COMMONWEALTH OF MASSACHUSETTS
EXECUTIVE OFFICE OF ENVIRONMENTAL AFFAIRS
DEPARTMENT OF ENVIRONMENTAL PROTECTION
ONE WINTER STREET, BOSTON, MA 02108 617-292-5500

ARGEO PAUL CELLUCCI
Governor

JANE SWIFT
Lieutenant Governor

ROBERT DURAND
Secretary

EDWARD KUNCE
Acting Commissioner

PRESERVATION TECHNIQUES FOR VOLATILE ORGANIC COMPOUND (VOC) SOIL SAMPLE ANALYSES

WSC # 99-415

This policy describes acceptable techniques and approaches for the preservation of volatile organic compounds contained in soil samples that are analyzed and used in support of response action decisions at disposal sites regulated under the Massachusetts Contingency Plan (310 CMR 40.0000).

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Date

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Deirdre C. Menoyo
Assistant Commissioner,
Bureau of Waste Site Cleanup

BACKGROUND

Since 1990, a growing and overwhelming body of scientific evidence has accumulated indicating that the failure to use accurate and up-to-date methods to preserve soil samples during sample collection and storage can result in substantial under-reporting of VOC concentrations (in some cases by over 99%) and, consequently, substantial underestimating of risk. Three mechanisms are to blame: (1) initial sampling and sub-sampling activities that disturb/destroy soil structure and/or aerate samples, (2) volatilization/diffusion out of the sample container during storage, and (3) biodegradation of contaminants during storage.

With the goal of minimizing loss of VOCs from the field to analysis, EPA developed and issued Method 5035 (December 1996). With its publication in the 6/13/97 Federal Register, this method was formally incorporated in SW-846, with an "immediate" effective date. The method refers to a variety of soil sampling and analytical procedures. **The method's most significant element is the preservation of soil samples containing VOCs with methanol prior to analysis**. Massachusetts has already adopted the methanol preservation requirement for its Volatile Petroleum Hydrocarbon method (VPH), effective as of October 31, 1997. The improved sample collection and preservation techniques maintain the integrity of the soil sample, control biological degradation, and minimize the potential loss of VOCs from the soil during sample collection and handling.

REGULATORY AUTHORITY

DEP is distributing this policy as an advisory of the following regulations under the Massachusetts Contingency Plan (the "MCP" or 310 CMR 40.0000) and to promote the collection of scientifically valid and defensible data. Relevant sections of the MCP appear below in bold:

310 CMR 40.0017 Environmental Sample Collection and Analysis

(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.

(2) Procedures and methodologies employed for the collection and analysis of soil, sediment, water, vapor, air, and/or waste samples shall consist of:

(a) methods published by the Department, EPA, the American Society for Testing and Materials (ASTM), the American Public Health Association (APHA), the National Institute for Occupational Safety and Health (NIOSH), the American Water Works Association (AWWA), and other organizations with expertise in the development of standardized analytical testing methods;

(b) modification of published methods, provided that all modifications are completely documented; or

(c) unpublished methods, including analytical screening methods, provided that such methods are scientifically valid, are of a known and demonstrated level of precision and accuracy, and are completely described and documented in response action submittals.

310 CMR 40.0191 Response Action Performance Standards (RAPS)

(2) RAPS shall be employed during the performance of all response actions conducted pursuant to 310 CMR 40.0000, and shall include, without limitation, the following:

(a) consideration of relevant policies and guidelines issued by the Department and EPA;

(b) use of accurate and up-to-date methods, standards and practices, equipment and technologies which are appropriate, available and generally accepted by the professional and trade communities conducting response actions in accordance with M.G.L. c. 21E and 310 CMR 40.0000 under similar circumstances; and

(c) investigative practices which are scientifically defensible, and of a level of precision and accuracy commensurate with the intended use of the results of such investigations.

Under these performance-based regulations, any person conducting response actions under the MCP should recognize and understand the relevance of:

- Extensively documented scientific evidence dating back to 1990 that failure to properly preserve soil samples can result in substantial under-reporting of VOC concentrations (see Appendix 1 for a partial list of references);
- Numerous DEP publications, training, and communications to LSPs on this subject dating back to August 1995, when the draft VPH method was published; and
- Publication of EPA Method 5035, which became effective on June 13, 1997.

It is DEP's position that VOC data from improperly preserved or mis-handled samples are not scientifically valid or defensible and, as a result, do not meet the performance standards described at 310 CMR 40.0017 or 40.0191.

APPLICABILITY

The need to use proper preservation methods applies to all VOC soil samples collected as part of a response action, including the characterization of Remediation Wastes, at any site regulated under the provisions of M.G.L. c. 21E and 310 CMR 40.0000. Unless technical justification is provided to the contrary, these methods also apply to sediment samples. VOCs include but are not limited to those analytes reported by EPA Methods 8015A, 8021A, and 8260A as listed in Final Update III of SW-846. (Note: Chemical preservatives are not allowed for samples collected for TCLP analysis.)

