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)

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VII Sampling, Data Evaluation and Reporting Procedures for MCP Activities

A Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data

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1.0 INTRODUCTION

The purpose of this document is to provide the regulated community with quality assurance and quality control (QA/QC) guidance regarding the acquisition and reporting of analytical data submitted in support of response actions conducted at disposal sites regulated under M.G.L. c. 21E and 310 CMR 40.0000, the Massachusetts Contingency Plan (MCP).

Section 2.0 of this document articulates the analytical components of a recommended QA/QC and data reporting program that may be electively utilized by parties conducting MCP response actions. Data conforming to the specifications of this program will be considered by the Department to meet the broad requirements of 310 CMR 40.0017 and 40.0191 regarding scientific defensibility, precision and accuracy, and documentation and reporting, and will assure parties of overall "Presumptive Certainty" for analytical data submittals.

Section 3.0 provides general guidance regarding the principles of QA/QC programs, along with regulatory performance standards and agency expectations for MCP data submittals. This information is provided as background for all parties and as relevant guidance for parties who elect not to use the Presumptive Certainty option described below in Section 2.0.

2.0 PRESUMPTIVE CERTAINTY FOR ANALYTICAL DATA

2.1 Overview Of Presumptive Certainty Process

310 CMR 40.0017 and 40.0191(2)(c) require that analytical and environmental monitoring data be scientifically valid and defensible, and of a level of precision and accuracy commensurate with its stated or intended use, taking into consideration relevant policies and guidelines issued by the Department and the Environmental Protection Agency (EPA). 310 CMR 40.0017 (3)(i) further provides that all response action submittals to the Department shall include details on any known conditions or findings which may affect the validity of analytical data, including unsatisfactory results obtained for blank, duplicate, surrogate or spiked samples.

To facilitate application of these broad performance standards, MADEP has published a "Compendium of Analytical Methods (CAM)", which provides a series of recommended protocols for the acquisition, analysis, and reporting of analytical data in support of MCP decisions. While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" for analytical data acceptance by agency reviewers.

In order to achieve Presumptive Certainty, parties must:

(a) Use the "MCP Analytical Methods" detailed in the CAM;
(b) Comply with the applicable QC analytical requirements prescribed for the individual testing procedures in the CAM;
(c) Evaluate, and narrate, as necessary, compliance with performance standards described for the individual testing procedures in the CAM; and
(d) Adopt the reporting formats and elements specified in the CAM

In achieving the status of Presumptive Certainty, parties will be assured that analytical data sets[1]:

- ✓ 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;
- ✓ May be used in a data usability assessment, and, if in compliance with all MCP Analytical Method standards, laboratory QC requirements, recommended limits and action levels the data set will be considered usable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to support a data representativeness assessment.

Presumptive Certainty requirements are to be considered minimum requirements. Efforts that go beyond these minimum requirements (e.g., including additional analytes in a specific methodology) are considered compliant with the Presumptive Certainty concept and provisions, and need not be identified and discussed as an "exception".

A logic diagram detailing the Presumptive Certainty approach is presented in Figure VII A-1. Additional details on the concept and status of Presumptive Certainty may be obtained in WSC-CAM-I, *Overview of the Analytical Data Enhancement Process for the Massachusetts Contingency Plan (MCP)* at www.mass.gov/dep/bwsc/files/data/overmcp.pdf

Parties who elect not to utilize the Presumptive Certainty option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document that the overall level of *analytical data quality* is adequate for the intended use of the data, including but not limited to data usability and data representativeness assessments.

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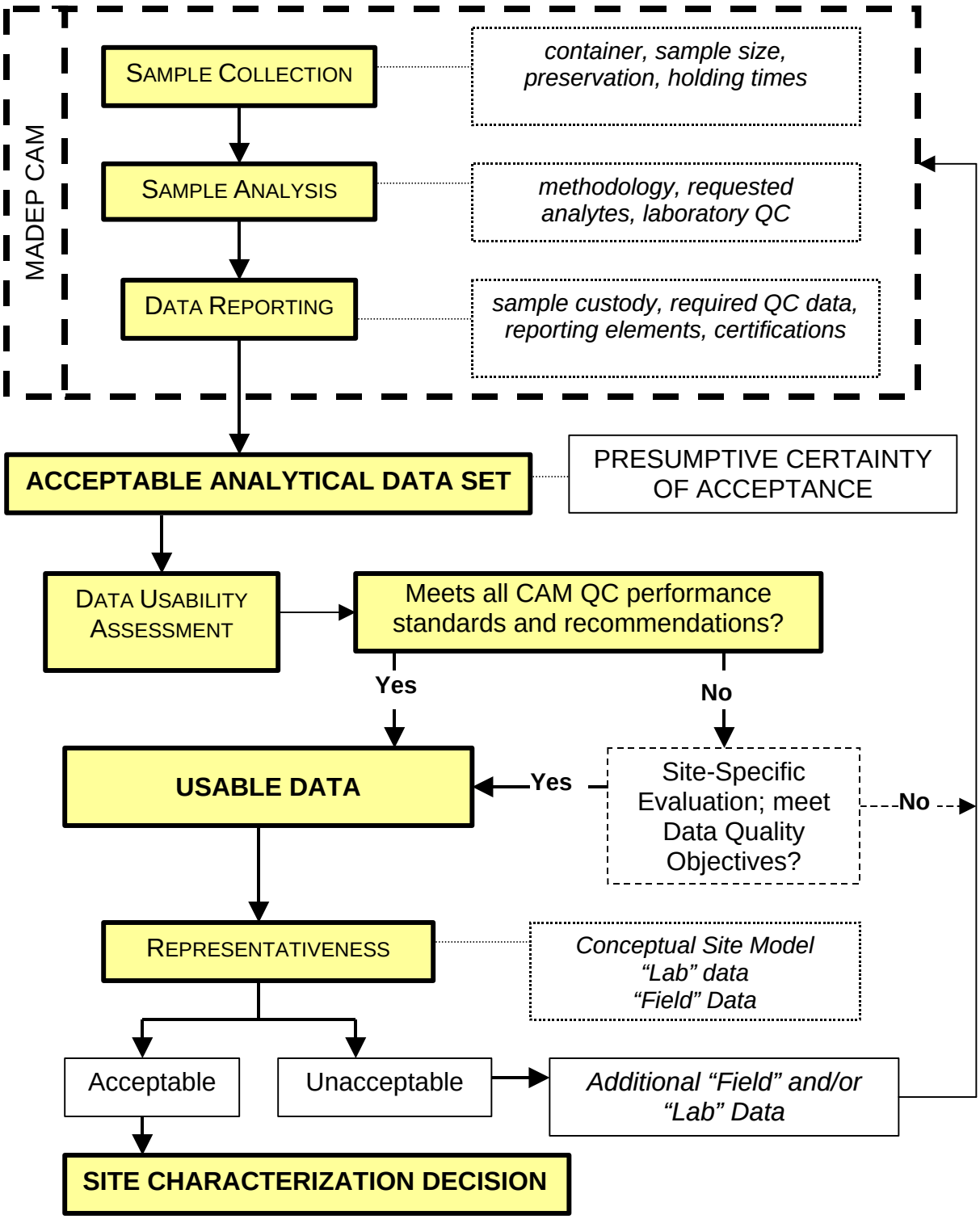
1. A group of samples collected, processed, and transported to a laboratory for analyses under similar conditions.

