after each initial calibration. (2) Concentration level near midpoint of curve. (3) Prepared using standard source different than used for initial calibration. (4) Must contain all target analytes. (5) Percent recoveries must be between 70-130% for target analytes except for "difficult" analytes(**) which must exhibit percent recoveries between 40-160%.	No	NA	Locate source of problem; recalibrate if >10% of all analytes are outside of criteria.	If recovery is outside of 70-130% for any analyte, including "difficult" analytes(**), report non-conforming compounds in laboratory narrative.
Continuing Calibration	Laboratory Analytical Accuracy	(1) Every 12 hours prior to the analysis of samples. (2) Concentration level near midpoint of curve. (3) Must contain all target analytes. (4) %D must be ≤20 for each target analyte except for "difficult" analytes(**) which must exhibit %Ds <60. (5) Minimum RFs as per Table 4 of SW-846 8260C. (6) Area counts of internal standards in continuing calibration must be between	No	RF <0.05; affects nondetect results for affected analyte in all samples analyzed under this continuing calibration.	(1) Recalibrate if >20% of target analytes exceed %D criteria. (2) If internal standard is outside of criteria, locate source of problem and reanalyze the continuing calibration. (3) If ≤20% of compounds exceed criteria, recalibration is not required as long as %D <40 (or <60 for "difficult	Report non-conforming compounds (%D >20 or minimum RF not met) and associated samples in laboratory narrative.

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
		50 – 200% of the area counts in the associated mid-level initial calibration standard.			analytes").	
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Every 20 samples prior to sample analysis and after calibration standards. (2) Matrix and preservative-specific (e.g., water, methanol). (3) Target analytes must be <RL except for common laboratory contaminants (acetone, methylene chloride, and MEK) which must be <5x the RL.	Yes	NA	(1) If concentration of contaminant in sample is <10x concentration in blank, locate source of contamination; correct problem; reanalyze method blank and associated samples. (2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample.	(1) If sample reanalysis is not possible, report non-conformance in laboratory narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" or some other convention, should qualify the sample results. Blank contamination should also be documented in the laboratory narrative. (3) If re-analysis is performed within holding time and yields acceptable method blank results, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and re-analysis.
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) Every 20 samples or for each new tune clock, whichever is more frequent.	Yes	Recovery <10%; affects nondetect	(1) Locate source of problem; reanalyze LCS	(1) If sample reanalysis is not possible, report non-

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
		(2) Concentration level near midpoint of curve. (3) Must contain all target analytes. (4) Matrix and preservative-specific (e.g., water, methanol). (5) Percent recoveries must be between 70-130% for target analytes except for "difficult" analytes(**) which must exhibit percent recoveries between 40-160%. (6) Can also be used as continuing calibration. NOTE: If used as continuing calibration standard, must be evaluated using Performance Standards, Corrective Actions, and Analytical Response Actions listed above for Continuing Calibration.		results for affected analyte in all samples analyzed under the LCS.	and associated samples if >10% of all analytes are outside of criteria. (2) If ≤10% of compounds are outside of the acceptance criteria, reanalysis is not required as long as recoveries are >10%. (3) If >10% of compounds are above the acceptance criteria (>130%), reanalysis is not required if affected compounds were not detected in associated samples.	conformance in laboratory narrative. (2) If recovery is outside of 70-130% for any analyte, including "difficult" analytes(**), report non-conforming compounds in laboratory narrative. (3) If re-analysis is performed within holding time and yields acceptable LCS results, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and re-analysis.
LCS Duplicate	Laboratory Analytical Accuracy & Precision	(1) Every 20 samples or for each new tune clock, whichever is more frequent. (2) Concentration level near midpoint of curve. (3) Must contain all target analytes. (4) Matrix and preservative-specific (e.g., water, methanol). (5) Percent recoveries must be between 70-130% for target analytes except for "difficult" analytes(**) which must exhibit percent recoveries between 40-160%. (6) Recommended to be run immediately after LCS in analytical sequence. (7) RPDs must be ≤20 for waters and solid.	Yes	Recovery <10%; affects nondetect results for affected analyte in all samples analyzed under this LCS.	(1) Locate source of problem; reanalyze LCS and associated samples if >10% of all analytes are outside of the recovery acceptance criteria. (2) If ≤10% of compounds are outside of the recovery acceptance criteria, reanalysis is not required as long as recoveries are >10%. (3) If >10% of compounds are above the recovery acceptance criteria	(1) If sample reanalysis is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of 70-130% for any analyte, including "difficult" analytes(**) or RPD >20 for any analyte, including "difficult" analytes**, report non-conforming compounds in laboratory narrative. (3) If re-analysis is performed within holding