PREVIOUSLY OBTAINED AND/OR SUBMITTED DATA

The following table describes how unpreserved VOC soil data will be managed based upon the sample collection date and the date of any submittal that relies on these data:

COLLECTION DATE	**SUBMISSION DATE**	***MANAGEMENT STANDARD***
Before 3/15/99	Before 3/15/99	In general, DEP will not require data reevaluation but reserves the right to do so, if evidence exists of direct and compelling health concerns. The data evaluation criteria listed below will be considered in making these decisions.
Before 3/15/99	On or After 3/15/99	RPs, PRPs and/or Other Persons, in conjunction with their LSPs and/or Consultants-of-Record, must evaluate data and relevant site characterization parameters on a case-by-case basis to determine whether VOCs in soils present at the site pose a risk of harm to human health, or act as a continuing and significant source of groundwater contamination. DEP recommends that the data evaluation criteria listed below be used when conducting these evaluations.
On or After 3/15/99	On or After 3/15/99	Proper preservation techniques must be used, or data will be rejected by DEP.

Data Evaluation Criteria

1. VOC headspace and other screening data indicating significant levels of VOCs;
2. The type, toxicity and persistence of VOC present (e.g., Chlorinated compounds and MtBE are generally more problematic in the environment than petroleum hydrocarbon compounds);
3. High and/or consistent levels of VOCs in groundwater indicating VOCs in soil may be a continuing source; and
4. Presence of sensitive receptors or exposure pathways at or in the vicinity of the disposal site (e.g., humans, surface water or drinking water supplies).

(Revised page April 12, 1999)

ACCEPTABLE SOIL PRESERVATION TECHNIQUES AND APPROACHES

High VOC Concentrations (> 200 ug/kg):

At most sites and for most concentration ranges of interest, field preservation **using methanol** alone should be sufficient, without the need to obtain additional samples using other preservation techniques.

- Sampling Logistics – When using methanol, **preservation must occur in the field**, following the procedures described in either EPA Method 5035, Appendix 1 *of Implementation of MADEP VPH/EPH Approach; Public Comment Draft; October 31, 1997 or, Appendix 4 of Method for the Determination of Volatile Petroleum Hydrocarbons (VPH); January 1998*. The differences between EPA Method 5035 and the VPH procedure are not deemed to be significant, and either meets the performance standards articulated in the MCP. Important preservation guidelines include the following:

  - Between 5 to 25 grams of soil should be collected.
  - Methanol must be "purge and trap" grade or equivalent quality.
  - The desired ratio of grams soil/mL methanol is 1:1, within a tolerance of +/- 25%. Ratios outside this range may be acceptable, depending upon data quality objectives. In all cases, however**, the soil sample must be completely immersed in methanol.**
  - It is permissible to estimate the mass of soil addition in the field based upon the volume of the sample, provided that the mass of soil and volume of methanol can be subsequently discerned, and provided that the grams soil/mL methanol ratio is acceptable.
  - An additional sample of (unpreserved) soil must be collected to allow for a determination of moisture content, and the normalization of data to a dry-weight basis.
  - An EnCore™ sampler or similar device with proven effectiveness may be used to obtain samples in the field without preservation, provided the sample is extruded into methanol within 48 hours.

- Moisture - Because water is completely miscible with methanol, naturally occurring moisture contained in the soil sample may result in under-reporting of the true, dry weight VOC concentrations. In general, every percent of moisture (by weight) present in a soil sample will result in a negative bias of about 1 percent. It is the responsibility of the data user to determine the significance of this effect on a site-specific basis, however, moisture contents less than 25% by weight are generally not considered a significant concern by DEP. No data adjustments are to be done by the laboratory relative to this issue, although laboratories may reference this phenomenon as a reason for low surrogate recoveries, as appropriate.

Low VOC Concentrations (< 200 ug/kg):

Because methanol preservation introduces a dilution factor into the sample analysis, EPA Method 5035 recommends sodium bisulfate preservation for detecting VOCs at concentrations below 200 ug/kg. In Massachusetts, there are 11 VOCs with Method 1 soil standards below 200 ug/kg, all of which are controlled by the leaching pathway as opposed to risks from direct human contact. At sites where an applicable Method 1 soil standard is less than 200 ug/kg, the following options are available:

1) Continue to use methanol if the laboratory can demonstrate that their Reporting Limits/PQLs are at or below the cleanup standard of interest. Stakeholder comments received during the

development of this policy indicated that Method Detection Limits (MDLs) as low as 25 ug/kg (or Reporting Limits/PQLs as low as 75 to 125 ug/kg) are achievable using most existing laboratory GC equipment. In such cases, however, it will be incumbent upon the laboratory to document the validity of this Reporting Limit/PQL through the use of MDL studies and appropriate calibration and QA/QC procedures.