Title: Logic Diagram for Presumptive Certainty Concept for MADEP Compendium of Analytical Methods (CAM)



2.2 Summary of Field Requirements for Presumptive Certainty

2.2.1 Sample Acquisition and Submittal

Parties seeking Presumptive Certainty are required to provide the laboratory with a sufficient volume of sample, in an appropriate container, properly preserved and within a time period that will not compromise analytical holding times for the analysis specified. Sample collection, preservation and holding time information for individual analytical methods and matrices are described in Appendix VII A-1. In addition, sample collection information and analytical instructions should be clearly documented on a Chain-of-Custody form that must accompany all samples submitted to the laboratory for analysis in support of MCP decision making. It is also recommended that a Supplemental MCP Analytical Services Request Form (see Section 2.4.7), or equivalent analytical instruction, be provided to the laboratory with each data set.

It should be noted that this document does not provide any specific guidance regarding proper sampling procedures, approaches to achieve representative sampling nor the type and frequency of field quality control samples required to evaluate overall data usability.

2.3 Use of MCP Analytical Methods and Analyte Lists in CAM

The MADEP Compendium of Analytical Methods (CAM) is a compilation of information regarding commonly used analytical protocols (e.g., EPA's SW-846 Methods, MADEP's VPH, etc.). In addition to providing a succinct summary of each analytical method, the CAM further articulates detailed quality control procedures and performance standards, analyte lists, reporting formats, and other methodological elements – details that may not have been specified and/or are cited as discretionary in the original publications (e.g., EPA's SW-846 Methods). Incorporation of all such provisions into a method is referred to as an "MCP Analytical Method".

Specifications for each MCP Analytical Method of interest are available in the CAM at: www.mass.gov./dep/bwsc/files/data/qaqcdocs.htm.

2.3.1 Performance Standards for MCP Analytical Methods

Individual MCP Analytical Methods describe detailed method-specific quality control requirements with associated performance standards. Conformance with these performance standards is evaluated by the analysis of various batch quality control samples (data quality indicators such as LCSs, etc.) and the comparison of these analytical results to pre-established ranges of acceptable analytical variability.

While it is not expected that every performance standard will be met in every analytical batch for each method analyte, it is required that each non-compliance be narrated in the Environmental Laboratory case narrative. This information must be given due consideration when evaluating overall analytical data usability in support of MCP decision-making.

2.3.2 Analyte Lists for MCP Analytical Methods

While it is not necessary to request and report all listed analytes in an MCP Analytical Method to obtain Presumptive Certainty, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP 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:

- ✓ Uncharacterized 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 that a desire to avoid detection and quantitation of a contaminant that is present or likely present at a site above background levels is <u>not</u> a valid reason to limit an analyte list, and that such an action could constitute a criminal violation of MGL c. 21E.

In cases where a truncated list of method analytes is selected, laboratories must still employ the method-specific quality control requirements and performance standards associated with the requested analytes list to obtain Presumptive Certainty status.

2.4 Environmental Laboratory Reporting

Parties seeking Presumptive Certainty must direct the laboratory to include the information specified in this section in their analytical data report as a component of the Presumptive Certainty process.

Certain QA/QC reporting recommendations are method-specific; therefore, the QA/QC information included in the Environmental Laboratory report is dependent on the analyses

performed. In addition, it is recommended, consistent with Safe Drinking Water Act (SDWA) certification requirements, that additional information be kept on file for ten (10) years to facilitate further in-depth review or for audit support. The associated performance standards for the MCP Analytical Method of interest should be consulted for the required QA/QC reporting elements.

2.4.1 Laboratory Information

This section must contain all laboratory identification information, including:

- Laboratory Name, Address, Phone Number
- Current Certifications the laboratory may hold and Certification ID #s
- Client Name, Client Contact, Address, Phone Number
- Project Identification
- Sample Identification - Field & Laboratory

2.4.2 Sample Results Section

The results section must contain, but is not necessarily limited to, the following information:

- Sample Identification: Field and Laboratory
- Method Reference
- Preparation Method
- Analysis Method
- Analyst Initials
- Target Analytes and Concentrations
- Units (mass/mass or mass/volume – not “ppm” or “ppb”; Solids must be reported on a dry weight basis)
- Reporting Limits – based upon the lowest calibration standard and adjusted for sample size, % moisture, dilution factors, etc.
- Data Qualifiers, if applicable,
- Date of Collection
- Date of Preparation, if applicable
- Date and Time of Analysis
- Dilution/Concentration Factors
- % Moisture or % Solid for solid samples
- Matrix

2.4.3 Required Sample- and Batch-Specific Quality Control Information

The quality control information reported must be method-specific. A summary of this information is included in the QA/QC Requirements and Performance Standards tabulations for each MCP Analytical Method. In general, the Environmental Laboratory report must include, but is not necessarily limited to, the following project and/or method specific performance and QA/QC related information:

- Method Blank Results
- Surrogate Spike Recoveries (organics only)
- Laboratory Control Sample (LCS) Recoveries
- LCS Duplicate Recoveries
- Matrix Spike Recoveries, if applicable
- Matrix Spike Duplicate Recoveries and Relative Percent Differences (RPDs), if applicable
- Laboratory Matrix Duplicate RPDs, if applicable
- Analytical Holding Time and Preservation Information

2.4.4 Environmental Laboratory Report Certification Statement

Every Environmental Laboratory report must include a certification pertaining to the analytical procedures and associated QC criteria and performance standards for all data included in the report.

As with the VPH/EPH Methods, the Department is specifying a required reporting content for presenting and certifying data. The required information is provided in Exhibit VII A-1. While laboratories are not required to adopt the specific format provided in this Exhibit for MCP Analytical Methods, all specified information and data must be succinctly and clearly presented. Moreover, the certification form must clearly indicate each and every sample for which the attestations are being made, to be included towards the front of such submittals.

The analytical report certification includes a series of “yes” or “no” questions, followed by a statement attesting to the accuracy and completeness of those responses and of the attached laboratory report(s), which is signed by an authorized laboratory representative. In order to achieve a status of Presumptive Certainty, it is necessary to answer **YES** to the first 4 questions. A **NO** designation must be fully discussed in an attached Environmental Laboratory case narrative (although the associated submittal will not have Presumptive Certainty due to a **NO** designation, the use of the CAM procedures and Certification Form is still recommended to facilitate site-specific review by DEP staff.)

Two additional questions are asked that have relevance to data usability and representativeness considerations. In order to achieve a status of Presumptive Certainty, both questions must be answered – although it is NOT necessary to respond in the affirmative to preserve the Presumptive Certainty Option. Once again, a **NO** designation must be fully discussed in an attached Environmental Laboratory case narrative.

MADEP MCP Response Action Analytical Report Certification Form

MADEP MCP ANALYTICAL METHOD REPORT CERTIFICATION FORM

Laboratory Name:	Project #:
Project Location:	MADEP RTN[1]:

This Form provides certifications for the following data set: [list Laboratory Sample ID Number(s)]

Sample Matrices: ☐ Groundwater ☐ Soil/Sediment ☐ Drinking Water ☐ Other: _____

MCP SW-846 Methods Used	8260B ( )	8151A ( )	8330 ( )	6010B ( )	7470A/1A ( )
	8270C ( )	8081A ( )	VPH ( )	6020 ( )	9014M [2] ( )
As specified in MADEP Compendium of Analytical Methods. (check all that apply)	8082 ( )	8021B ( )	EPH ( )	7000 S[3] ( )	7196A ( )

1 List Release Tracking Number (RTN), if known
2 M – SW-846 Method 9014 or MADEP Physiologically Available Cyanide (PAC) Method
3 S – SW-846 Methods 7000 Series List individual method and analyte.