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
					(>130%), reanalysis is not required if affected compounds were not detected in associated samples.	time and yields acceptable LCS results, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and re-analysis.
MS/MSD	Method Accuracy & Precision in Sample Matrix	(1) Every 20 samples (at discretion of laboratory or at request of data user). (2) Matrix-specific. (3) Concentration level near midpoint of curve. (4) Must contain all target analytes. (5) Percent recoveries between 70 – 130%. (6) RPDs ≤20 for waters and ≤30 for solids.	Yes ONLY when requested by the data user	Recovery <10%; affects nondetect result for affected analyte in unspiked sample only.	Check LCS; if recoveries are acceptable in LCS, narrate non-conformance.	Note exceedances in laboratory narrative.
Surrogates	Method Accuracy in Sample Matrix	(1) Minimum of 3 surrogates, at retention times across GC run. (2) Percent recoveries must be between 70-130% for individual surrogate compounds.	Yes	Recovery <10%; affects all nondetect VOC results in affected sample.	If one or more surrogates are outside of limits, reanalyze sample unless one of the following exceptions applies: (1) Obvious interference present (e.g., UCM). NOTE: If obvious interference is present and surrogate recovery would cause rejection of data (i.e., <10%), reanalyze sample on dilution. (2) Methanol-preserved samples: re-analysis is not	(1) Report recoveries outside of 70-130% in laboratory narrative. (2) If reanalysis yields similar surrogate non-conformances, the laboratory must report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the reanalysis only.

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
					required if % moisture >25 and surrogate recovery is >10%. (3) If one or more surrogates exhibit high recoveries and target analytes are not detected in sample, reanalysis is not required.	(4) If reanalysis is performed outside of the holding time and yields acceptable surrogate recoveries, the laboratory must report results of both analyses. (5) If sample is not re-analyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Internal Standards	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Minimum of 3 at retention times across GC run. (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard. (3) Retention times of internal standards must be within ±30 seconds of retention times in associated continuing calibration standard.	No	Recovery <20%; affects all nondetect results quantitated using affected internal standard in associated sample.	If one or more internal standards are outside of limits, reanalyze sample unless obvious interference present (e.g., UCM). NOTE: If obvious interference is present and internal standard area would cause rejection of data (i.e., <20%), reanalyze sample on dilution.	(1) Report nonconformances in laboratory narrative. Include actual recovery of internal standard and provide summary of analytes quantitated using the internal standard. (2) If reanalysis yields similar internal standard non-conformances, the laboratory must report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of the holding time and yields

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
						acceptable internal standard recoveries, the laboratory must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Quantitation	NA	(1) Quantitation must be based on internal standard calibration. (2) The laboratory must use the average response factor, linear or non-linear regression curve generated from the associated initial calibration for quantitation of each analyte. (3) The internal standard used for quantitation must be the one nearest the retention time of the subject analyte. (4) 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".[3]	NA	NA	NA	NA
Identification	NA	Refer to SW-846 8260B, Section 7.6.	NA	NA	NA	NA
General Reporting Issues	NA	(1) The laboratory must only report values ≥ the sample-specific reporting limit; optionally, values below the sample-specific reporting limit can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory	NA	NA	NA	(1) Qualification of the data is required if reporting values below the sample-specific reporting limit. (2) Complete analytical documentation for diluted and undiluted analyses must be made available for review

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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
		should report results for the lowest dilution within the valid calibration range for <u>each</u> analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported. (3) Refer to Section 3.3, TICs by GC/MS, for guidance. (4) All soil/sediment sample results preserved in methanol must be corrected for the methanol dilution as per Section 3.2.1 of this CAM protocol. (5) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (6) Refer to Appendix II A-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times.				during an audit. (3) TICs will be evaluated at the discretion of the data user consistent with the guidelines presented in Appendix II A–3. (4) The performance of dilutions must be documented in the laboratory narrative or on the report form. Unless due to elevated concentrations of target compounds, reasons for dilutions must be explained in the laboratory narrative. (5) If samples are not properly preserved (pH >2 for aqueous samples, solid samples not completely covered with appropriate preservative) or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (6) If samples are preserved and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative.

** Potentially "difficult" analytes include: acetone, methyl ethyl ketone, 4-methyl-2-pentanone, 2-hexanone, dichlorodifluoromethane, bromomethane, chloromethane, and 1,4-dioxane.

[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]If the RL is estimated due to unacceptable recovery of the lowest standard, the CAM RL has not been achieved; Question G of the "MassDEP MCP Analytical Protocol Certification Form" must be answered

Table II A-1: Specific QC Requirements and Performance Standards for VOCs (SW-846 8260B) Using WSC-CAM-II A

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

"NO" and this must be addressed in the laboratory narrative.

[3]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-II A

The MCP analyte list for WSC-CAM-II A is presented in Table II A-2. The list is comprised of potential contaminants that are readily-analyzable by WSC-CAM-II A.

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/service-details/oil-hazardous-material-list
- 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/lists/waste-site-cleanup-laws-and-regulations

Most of the analytes listed in Table II A-2 have a promulgated MCP Method 1 groundwater/soil standard. The remaining analytes listed are designated “consensus contaminants” and do not have promulgated MCP Method 1 Standards as of the publication date of this revision.

1.7.1 Analyte List Reporting Requirements for WSC-CAM-II A

While it is not necessary to request and report all the WSC-CAM-II A analytes listed in Table II A-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 a limited number of 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-II A to obtain “Presumptive Certainty” status.

Table II A-2: Analyte List for WSC-CAM-II A (SW-846 8260B)

Analyte	CASN	Analyte	CASN
Acetone [PP]	67641	Dichlorodifluoromethane (Freon 12)	75718
Amyl Methyl Ether (TAME), *tert*- [OXY]	994058	Dichloroethane, 1,1-	75343
Benzene	71432	Dichloroethane, 1,2-	107062
Bromobenzene	108861	Dichloroethylene, 1,1-	75354
Bromochloromethane	74975	Dichloroethylene, cis-1,2	156592
Bromodichloromethane	75274	Dichloroethylene, trans-1,2	156605
Bromoform	75252	Dichloropropane, 1,2-	78875
Bromomethane	74839	Dichloropropane, 1,3-	142289
Butylbenzene, sec- [2]	135988	Dichloropropane, 2,2-	594207
Butylbenzene, n- [2]	104518	Dichloropropene, 1,1-	563586
Butylbenzene, tert- [2]	98066	Dichloropropene, cis-1,3- [3]	10061015
Carbon Disulfide	75150	Dichloropropene, trans-1,3- [3]	10061026
Carbon Tetrachloride	56235	Diethyl Ether [OXY]	60297
Chlorobenzene	108907	Diisopropyl Ether (DIPE) [OXY]	108203
Chlorodibromomethane	124481	Dioxane, 1,4- [PP, 1]	123911
Chloroethane	75003	Ethyl Tertiary Butyl Ether (ETBE) [OXY]	637923
Chloroform	67663	Ethylbenzene	100414
Chloromethane	74873	Hexachlorobutadiene	87683
Chlorotoluene, 2-	95498	Hexanone (MNBK), 2- [PP]	591786
Chlorotoluene, 4-	106434	Isopropylbenzene (Cumene) [2]	98828
1,2-Dibromo-3-chloropropane [PP]	96128	Isopropyltoluene, p- [2]	99876
Dibromoethane, 1,2- (EDB)	106934	Methyl Ethyl Ketone (MEK) [PP]	78933
Dibromomethane	74953	Methyl Isobutyl Ketone (MIBK) [PP]	108101
Dichlorobenzene, 1,3- (m-DCB)	541731	Methyl Tertiary Butyl Ether (MTBE) [OXY]	1634044
Dichlorobenzene, 1,2- (o-DCB)	95501	Methylene Chloride	75092
Dichlorobenzene, 1,4- (p-DCB)	106467	Naphthalene	91203
Propylbenzene, n- [2]	103651	Trichloroethane, 1,1,2-	79005