An affirmative response to questions A, B, C and D is required for "Presumptive Certainty" status

A	Were all samples received by the laboratory in a condition consistent with that described on the Chain-of-Custody documentation for the data set?	☐ Yes ☐ No[1]
B	Were all QA/QC procedures required for the specified analytical method(s) included in this report followed, including the requirement to note and discuss in a narrative QC data that did not meet appropriate performance standards or guidelines?	☐ Yes ☐ No[1]
C	Does the data included in this report meet all the analytical requirements for "Presumptive Certainty", as described in Section 2.0 (a), (b), (c) and (d) of the MADEP document CAM VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data"?	☐ Yes ☐ No[1]
D	***VPH and EPH Methods only***: Was the VPH or EPH Method conducted without significant modifications (see Section 11.3 of respective Methods)	☐ Yes ☐ No [1]

A response to questions E and F below is required for "Presumptive Certainty" status

E	Were all analytical QC performance standards and recommendations for the specified methods achieved?	☐ Yes ☐ No[1]
F	Were results for all analyte-list compounds/elements for the specified method(s) reported?	☐ Yes ☐ No[1]

[1] *All Negative responses must be addressed in an attached Environmental Laboratory case narrative.*

I, the undersigned, attest under the pains and penalties of perjury that, based upon my personal inquiry of those responsible for obtaining the information, the material contained in this analytical report is, to the best of my knowledge and belief, accurate and complete.

Signature:_____	**Position:**_____
Printed Name:_____	**Date:**_____

2.4.5 Environmental Laboratory Environmental Laboratory case narrative

The purpose of the Environmental Laboratory case narrative is to provide a means of communication (and documentation) from the laboratory to the data user. The objective of this communication is to concisely inform the data user of any analytical issues associated with project-specific or method-specific performance and/or QA/QC requirements. The scope of the narrative is to include all relevant information so that the data user will be able to make informed decisions concerning the use of the data reported. The narrative must address all relevant information, including information the laboratory is required to retain (and be made available to the Department on request for reviews and/or audits) as well as the information required to be included in the report.

The Environmental Laboratory case narrative is to be in the form of an exception report where only the anomalies related to project- and/or method-specific performance and QA/QC are disclosed and discussed.

As applicable and appropriate, the following specific information is to be provided in the narrative:

- Problems with sample condition, preservatives, and/or temperature;
- Qualifications regarding the identification of Tentatively Identified Compounds (TICs), where required and applicable;
- Non-routine QC Requirements, if provided to laboratory;
- Laboratory report certification section follow-up to “no” answers appearing on the Analytical Report Certification Form (Exhibit VII A-1);
- QA/QC nonconformance for performance standards (e.g., blanks and LCS), as well as nonconformances not required to be provided in the Environmental Laboratory report (e.g., calibration);
- Method modifications and corrective actions, if applicable;
- Holding time exceedances; and
- Obvious discrepancies in sample description information recorded on the Chain-of-Custody form supplied by the sampler, as applicable.

If there are no exceptions or analytical issues to report, the narrative must include (and may consist solely of) a statement that documents that there are no relevant data issues to discuss.

2.4.6 Completed Chain of Custody

The Environmental Laboratory report must append a copy of the chain of custody submitted with the samples. If no chain of custody is provided, the Environmental Laboratory case narrative should so indicate. The chain of custody must include the following information if applicable to the samples being analyzed:

- Sample identification
- Sample type
- Date and time of collection
- Sample collector's name
- Sample preservative
- Field filtration or other field preparation procedures used, and
- Relinquished and receipt signatures, dates, times

2.4.7 Supplemental MCP Analytical Services Request Form

In many instances, the information provided with the chain-of-custody form does not provide adequate instruction to the laboratory for MCP analytical requests, whether or not "Presumptive Certainty" status is requested. At a minimum, it is recommended that the data user provide the laboratory with additional information that clearly articulates whether MCP "Presumptive Certainty" status is being requested or not; affirms that samples were collected in appropriate containers, and properly preserved or require additional laboratory preservation; specifies required analyte lists and reporting limits; and identifies any field QC support to be provided by the laboratory. In addition, drinking water samples, as described in Section 2.5, should be identified and specific instruction regarding tentatively identified compound (TIC) reporting and the analysis of contingency field quality control samples as described in Table VII A-1must be provided, as appropriate.

Exhibit VII A-2, Supplemental MCP Analytical Services Request Form, provides a convenient means for providing this pertinent information to the laboratory. It is recommended that this form, or an equivalent listing of supplemental information, be attached to the Chain-of-Custody Form for each data set for which MCP analytical services are being requested. Use of this form (see Exhibit VII A-2) is <u>not</u> a prerequisite for obtaining "Presumptive Certainty" status.

Exhibit VII A-2 Supplemental "Presumptive Certainty" Status Analytical Services Request Form

SUPPLEMENTAL "PRESUMPTIVE CERTAINTY" STATUS REQUEST FOR MCP ANALYTICAL SERVICES FORM

Client Name: _____	Project Name: _____
Project Location: _____	MADEP RTN [1] _____
Chain of Custody Reference: _____	Data Set[2] Reference: _____

General Questions:

Is MCP Analytical Presumptive Certainty status being requested for the referenced data set*? ** Laboratory must use approved MCP Analytical Methods*	☐ Yes[3] ☐ No
Were all samples comprising this data set collected in appropriate containers as specified in CAM VII A, Appendix VII A-1 for requested analytes ?	☐ Yes ☐ No
Were all samples preserved as specified in CAM VII A, Appendix VII A-1 for requested analytes ?	☐ Yes ☐ No
Were all samples that require preservation at 4 °C maintained at this temperature from time of collection to the time samples were received by the laboratory?	☐ Yes ☐ No
Are any of the soil/sediment samples in the data set preserved by freezing or require freezing (< 7 °C) by the laboratory (within 48 hours of the time of collection)	☐ Yes ☐ No
Should laboratory report standard MCP Analyte List for requested analytical methods?	☐ Yes ☐ No[4]
Specify minimum Reporting Limits (RLs) for aqueous samples (Method 1 GW-1, RC[5] GW-2, etc.)	
Specify minimum Reporting Limits (RLs) for soil/sediment samples (Method 1 S-1 Soil & GW-3, etc.)	
Are Matrix Spikes (MS) or MS Duplicates required for this data set? Has adequate sample volume/duplicate samples been identified and/or provided?	☐ Yes[6] ☐ No ☐ Yes ☐ No
Are any of the samples in the data set characterized as "drinking water" as described in CAM VII A, Section 2.5? If **YES**, samples identified as "drinking water" must be analyzed using analytical methods specified in 310 CMR 22.06 B (10), i.e., EPA 500 Series for organics, EPA 200 Series for metals, etc., and require analysis of Tentatively Identified Compounds (TICs), if GC/MS analyses requested, Field Duplicates, and Trip Blanks as described in CAM VII A, Section 2.5.	☐ Yes ☐ No
Field Duplicate Samples provided and identified for all "drinking water" samples*.	☐ Yes ☐ No
Trip Blanks provided and identified for all "drinking water" samples *. **** Complete analysis only if target Analyte is encountered above RL.***	☐ Yes ☐ No
Is any alternative, supplemental or non-routine QC required for this data set?	☐ Yes[7] ☐ No

1. MCP Release Tracking Number
2. A group of samples collected, processed and transported to a laboratory for analyses under similar conditions
3. Laboratory must use approved MCP Analytical Methods
4. Attach modified analyte list (may include non-standard Analyte List compounds)
5. MCP Reportable Concentration (310 CMR 40.1600, Massachusetts Oil and Hazardous Material List)
6. List identifying candidate samples for MS and/or MSD attached. **Data user responsible to provide laboratory with adequate sample volume to prepare field QC samples**.
7. Attached description of alternative, supplemental or non-routine QC.