Table II A-2: Analyte List for WSC-CAM-II A (SW-846 8260B)

Analyte	CASN	Analyte	CASN
Styrene	100425	Trichloroethylene (TCE)	79016
Tetrachloroethane, 1,1,1,2-	630206	Trichlorofluoromethane (Freon 11)	75694
Tetrachloroethane, 1,1,2,2-	79345	Trichloropropane, 1,2,3-	96184
Tetrachloroethylene	127184	Trimethylbenzene, 1,2,4-[2]	95636
Tetrahydrofuran (THF)	109999	Trimethylbenzene, 1,3,5-[2]	108678
Toluene	108883	Vinyl Chloride	75014
Trichlorobenzene, 1,2,4-	120821	Xylene, o-[4]	95476
Trichlorobenzene, 1,2,3-	87616	Xylene, m-[4]	108383
Trichloroethane, 1,1,1-	71556	Xylene, p-[4]	106423

PP – Poor purging efficiency may result in high reporting limits, as described in SW-846 Method 8260B, Section 1.1. May not meet some CAM QC performance standards for this method.

OXY – Oxygenate: gasoline additives, indicators of historical gasoline releases.

[1]Standard RL for this compound may not be able to achieve regulatory compliance limit.

[2]Evaluate results for these compounds using the standard/criteria for C_9 – C_{10} Aromatics. If the sum of these compounds exceeds the C_9 – C_{10} Aromatics standard/criteria, it may be prudent to conduct an independent volatile petroleum hydrocarbon (VPH) analysis (MADEP-VPH-04-1.1).

[3]Regulated as 1,3-Dichloropropene, Mixed Isomers (CAS Number: 542756). Report as the additive sum of the concentrations of cis-1,3-Dichloropropene and trans-1,3-Dichloropropene.

[4]Regulated as Xylenes (Mixed Isomers). Report as Total Xylenes or as individual Xylene isomers, if separated chromatographically.

CASN – Chemical Abstracts Service Numbers

NOTE: Other VOCs may also be analyzed using the WSC-CAM-II A 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-II A

3.1 General Reporting Requirements for WSC-CAM-II A

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-II A

Specific QC requirements and performance standards for WSC-CAM-II A are presented in Table II A-1. Specific reporting requirements for WSC-CAM-II A are summarized below in Table II A-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 II A-3 Routine Reporting Requirements for WSC-CAM-II A (SW-846 8260B)

Parameter	Required Analytical Deliverable
GC/MS Tunes	***NO***
Initial Calibration	***NO***
Initial Calibration Verification	***NO***
Continuing Calibration (CCAL)	***NO***
Method Blank	***YES***
Laboratory Control Samples (LCSs)	***YES***
LCS Duplicates	***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)***
Surrogates	***YES***
Internal Standards	***NO***
Tentatively Identified Compounds (TICs)	***YES (if requested by data user)***
Identification and Quantitation	***NO***
General Reporting Issues	***YES***

3.2.1 Data Correction for VOC Concentrations Due To Methanol Preservation Dilution Effect

VOC analytical results for soil/sediment samples must be corrected by the laboratory for the methanol preservation dilution effect. If this correction is neglected, the potential for under reporting volatile organic concentrations is more pronounced as the "as-received" % moisture content of the soil/sediment sample increases.

VOC concentrations and the recovery of matrix spikes and/or surrogates in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume, as a consequence of the moisture content of the sample, is not considered. The total solvent volume is the additive sum of the volume of methanol and the sample moisture content that partitions into the methanol. The total solvent/water volume (Vt) is calculated using the following equation:

$$\text{mL solvent/water (Vt)} = \text{mL of methanol} + ((\%\ \text{moisture}/100) \times \text{g of sample})$$

This "corrected" Vt value should be substituted directly for the Vt value in the equation shown in SW-846 Method 8000B, Section 7.10.1.2. It should be noted that whether corrected or uncorrected, the Vt value

used to calculate VOC concentrations must also take into consideration the volume of any surrogate/spiking solution added to soil/sediment samples.

3.2.2 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the target analytes exceed the concentration of their respective highest calibration standard or any non-target peak exceeds the dynamic range of the detector (i.e., "off scale"), the RL for each VOC must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL for the diluted sample, RL_d:

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

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.

NOTE: **Over dilution is an unacceptable laboratory practice.** The post-dilution concentration of the target analyte with the highest concentration must be at least 60 to 80% of its associated highest calibration standard. This will avoid unnecessarily high RLs for other target analytes which did not require dilution.

3.3 Tentatively Identified Compounds (TICs) by GC/MS

The evaluation of TICs in conjunction with GC/MS analyses (WSC-CAM-II A and WSC-CAM-II B) is a powerful and cost-effective analytical tool that can be particularly effective in assessing locations with suspect disposal practices, complex or uncertain site history, and/or sites that require detailed evaluation of critical exposure pathways. When GC/MS analytical methods are utilized in support of MCP decision-making, an analysis of TICs is:

Required when drinking water samples are analyzed (Refer to WSC-CAM-VII A for a definition of "drinking water"),
Should be considered in support of site characterization activities for releases at locations with complex and/or uncertain history,
Not usually expected at petroleum-only sites,
Not usually expected when the contaminants of concern have been previously identified, and/or
Not usually expected when used to determine the extent and magnitude of contamination associated with a "known" release of OHM.

It should be noted that TICs only need to be evaluated by the laboratory when specifically requested by the data user.

3.3.1 Reporting of TICs

If evaluated, all TICs that meet the chromatographic criteria presented in Section 1.0 of Appendix II A-3 must be reported by the laboratory either in the laboratory report or in the laboratory narrative. In turn, the data user must include a discussion regarding the disposition of all reported TICs as part of the MCP submittal. Depending on specific site circumstances (e.g., a potentially toxic contaminant is found in a private drinking water supply well, etc.), resampling/re-analysis with analyte-specific calibration and QC may be required to definitively assess the risk posed by the TIC to human health and the environment. Guidance for the evaluation of TICs for MCP decision-making is presented in Appendix II A-3 of this document.

Appendix II A-1

Sample Collection, Preservation, and Handling Procedures for Volatile Organic Compound Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for VOCs 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)*. The selection of preservation for samples analyzed for VOCs should be based on the data quality objectives of the sampling program.

Aqueous Samples				
Matrix	**Analyte**	**Container[1]**	**Preservative[2,3]**	**Holding Time[5]**
Aqueous Samples, with no Residual Chlorine	Most Volatile Organic Compounds	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	Adjust pH to < 2.0 by addition of HCl or $NaHSO_4$ to container before sampling. Cool to ≤ 6ºC but not frozen.	14 days
	MTBE or other fuel oxygenates with heated purge-and-trap (>40ºC) sample introduction only	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	0.7 g of trisodium phosphate dodecahydrate (TSP) per 40 ml. Verify pH >11.0. Cool to ≤ 6ºC but not frozen.[4]	14 days
	Volatile organics susceptible to acid hydrolysis, abiotic degradation or loss during storage	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	Cool to ≤ 6ºC but not frozen.	Analyze ASAP but not more 7 days
Aqueous, with Residual Chlorine	Presence of chlorine residual is usually associated with drinking water samples. Collect sample in at least two (2) x 40-mL VOC vials w/ Teflon-lined septa screw caps containing either 25 mg of Ascorbic Acid or 3 mg of Sodium Thiosulfate. If Residual Chlorine > 5 mg/L, additional dechlorination agent may be required After dechlorination is confirmed, preserve as above based on compound classes.			

[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]Preservation of samples by acidification to pH <2.0 and analysis within 14 days is considered a suitable preservation technique for samples not expected to contain reactive contaminants of concern.

[3]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.

[4]TSP may also be used to preserve samples for BTEX and/or VPH analysis (i.e., it would not be necessary to obtain samples in separate vials).

[5]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.