Signature _____ Date _____

2.5 Special Consideration for Drinking Water Samples

Any sample collected for MCP purposes from a residential or public water supply well and submitted to a laboratory for analysis must be accompanied by the field quality control samples as specified in Table VII A-1. These specific field quality control sample requirements for "drinking water samples" are to insure a high confidence in the results should an oil or hazardous material be detected in water that is actually used for human consumption.

TABLE VII A-1 MINIMUM FIELD QC SAMPLE FREQUENCY FOR SAMPLES REGULATED UNDER 310 CMR 22 (DRINKING WATER SAMPLES ONLY)

ANALYTES	METHOD(S)	QC ELEMENT		
		Matrix Spike (MS) [a]	Field Duplicate [b]	Trip Blank [c]
VOCs & VPH Target Analytes	EPA Method 524.2	Not Mandatory [d]	If analyte detected	1 per cooler
SVOCs, Pesticides; PCBs Herbicides, Nitroaromatics & EPH Target Analytes	EPA Series 500 Methods	Not Mandatory [d]	If analyte detected	Not Mandatory [d]
VPH Ranges	MADEP VPH	Not Mandatory [d]	If analyte detected	1 per cooler
EPH Ranges	MADEP EPH	Not Mandatory [d]	If analyte detected	Not Mandatory [d]
Metals	EPA Series 200 Methods	1 per 20 samples	If analyte detected	Not Mandatory [d]
Total Cyanide & Physiologically Available Cyanide (PAC)	SW-846 Method 9014; and MADEP PAC	1 per 20 samples	If analyte detected	Not Mandatory [d]

[a] Matrix Spikes must be selected that represent the most significant exposure points to human health and the environment.

[b] Field Duplicate MUST be analyzed if one or more analytes are detected in the primary sample above the RL. Duplicate samples MUST be collected for every drinking water sample for such purposes.

[c] Trip Blank MUST be analyzed if one or more analytes are detected in the primary sample above the RL. A Trip Blank MUST accompany all drinking water samples for such purposes.

[d] On a site and project-specific basis, the use of one or more of these and/or other QC elements (e.g. equipment rinsate blanks, etc.) samples designated "Not Mandatory" may be advisable and/or necessary to demonstrate usability of the data, and/or to determine if the data are biased high due to contamination by sampling equipment/storage conditions. See Section 3.3.

Examples that would be considered "drinking water" in this context include samples taken directly from a tap, as well as water collected from a private well in the delivery system prior to the tap. Conversely, examples that would ***not*** be considered "drinking water" in this context include water collected from a well that is subsequently treated prior to consumption, and water collected from a surface water supply or cistern.

For "drinking water", field duplicates must be collected for all samples but need only be analyzed if an oil or hazardous material is detected in the primary sample above the analyte's Reporting Limit. For VOCs and VPH, a trip blank must also be collected but need only be analyzed if an oil

or hazardous material is detected in the primary or duplicate sample above the analyte's Reporting Limit. Any non-compliance with the field QC sample requirements for "drinking water" samples described in Table VII A-1 must be identified and discussed in the data usability assessment. ***It should be noted that compliance with field QC sample requirements for "drinking water" samples is not a prerequisite for "Presumptive Certainty" status.*** However, compliance with these field QC requirements insure a high level of confidence in results used to support decisions concerning drinking water consumption

2.5.1 Compliance with DEP Drinking Water Program (310 CMR 22) Requirements

All samples, including samples analyzed in support of MCP decision making, collected from a source regulated by the DEP Drinking Water Program under 310 CMR 22 (Public Water Supplies, Distribution Systems or Surface Water Sources) must be analyzed using the analytical methods specified in 310 CMR 22.06 B (10), i.e., EPA 500 Series for organics, EPA 200 Series for metals, etc. Since there are no approved organic methods for the identification and quantification of aliphatic and aromatic petroleum hydrocarbon ranges under the drinking water program, MADEP VPH and/or EPH Methods are acceptable for this purpose (see "Implementation of MADEP VPH/EPH Approach" (April 2002), Section 3.9). It should be noted that for "drinking water" samples, VPH and/or EPH target analytes ***must*** be analyzed by the appropriate analytical method specified in 310 CMR 22.06 B (10).

Samples collected from these regulated sources must be identified as "drinking water" to the laboratory on the chain-of-custody form. It is the responsibility of the data user to request regulatory-compliant analyses from the laboratory if the data is to be used in support MCP decision-making. The analytical methods specified in 310 CMR 22.06 B (10) should also be consulted to determine if any additional method specific sampling and/or analytical quality control is required for compliance with the DEP Drinking Water Program.

2.5.2 "Presumptive Certainty Status" for Drinking Water" Analyses

For purposes of "Presumptive Certainty" status, the Department stipulates that the analytical methods specified in 310 CMR 22.06 B (10) are equivalent to the corresponding MCP Analytical Methods (i.e., EPA 500 Series Method 524.2 and SW-846 Method 8260 B) **for the analysis drinking water only** (see Section 2.5.1). Analytical data produced utilizing corresponding Drinking Water Program methods may be used in support of MCP decision making providing the samples are analyzed by a laboratory currently certified by the State of Massachusetts for drinking water for the analytes of interest, and have reporting limits, quality control requirements and performance standards consistent with the equivalent MCP Analytical Method. It must be emphasized that although the Drinking Water Program methods are deemed equivalent to the MCP Analytical Methods for the purpose of "Presumptive Certainty" when analyzing drinking water samples, the MCP Analytical Methods should **never** be used for drinking water analysis.

2.5.3 Reporting and Evaluation of Tentatively Identified Compounds (TICs)

For drinking water samples, as described in Section 2.5, parties are required to instruct laboratory personnel to report Tentatively Identified Compounds (TICs) when GC/MS

organic methods are used in the analysis of the samples. If identified, these compounds must be reported by the laboratory in the Environmental Laboratory case narrative, as described in Section 2.4.5.

All reported concentrations of TICs are by definition estimated values. The party conducting response actions may either accept the estimated TIC concentration without further qualification, or improve the identification and the accuracy of the estimated concentration by post-calibration, re-sampling and/or re-analysis with a more appropriate analytical method.

If the presence of the TIC at the concentration reported by the laboratory appreciably changes the overall risk posed by the site or the utility of the potential remedial measures under consideration, the Department recommends (and may require) the latter option be exercised.

3.0 PERFORMANCE STANDARDS AND QA/QC CONCEPTS

This section contains general information on key regulatory and scientific principles pertaining to data quality and their applicability under the MCP. It is provided as background information for all parties, and relevant guidance for parties who elect to forgo the Presumptive Certainty option detailed in Section 2.0.

3.1 MCP Performance Standards for Data Quality

Under the provisions of 310 CMR 40.0017 (1), “Any person undertaking response actions under the provisions of this Contingency Plan shall ensure that analytical and environmental monitoring data used in support of recommendations, conclusions, or LSP Opinions with respect to assessment, removal, or containment actions is scientifically valid and defensible, and of a level of precision and accuracy commensurate with its stated or intended use.”

The level of QA/QC for these activities should be commensurate with the complexity of the response action conducted at a disposal site, the potential risk posed to human health and the environment by the contaminants of concern, and the intended use of the data. Data acquired from QC procedures are used to:

- Estimate the overall quality (precision, accuracy and representativeness) of analytical data;
- Determine the need for corrective action in response to identified data deficiencies;
- Interpret results after corrective actions are implemented; and
- Demonstrate that remedial goals have been achieved.

A total program to produce data of suitable and acceptable quality should include both a QA component, which encompasses management procedures and controls, as well as an operational QC component, to assess the precision, accuracy (bias) and representativeness of the site data set. An effective program should identify and document data quality objectives to support the disposal site’s response action requirements, and establish sampling design criteria; not only to acquire adequate site data but also to acquire the supporting data quality indicators. The disposal site assessment should include an evaluation

of the data quality indicators associated with each site data set to determine if the pre-established data quality objectives for the disposal site assessment were achieved.

3.2 Field Sampling Quality Assurance and Quality Control

Considerations regarding the necessary level of field quality control should be premised on the governing regulatory jurisdictions and on the intended use of the data. This evaluation is a prospective activity and should be conducted prior to the initiation of any field sampling. QA/QC is an integral component of the field and laboratory planning process.

The criteria commonly used to specify QA goals are precision, accuracy, representativeness, completeness, comparability, and sensitivity (PARCCS). Field sampling activities should incorporate methods and/or measures to allow for assessment of relevant PARCCS parameters using appropriate data quality indicators. Each of the PARCCS parameters is described below with a summary of potential assessment methods and measures.

3.2.1 Precision

Precision is a measure of mutual agreement among individual measurements of the same property, under prescribed conditions (i.e. random error). Precision may be evaluated qualitatively or quantitatively. Qualitative assessments of precision are based upon evaluations of larger data sets. Quantitative measurements of precision have historically been based upon the testing of duplicate samples.

Qualitative assessments of precision consider the range of concentrations encountered for a complete data set for a location or an area. For example:

- Groundwater samples collected over time from a single monitoring well in a steady-state environment could be assessed qualitatively as to the reproducibility and consistency of the measurements.
- Multiple soil sample results from a single area may be assessed qualitatively for variability in the range of reported concentrations.

Quantitatively, precision is generally expressed as Relative Percent Difference (RPD) between duplicate samples. Duplicates are two samples that are handled in an identical manner and the RPD of the measured results represents the precision (reproducibility) of the measurements. Laboratory duplicates are used to assess analytical precision. Field duplicates assess sample data repeatability that combines the cumulative precision of the sampling technique, non-homogeneity of the matrix, and the analytical method.

A field duplicate is a replicate sample taken at the same location and time using the same sampling method used to collect the initial sample and submitted along with the initial sample for testing. Samples are homogenized or not homogenized depending on whether laboratory precision or matrix non-homogeneity is being evaluated. Precision of field duplicates is reported as the RPD between the initial sample and the field duplicate results. U.S. EPA data

validation guidelines typically use criteria for RPDs of field duplicates as <50 for soils and <30 for waters. Care should be taken in the evaluation of RPDs as the precision of testing results decreases as concentrations approach the reporting limits. It is recommended that a matrix spike duplicate (MSD) be substituted for the field duplicate as a measure of precision for samples that are expected to be at or near the Reporting Limit (RL) of the analytical method. As a general rule, samples selected to assess precision should have an average concentration of at least ten times (10 X) the RL for the analytical method.

RPDs are calculated as follows:

$$RPD = \frac{\text{Range}}{\text{Mean}} \times 100$$

Range = Absolute Value of (Sample Concentration – Duplicate Concentration)
Mean = (Sample Concentration + Duplicate Concentration) / 2

Other methods of assessing the precision of the reported results of response actions may also be appropriate. For example, in lieu of the collection and analysis of field duplicates, sampling precision related to the non-homogeneity of the impacted matrix may in many cases be most appropriately and cost-effectively addressed via the analysis of a large data set of samples using field screening techniques.

3.2.2 Accuracy

Accuracy is the degree of agreement of a measurement with an accepted reference or true value. The difference between the measurement and the true value is usually expressed as a percentage or ratio. Accuracy is a measure of the bias that exists in a system. The measure of accuracy of a method is generally evaluated using laboratory control samples. The measurement of accuracy in a sample matrix is generally evaluated using matrix spikes (MS). Other data quality indicators used to assess accuracy are described in detail in Section 3.3.

Upon submittal of samples to the laboratory, parties conducting response actions must designate which sample(s) will be used for the matrix spike, as required. The laboratory will add known concentrations of representative contaminants (spikes) to an aliquot of the submitted sample and prepare and analyze it in accordance with the requested methods Samples must be fortified with all surrogates and matrix spikes ***before*** the sample is processed (i.e. extraction, cleanup, etc.) if recovery information will be used to assess matrix effects.

Accuracy is reported as the percent recovery of the known concentrations that were added to the sample aliquot. The measured percent recovery provides an indication of whether the sample matrix (soil, water, etc.) is influencing the recovery of the contaminant from the matrix and thus the accuracy of the results. Results may be biased high or low. Matrix spike samples are sometimes prepared in duplicate and are called a matrix spike/matrix spike duplicate (MS/MSD). In addition to accuracy information, MS/MSD analysis also provides additional precision information.

The sample selected for MS/MSD evaluation should not contain significant concentrations of the contaminants as compared with the spike concentrations as this may prevent accurate measurements of the spiked compound's recovery. Ideally, the cumulative concentration of the undiluted sample and matrix spike should not exceed seventy-five (75) percent (%) of the highest analytical standard used in the applicable calibration curve and the ratio of spiked contaminant to the native concentration of the contaminant in the undiluted sample should be five (5) to one (1), or greater. Furthermore, it is critical that the sample submitted to the laboratory for MS evaluation is representative of the potentially contaminated matrix. The laboratory requires additional sample quantity when matrix spikes are requested, especially on aqueous samples (i.e. the sample volumes specified in Appendix VII A should be tripled).

Other methods of assessing the accuracy of the reported results of response actions may also be appropriate. However, documentation is required when alternative methods for assessing accuracy are utilized. [See 310 CMR 40.0017(2)].

3.2.3 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variation, or environmental condition. Representativeness is a qualitative assessment based upon observed conditions and measurements. Sampling design, the logic used to determine specific sampling locations and the procedures used for sample collection, plays a major role in determining how representative a given sample set may be.

The RPD of field duplicates is one quantitative measure of representativeness. In addition to the measurements of precision and accuracy discussed above, the assessment of representativeness should also consider qualitative observations such as:

- Site history – Were the samples collected in areas of suspected contamination?
- Conceptual Site Model (CSM) – Are sample results consistent with the CSM?
- Visual and olfactory observations – Was there evidence of contamination compared with other areas?
- Physical features – Were sample locations consistent with respect to soil types, groundwater flow direction, and/or bedrock fracture patterns?
- Sample collection procedures – Were the appropriate methods used to representatively collect samples?
- Sample preservation – Were the samples properly preserved to prevent losses of contaminants?
- Testing methods – Were the appropriate methods used to test for the contaminants of concern?