Soil, Sediment and Waste Samples			
Matrix	**Container[a]**	**Preservation[1,2,3]**	**Holding Time[1,4]**
Soil/Sediment Samples ***High-Level Analysis***	Extrude soil/sediment sample directly into a pre-weighed vial* w/ Teflon-lined septa screw caps: Vials must contain 1 mL purge-and-trap grade methanol for every gram soil/sediment. *(1) x 60-mL vial or (1) x 40-mL vial	1 mL methanol for every gram soil/sediment; add methanol before or at time of sampling; Cool to ≤ 6ºC but not frozen; protect from light	14 days
	EnCore samplers[5] or other suitable coring device	Cool to ≤ 6ºC (but not frozen) in field; 48 hours from date collected until methanol preservation (1 mL methanol for every gram soil/sediment).	
Soil/Sediment Samples ***Low-Level Analysis*** by Closed-System Purge-and-Trap Process (SW-846 Method 5035A)	5 g EnCore samplers[5] or other suitable coring device.	Cool to ≤ 6ºC in field; 48 hours from date collected until extrusion in reagent water followed by freezing (< -7ºC) or analysis within 48 hours of sample collection (see Note 2). Alternatively, samples may be frozen to < -7ºC in the field using gel packs.	14 days[7]
	Extrude 5 grams of sample directly into (2) x pre-weighed 40 ml VOC vials containing 5 mL of reagent water (with or without chemical preservation; see Note 2) and a Teflon-coated magnetic stir bar[6].	Cool to ≤ 6ºC in field and deliver to laboratory for freezing (< -7ºC) or analysis, both within 48 hours of sample collection. Alternatively, samples may be frozen to < -7ºC in the field using gel packs.	
Waste Samples	Collect sample in one (1) x 500 mL amber wide mouth jar with a teflon lined screw cap.	No special preservation required	14 days

[a]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. Caution: samples to be frozen should not be stored vertically. These samples should be stored horizontally or at least at a 45 degree angle to avoid breakage from expansion.

[1]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 or if soil/sediment samples are not properly preserved, data users should consider nondetect results as unusable and positive results as estimated with a significantly low bias.

[2]A number of acceptable alternative preservation techniques requiring close communication with the receiving laboratory that require field cooling (≤ 6°C) with subsequent laboratory preservation (freezing, methanol, $NaHSO_4$, etc.) and/or expedited analysis (48 hours) are presented in Appendix A, "Collection and Preservation of Aqueous and Solid Samples for Volatile Organic Compounds (VOC) Analyses" of the document entitled , "Closed System Purge-and-Trap and Extraction for Volatile Organics In Soil and Waste Systems", an updated version of SW-846 Method 5035A published by US EPA In July 2002. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5035a_r1.pdf

[3]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.

[4]Holding time is calculated from the time of sample collection and only applies to samples that have been frozen and chemically preserved.

[5]EnCore Sampler may not be suitable for certain soil types; refer to guidance in SW-846 Method 5035A.

[6]Not required if closed system purge-and-trap device employs a means of stirring the sample other than a magnetic stirrer.

[7]Any samples which are frozen must be analyzed within 48 hours of thawing.

Additional Sample Handling and Preservation Notes:

Aqueous Samples:

1. The most common preservation technique for aqueous samples analyzed for VOCs is the addition of HCl to the container prior to sampling (pH to < 2.0) and cooling to ≤ 6°C. Because of their reactivity, solubility and/or volatility, alternative preservation techniques may be required for some classes of analytes (reactive, MTBE and other fuel oxygenates, etc.). In the unusual circumstance that contaminants of concern at a disposal site require mutually exclusive preservation techniques (acid preservation/with cooling for BTEX and no acid preservation/with cooling for reactive compounds), separate sampling containers to accommodate the different preservation techniques may be required. In all cases the selection of preservation technique for samples analyzed for VOCs should be based on the data quality objectives of the sampling program.

2. If effervescence occurs upon addition of HCl, samples should be collected without the acid preservative. Where acid preservation is not used, the analysis holding time is seven (7) days from date collected to date analyzed.

Low-Level and High-Level Solid Samples:

An extra aliquot of sample must be collected in a 4 oz. glass jar with no preservative so that the laboratory can perform a percent solids analysis. If the same sample is being submitted to the laboratory for additional analyses which require no preservative, the percent solids analysis can be measured using an aliquot from these sampling containers. Otherwise, a separate bottle will be required.