- Field screening data – Are sample results consistent with field screening data? It is critical in assessing representativeness to evaluate the testing results, field observations, and methods and procedures utilized.

3.2.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount expected under normal conditions. Completeness is usually expressed as a percentage. If the completeness goal is 100%, this means that all samples collected and submitted to the laboratory must be useable in support of response actions. A completeness goal of 85-90% is generally considered a more reasonable target, except for critical samples (discussed below). Completeness targets are set to estimate the minimum amount of data required to support recommendations, conclusions, or LSP Opinions.

3.2.5 Critical Samples

It should be noted that some samples are critical to meeting the objectives of a specific MCP response action. For example, in an assessment to determine the risk associated with a release to groundwater, all samples from identified private and municipal water supply wells in the study would be considered critical samples. **The target completeness for critical samples should be 100%.**

3.2.6 Comparability

Comparability expresses the confidence with which one data set can be compared to another. Comparability may be determined quantitatively or qualitatively. Quantitative determinations of comparability are usually based on the comparison of internal control samples (a sample collected at the same location using the same sampling and analytical method) included in consecutive sampling events. A qualitative assessment of comparability is generally based upon a review of sampling and testing procedures. Typical issues would include sampling and analytical methods, units of concentration and detection limits. Site conditions and other site-specific factors should also be considered in this assessment.

3.2.7 Sensitivity

Sensitivity is the ability of the method to detect the contaminant of concern at the concentration of interest (e.g., MCP Method 1 Cleanup Standards), expressed as the Reporting Limit. Several QC samples and procedures are commonly used to provide sensitivity consistent with project needs. These measures also assist in the assessment of the accuracy of an analytical result. These measures include equipment blanks, trip blanks, laboratory method and instrument blanks, laboratory instrument calibration QC and the requirement that the low-level standard in the calibration curve be equal to the analyte Reporting Limit. If sample dilution is required, the Reporting Limit (RL) for all target analytes must be adjusted (increased) accordingly in direct proportion to the Dilution Factor (DF). All dilutions must be fully documented in the Environmental Laboratory case narrative.

It should be noted that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the "adjusted" RL 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 enables quantification of target analytes which exceed the calibration range.

Data users should reference the method-specific QA/QC requirements and performance standards for individual methods provided by the Department on the Data Enhancement Web Page (www.mass.gov/dep/bwsc/files/data/qaqcdocs.htm) for details of the type, frequency, and criteria of the laboratory quality measures.

Parties should evaluate the usability of non-detected results with Reporting Limits greater than project DQOs (e.g., greater than the MCP standards), on a case-by-case basis.

3.3 Summary of Field QC Considerations under the MCP

3.3.1 Approach

Pursuant to 310 CMR 40.0017(i), "all response actions submittals to the Department under the MCP that contain the results of sample collection and analyses ***shall*** include details on any known conditions or findings which may effect the validity of analytical data". The most common approach to evaluate the validity of such data is a data usability assessment, which includes both a laboratory and field component. Analytical requirements for data usability are described in detail elsewhere in this document. This section provides a brief discussion of a number of field QC elements that should be considered for inclusion in any sampling program conducted to support of MCP response actions. Some combination of the following common field QC elements should be incorporated selectively into MCP site characterization efforts to provide quantitative information for the evaluation of the overall accuracy, precision, representativeness, sensitivity and comparability of sampling data:

Matrix Spikes, a direct measurement of matrix effects and overall measurement of data accuracy, are not mandated for a number of common organic methods. Rather, MADEP believes recovery of surrogates (which are used on 100% of samples) should provide sufficient information on accuracy in the sample matrix for most site assessment efforts and data quality objectives.

Field Duplicates, a measure of sampling precision, representativeness, (site heterogeneity), and laboratory operations (when submitted as blind samples), are not mandated for most analytical methods. Rather, except for drinking water samples, MADEP believes that characterization of site heterogeneity may be best and/or most economically measured using field-screening data, and is best evaluated as part of data representativeness considerations.

Equipment Blanks, a measure of "false positive" contamination during sample acquisition and/or storage. Contaminant-free water is poured over sampling equipment and then collected for analysis. The presence of measurable concentrations of contaminants in an equipment blank indicates the potential for cross

contamination between sampling locations when sample collection equipment is used to collect samples at more than one location.

Because equipment blanks are a measure of cross contamination, they may be helpful in assessing the accuracy and representativeness of field measurements. The detection of measurable concentrations of contaminants in an equipment blank is indicative of the potential for the reported concentrations to be higher than the actual concentrations in the samples (false positives). Care must be taken in interpreting any measurable concentrations of contaminants in equipment blanks particularly when aqueous equipment blanks are compared to different solid sample matrices (soil, sediment). It should be noted that an assessment of accuracy can not be made by evaluating equipment blank data unsupported by other data quality indicators (e.g., matrix spikes, etc.). For other sampling efforts, it is up to the party conducting work to determine if the acquisition and/or analysis of an equipment blank is appropriate, as false positive data will lead to more conservative, not less conservative, assessments and cleanups.

Trip Blanks, are used in conjunction with VPH and VOC analyses to assist in the assessment of field accuracy and representativeness and are a measure of "false positive" contamination during sample acquisition and/or storage. For water samples submitted for VPH and VOC analyses, trip blanks consist of VOC-free water in VOA vials preserved in the same manner as the samples. For solid samples submitted for VPH analysis, trip blanks consist of a vial-containing methanol. For solid samples submitted for VOC analysis, trip blanks may consist of (a) VOC-free water or sodium bisulfate preservative solution for low level analysis, and/or (b) methanol for high-level analysis. Trip blanks accompany the empty sample containers from the laboratory to the field and return with the collected samples from the field to the laboratory.

The presence of measurable concentrations of contaminants in a trip blank indicates the potential for cross contamination with a potential for the reported concentrations of VOCs to be higher than the actual concentrations in the samples (false positives). The sources of the cross contamination may be associated with the transportation of containers to and from a site, ambient conditions present at a site, and/or other samples shipped with the trip blank. It should be noted that an assessment of accuracy can not be made by evaluating trip blank data unsupported by other data quality indicators (e.g., matrix spikes, etc.). Trip Blanks are not mandatory analyses, except for drinking water samples, and in such cases, only if there is a positive detection in the primary sample. For other sampling efforts, it is up to the party conducting work to determine if the acquisition and/or analysis of a trip blank is appropriate, as false positive data will lead to more conservative, not less conservative, assessments and cleanups.

Double-Blind Spikes, a double-blind spike, also known as a Performance Evaluation Sample (PES), is a sample prepared by a third party with known concentrations of contaminants that is submitted to the laboratory as part of a project-specific quality

control program. The double-blind spike is submitted to a laboratory along with other samples, and is not identified as a PES. The results of the analysis are assessed in the same manner as matrix spike results. The measured recovery of the analytes in a performance evaluation sample is an independent and external indication of the bias or accuracy of the laboratory testing procedures for a specific matrix. Results may be biased high or low.

It should be noted that once the supporting field QC data are evaluated, there may in some cases be a need to obtain and/or analyze additional samples to better evaluate data with low surrogate recoveries, suspected false positives, and/or other data quality concerns. Of course, nothing precludes parties from obtaining and analyzing field QC samples at a higher frequency initially if they cannot tolerate scheduling extensions to address possible problems that may become evident in this regard.

3.3.2 Specific Soil/Sediment Media Considerations

Most soil and sediment field QC samples should be included in the first sampling round, unless unusual circumstances warrant a delay to a latter round.

Parties may wish and/or otherwise may need to obtain and analyze supplemental soil and sediment field QC samples in order to investigate and evaluate data anomalies and/or inconsistencies, including sites and situations where the following is evident:

- Lab data are inconsistent with field screening/observations;
- Recovery of lab surrogate spikes is low;
- Natural organic material is present in sample that could interfere with recovery of target analyte(s); and/or
- The sample consists of a cohesive organic-clay soil mixture.

3.3.3 Specific Aqueous Media Considerations

Most aqueous field QC samples should be included in the first sampling round, unless unusual circumstances warrant a delay to a latter round.

Parties may wish and/or otherwise may need to obtain and analyze supplemental aqueous field QC samples in order to investigate and evaluate data anomalies and/or inconsistencies, including sites and situations where the following is evident:

- Lab data are inconsistent with field screening/observations; and/or
- Recovery of lab surrogate spikes is low.

Sample preservation, container specifications, and analytical holding time specifications for surface, groundwater, soil, sediment and waste samples analyzed in support of MCP Response Actions by matrix and media are presented in the following Tables:

Table Number	Matrix	Analyte	Page
VII A-2	Aqueous	Volatile Organics	25
VII A-3	Aqueous	SVOCs, Pesticides, PCBs, Herbicides and Nitroaromatics	26
VII A-4	Aqueous	Miscellaneous Organic and Inorganic Analytes	27-29
VII A-5	Soil/Sed	Volatile Organics	30
VII A-6	Soil/Sed	Miscellaneous Organic and Inorganic Analytes	31-32

Analytical Notes:

1. For certain "critical" aqueous samples to be analyzed for Methyl tertiary-butyl ether (MtBE) and/or other fuel additive oxygenates **using heated sample preparation techniques** (e.g., SW-846 Method 5030 heated to 80° C, heated purge and trap), alternative preservation techniques must be utilized to eliminate a negative bias attributable to acid hydrolysis. Critical samples include (1) all samples from a private or public drinking water supply, and (2) select samples from groundwater monitoring wells in GW-1 areas. It is recommended that such samples be preserved with trisodium phosphate dodecahydrate (TSP) rather than HCl. Between 0.40 and 0.44 grams of TSP are added to each 40 ml of sample to raise the pH of the sample to > 11.0. Preserved samples are kept at 4° C prior to analysis. Samples preserved with TSP may also be analyzed for BTEX with no adverse effects. See referenced web page for a complete discussion of this concern and recommendation: http://www.epa.gov/swerust1/mtbe/LL42Analytical.pdf

2. In July 2002, the US EPA published an updated version of SW-846 Method 5035A, "Closed System Purge-and-Trap and Extraction for Volatile Organics In Soil and Waste Systems". The updated method includes Appendix A, "Collection and Preservation* of Aqueous and Solid Samples for Volatile Organic Compounds (VOC) Analyses". See http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5035a_r1.pdf

Title: Sample Collection, Preservation, And Handling Procedures for Aqueous Volatile Organic Compound (VOC) Analyses

Sample preservation, container and analytical holding time specifications for surface water, and groundwater samples for volatile organic compounds analyzed in support of MCP decision-making are summarized below

Matrix	Analyte	Container [1]	Preservative [2]	Holding Time
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 4 ± 2^{O} C.**	14 days
	MTBE or other fuel oxygenates *only* **with heated purge-and-trap sample introduction**	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	Adjust pH to **> 11.0** by addition of 0.7 g of trisodium phosphate dodecahydrate (TSP) to container before sampling. **Cool 4 ± 2^{O} C.**[3]	14 days
	Reactive[4] 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 4 ± 2^{O} C.**	Analyze ASAP but not more 7 days [5,6]
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 A cid 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 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).

4 While there are chemicals that are described as *potentially* reactive on various lists of Volatile Organic Target Analytes (see Tables II A-2 and V A-2), at this time DEP does not consider any chemicals on these lists to be "reactive" and requiring special preservation and/or hold times.

5. Every reasonable effort should be made to analyze reactive samples as soon as possible (the goal should be 24 hours or sooner) after the time of collection. In all cases the holding time for reactive samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

6. In the unusual circumstance that contaminants of concern at a disposal site require mutually exclusive preservation techniques (e.g., acid preservation/with cooling for BTEX and no acid preservation/cooling-only for reactive compounds) separate sampling containers to accommodate the different preservation techniques may be required. The selection of preservation technique for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

Sample preservation, container and analytical holding time specifications for surface water, groundwater non-volatile organic compounds and wastes analyzed in support of MCP decision-making are summarized below.

Matrix	Container [1]	Preservation	Holding Time [2]
Aqueous Samples, with no Residual Chlorine	(2) 1-L amber glass bottles w/ Teflon-lined screw caps	Cool to 4°C	7 days to extraction; 40 days from extraction to analysis [3]
Aqueous Samples, with Residual Chlorine [4]	(2) 1-L amber glass bottles w/ Teflon-lined screw caps	Add 1-mL 10% sodium thiosulfate solution per container (or 0.008%) [5]. Addition of thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 4°C	7 days to extraction; 40 days from extraction to analysis [3]
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 to extraction; 40 days from extraction to analysis [3]

1 The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis
2 Holding time begins from time of sample collection.
3 SVOC samples extracts must be stored at – 10° C, protected from light, and stored in sealed vials (e .g., screw-cap or crimp-caped vials) with un-pierced PTFE-lined septa. See SW-846 Method 8270C, Section 6.1.
4 Presence of chlorine residual is usually associated with drinking water samples
5 Confirm dechlorination. If Residual Chlorine > 5 mg/L additional dechlorination agent may be required

Sample preservation, container and analytical holding time specifications for surface water and groundwater samples analyzed in support of MCP decision-making are summarized below.

Parameter	Sample Container(s) [1]	Preservative	Holding Time [2]
Volatile Organics	(2) 40-ml VOA vials, Teflon lined septa	See Table VII A-2	See Table VII A-2
Semi-Volatile Organics	(2) 1-L Amber Glass Bottles	See Table VII A-3	See Table VII A-3
PCBs	(2) 1-L Amber Glass Bottles	See Table VII A-3	See Table VII A-3
Pesticides	(2) 1-L Amber Glass Bottles	See Table VII A-3	See Table VII A-3
Chlorinated Herbicides	(2) 1-L Amber Glass Bottles	See Table VII A-3	See Table VII A-3
Nitroaromatics	(2) 1-L Amber Glass Bottles	See Table VII A-3	See Table VII A-3
Metals	(1) 500 ml Polyethylene Bottle for Total Metals (1) 500 ml Polyethylene Bottle for Dissolved Metals	HNO_3 to pH < 2 Preserved <u>after</u> filtration for dissolved metals	180 days: all metals except mercury 28 days: mercury
Cyanide	(1) 500 ml Polyethylene Bottle	NaOH to pH >12, cool to 4°C, 0.6 g ascorbic acid per liter, if residual chlorine present	14 days
Extractable Petroleum Hydrocarbons	(2) 1-Liter amber glass bottle with Teflon-lined screw cap	Add 5-ml of 1:1 HCl; Cool, 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction

Parameter	Sample Container(s) [1]	Preservative	Holding Time [2]
Volatile Petroleum Hydrocarbons	(3) 40-mL glass vials w/ Teflon-lined septa screw caps	See Table VII A-2	See Table VII A-2
TOC	(4) 40-ml VOA vials, Teflon lined septa	Cool, 4°C, H_2SO_4 to pH<2	28 days
Sulfate	(1) 500-mL Polyethylene Bottle	Cool, 4°C	28 days
Sulfide	(1) 500-mL Polyethylene Bottle	Cool, 4°C, 2N zinc acetate plus sodium hydroxide to pH >12	7 days
Nitrate-Nitrite Nitrogen	(1) 500-mL Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	28 days
Nitrate-Nitrogen	(1) 500-mL Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	48 hours
Nitrite-Nitrogen	(1) 500-mL Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	28 days
Ammonia	(1) 1-L Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	28 days
Total Kjeldahl Nitrogen	(1) 500-mL Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	28 days
Ortho- Phosphate	(1) 500-mL Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	48 hours
Total Phosphorus	(1) 500-mL Polyethylene Bottle	Cool, 4°C, H_2SO_4 to pH<2	28 days
Total Suspended Solids	(1) 1-L Polyethylene Bottle	Cool, 4°C	7 days
Chloride	(1) 500-mL Polyethylene Bottle	Cool, 4°C	28 days
Carbonate/ Bicarbonate Alkalinity	(1) 250-mL Polyethylene Bottle	Cool, 4°C	14 days

Parameter	Sample Container(s) [1]	Preservative	Holding Time [2]
Chlorophyll-a	(1) 500-mL Amber Bottle	Cool, 4°C, 0.5 mL of $MgCO_3$	As soon as possible
Calcium Magnesium (indicator parameters)	If metals being done: no extra sample bottle required. If no metals collected: (1) 500-mL Polyethylene Bottle	see metals	180 days
Hardness (requires calcium and magnesium analysis)	If metals being done: no extra sample bottle required. If no metals collected: (1) 500-mL Polyethylene Bottle	see metals	180 days (for calcium and magnesium analysis)
Methane, Ethane, and Ethene	(2) 40 mL VOA vials w/ Teflon-lined septa screw caps	HCl to pH < 2, Cool, 4°C	14 days

Notes and Precautions

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.

2 From date of sample collection.

Matrix	Container [a]	Preservation[1,2]	Holding Time[3]
Soil/Sediment Samples ***High-Level Analysis***	Extrude 5 grams of 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 g soil/sediment (+/- 25%). **Methanol must completely cover soil/sediment.** *(1) x 60-mL vial or (1) x 40-mL vial	Cool to 4 ± 2° C; protect from light	14 days
	5 g EnCore samplers[4] or other suitable coring device	Cool to 4 ± 2° C in field and deliver to laboratory within 48 hours of collection for freezing (< -7° C) or methanol preservation.	
Soil/Sediment Samples ***Low-Level Analysis*** by Closed-System Purge-and-Trap Process	5 g EnCore samplers[4] or other suitable coring device.	Cool to 4 ± 2° C in field and deliver to laboratory for freezing (< -7° C) or analysis within 48 hours of sample collection (see Note 1). Alternatively, samples may be frozen to < -7° C in the field using gel packs	14 days
	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 1) and a Teflon-coated magnetic stir bar[5].	Cool to 4 ± 2° C in field and deliver to laboratory for freezing (< -7° C) or analysis within 48 hours of sample collection. Alternatively, samples may be frozen to < -7° C 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

1. For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours after sample collection.

2 A number of acceptable alternative preservation techniques requiring close communication with the receiving laboratory that require field cooling (4 ± 2°) 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 Holding time is calculated from the time of sample collection.

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

5. Not required if Closed-System Purge-and Trap device employs a means of stirring the sample other than a magnetic stirrer

Parameter	Sample Container(s)	Preservative [1,2,3]	Holding Time [4]
Volatile Organics ***High-Level Analysis***	See Table VII A-5	See Table VII A-5	See Table VII A-5
Volatile Organics[2] ***Low-Level Analysis***	See Table VII A-5	See Table VII A-5	See Table VII A-5
Semi-Volatile Organics	(1) 8-oz. amber glass jar w/ a Teflon-lined screw cap	Cool to 4°C	14 days to extraction; 40 days from extraction to analysis
Pesticides	(1) 4-ounce glass jar	Cool, 4°C, protected from light	Extraction: within 14 days of collection Analysis: within 40 days of extraction
PCBs	(1) 4-ounce glass jar	Cool, 4°C, protected from light	Extraction: within 14 days of collection Analysis: within 40 days of extraction
Chlorinated Herbicides	(1) 4-ounce glass jar	Cool to 4°C	Extraction: within 14 days of collection Analysis: within 40 days of extraction
Nitroaromatics	16-oz. (500 mL) wide-mouthed amber glass jar with Teflon-lined screw cap	Store in dark ***Cool to 4°C***	Extraction: within 14 days of collection Analysis: within 40 days of extraction [5]
Metals	(1) 4-ounce glass jar	Cool, 4°C	180 days: all metals except mercury 28 days: mercury
Cyanide	(1) 4-ounce glass jar	Cool, 4°C	14 days

Parameter	Sample Container(s)	Preservative [1,2,3]	Holding Time [4]
Extractable Petroleum Hydrocarbons (EPH)	4-oz. (120 ml) widemouth amber glass jar with Teflon-lined screw cap	Cool, 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Volatile Petroleum Hydrocarbons (VPH)	(3) 40-mL VOC vials w/ Teflon-lined septa screw caps 40 ml vials: add 15 g soil 60 ml vials: add 25 g soil	1 mL purge-and-trap grade methanol for every g soil/sediment +/- 25%; MUST completely cover soil. Cool to 4°C; protect from light	28 days
AVS/SEM	(1) 4-ounce glass jar or 40-mL VOA vial no headspace	Cool, 4°C	AVS: evolution within 14 days, analysis within 24 hours of evolution SEM: analysis within 14 days of extraction
Grain Size	Shelby Tubes or (1) 8-oz Glass jar	None	NA
Total Organic Carbon	(1) 4-ounce glass jar	Cool, 4°C	28 days (14 days for Lloyd Kahn)

1. If a hermetically sealed sampling device such as an EnCore® sampler is utilized, the laboratory must be prepared to preserve the sample within 48 hours of sample collection. The sample must be analyzed within 14 days of sample collection. The EnCore™ samplers must be kept at 4ºC from time of collection to time of preservation. The preserved samples must be kept at 4ºC from time of preservation until the time of analysis.
2. Acceptable alternative to freezing in the field: keep samples cool at 4°C then freeze upon receipt at laboratory. Preservation with sodium bisulfate is also an acceptable alternative for BTEX analysis when soils are non-calcareous.
3. All samples for <u>extractable</u> organic, metals and cyanides analyses may be held for up to one (1) year if frozen within 24 hours of collection at < -10°C (with the exception of Nitroaromatics). <u>Sampling container should only be filled to 2/3 of capacity to avoid breakage caused by expansion during freezing</u>. Preparation or extraction must be commenced within 24 hours of thawing. Temperature must never be allowed to go below – 20 °C to avoid damage to seals, etc..
4. From the date of sample collection or date thawed (as discussed in Note # 3 above).
5. Soil samples for Nitroaromatic analysis that have been frozen within 24 hours of collection at < - 10°C may be held for up to eight (8) weeks prior to analysis.