Appendix II A-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-II A (VOCs by GC/MS: SW-846 8260B)	
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 sample weight logs Freezer logs
Initial Calibration Data	Summary of response factors for all standards in initial calibration; average response factors, %RSDs, correlation coefficients and coefficients of determination for all target compounds 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	Summary of percent recoveries for all target compounds Chromatograms for all ICVs Quantitation reports for all ICVs
Continuing Calibration Data	Summary of %Ds and response factors Chromatograms for all continuing calibration standards Quantitation reports for all continuing calibration standards Concentrations of standards used must be clearly presented
Sample Results	Chromatograms for all sample analyses, reanalyses, and dilutions Quantitation reports for all sample analyses,

DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-II A (VOCs by GC/MS: SW-846 8260B)	
	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 positive results in method blanks 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 Results (if performed)	Chromatograms for all MS/MSDs Quantitation reports for all MS/MSDs 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
GC/MS Tune Data	BFB tune raw data: chromatogram, mass listing of BFB, and summary of tune results
QC Summaries	Surrogate recoveries Internal standard performance
Other Information	Volume of surrogate added to methanol extracts Demonstration that ICV prepared from second source standard
Quantitation reports must exhibit area counts of target compounds, internal standards, and surrogates.	

Appendix II A-3

Guidance for Evaluation of Tentatively Identified Compounds (TICs) for WSC-CAM-II A under the MCP

A logic diagram for the Evaluation of Tentatively Identified Compounds (TICs) for WSC-CAM-II A under the MCP is presented in Exhibit II A-1. This exhibit graphically presents a systematic approach to evaluate TICs based on chromatographic, mass spectral, and toxic spectral characteristics criteria.

1.0 Specific Criteria for the Evaluation of TICs

1.1 Chromatographic Criteria

- Initially include all of the non-target compounds that have a peak area count of $\geq$ 10% of the nearest internal standard.

1.2 Mass Spectral Criteria

- All spectra must be evaluated by a qualified mass spectrometrist.
- The spectral library match must be $\geq$ 85% for a tentative identification to be made.
- The major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within $\pm$ 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or for the presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.
- Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different chromatographic retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs (as a mixture of two isomers).
- Spectra identified as “unknown” should be assigned to a general chemical class, if possible. Classification as a halogenated hydrocarbon, aldehyde/ketone, carboxylic acid, or cyano compound, etc. is acceptable. An explanation as to why more specific identification cannot be made (e.g., truncated spectra due to insufficient mass scanning range) must be provided in the laboratory narrative to support any “unknown” classification.
- TICs, which are identified as petroleum aliphatic hydrocarbons, do not have to be reported as TICs. However, there must be a statement in the laboratory narrative discussing the presence of these hydrocarbons in the sample(s).

After the above criteria are met, the top ten (10) compounds, chosen by comparing the area of the TIC to the area of the nearest internal standard, must be tentatively identified, quantitated, and reported.

1.3 Toxic Spectral Characteristics Criteria

Regardless of the peak area count in relation to the nearest internal standard, the laboratory must evaluate the spectra for any compound if the mass spectrum:

- Exhibits a characteristic chlorine or bromine spectral pattern.

2.0 Reporting Criteria

All TICs must be reported by the laboratory with the clear indication that the reported concentration is an estimated value unless analyte-specific calibration and QC were performed as discussed in Section 3.3.1. This reporting requirement may be fulfilled by discussion in the laboratory narrative, or by some other laboratory reporting convention to qualify the sample results. General laboratory reporting requirements are presented in WSC-CAM-VII A, Section 2.4.

If a data user determines that the presence of the TIC at the estimated concentration reported by the laboratory may appreciably increase the overall risk posed by the site or the utility/cost of the potential remedial measures under consideration, additional analytical work is recommended to verify the identification and/or concentration of the reported TIC either by reanalysis or resampling. This contingency will require additional coordination and communication between the laboratory and the data user.

Exhibit IIA-1

Analytical Note: TICs need only to be evaluated by the laboratory when specifically requested by the data user.