2) Use sodium bisulfate or any other suitable low level preservation method with demonstrated effectiveness. (Note: There are questions about the efficacy of sodium bisulfate preservation, including poor sample purging efficiencies, acetone production, and limited effectiveness in reducing VOC losses due to volatilization. Therefore, the Department recommends that sodium bisulfate preservation be used only when expected concentrations are likely to be less than 200 ug/kg, based upon site conditions, site history and screening data.)

3) Use a Method 2 (or Method 3) Risk Characterization, and demonstrate that the soil-to-groundwater leaching pathway has been adequately evaluated and the achievement of analytical detection limits less than 200 ug/kg is not necessary to document the presence of No Significant Risk.

OTHER ACCEPTABLE SAMPLING PRESERVATION TECHNIQUES AND APPROACHES:

An EnCore™ sampler or similar device with proven effectiveness may be used to obtain samples in the field without preservation, provided the sample is extruded into methanol or sodium bisulfate within 48 hours.

Unpreserved field and/or soil screening data may be acceptable, depending on the analytical techniques employed and the specific data quality objectives that need to be met. Examples of such field and/or screening approaches include PID/FID headspace screening, UV Fluorescence & Absorbance, Immunoassay Test Kits, and portable Gas Chromatograph units that analyze samples in the field on a real time basis with comparable laboratory QA/QC requirements.

The Department anticipates that as parties gain experience with the VPH method and EPA Method 5035 refinements and modifications will be identified and developed by scientific researchers, laboratories and data users. DEP expects and encourages innovations in this regard provided that these innovations are scientifically defensible and valid, and meet the performance standards contained in 310 CMR 40.0017.

FOR QUESTIONS AND FURTHER INFORMATION

DEP BWSC Help Line……(617) 338-2255
DEP on the World Wide Web……http://www.magnet.state.ma.us/dep

A partial list of reference materials and citations for VOC Soil Sampling/Storage Losses & Use of Methanol Preservation is provided in Appendix 1.

Appendix 1:

PARTIAL LIST OF REFERENCE MATERIALS AND CITATIONS VOC SOIL SAMPLING/STORAGE LOSSES & USE OF METHANOL PRESERVATION

Ball, W., et. al., "Hot Methanol Extraction for the Analysis of Volatile Organic Chemicals in Subsurface Core Samples from Dover Air Force Base, Delaware", Ground Water Monitoring Review, Winter 1997.

Hewitt, A., "Comparison of Sample Collection and Handling Practices for the Analysis of Volatile Organic Compounds in Soils", National Symposium on Measuring and Interpreting VOCs in Soils; State of the Art and Research Needs, Las Vegas, 1993.

Hewitt, A., "Review of Current and Potential Future Sampling Practices for Volatile Organic Compounds in Soils", National Symposium on Measuring and Interpreting VOCs in Soils; State of the Art and Research Needs, Las Vegas, 1993.

Hewitt, A., "Concentration Stability of Four Organic Compounds in Soil Subsamples", US Army Corps of Engineers, Cold Region Research and Engineering Laboratory Special Report, April, 1994.

Hewitt, A., "Comparison of Methods for Sampling Vadose Zone Soils for Determination of Trichloroethylene", J. Assoc of Anal Chem, Vol 77, No. 2, 1994.

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King, P., "Evaluation of Sample Holding Times and Preservation Methods for Gasoline in Fine Grained Soils", National Symposium on Measuring and Interpreting VOCs in Soils; State of the Art and Research Needs, Las Vegas, 1993.

Lewis, T., et. al., "Soil Sampling and Analysis for Volatile Organic Compounds", EPA/540/4-91/001, February, 1991.

Maskarinee, M .P., et. al., "Stability of Volatile Organics in Environmental Soil Samples", Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831, ORNI/TM-12128, 1992.

Massachusetts Department of Environmental Protection, "Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)", DRAFT Laboratory Standard Operating Procedures (SOPs), August 1995.

Massachusetts Department of Environmental Protection, "Issues Paper - Implementation of the VPH/EPH Approach", May 1996.

Massachusetts Department of Environmental Protection, "Beyond TPH - Understanding and Using the New VPH/EPH Approach", Slides and handouts from joint MADEP and LSP short course, June 1997.

Massachusetts Department of Environmental Protection, "Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of MADEP VPH/EPH Approach", Public Comment Draft, October 1997.

Massachusetts Department of Environmental Protection, "Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)", FINAL Laboratory Standard Operating Procedures (SOPs), January 1998.

Parr, J., et. al., "Sampling and Analysis of Soils for Gasoline Range Organics", Proceedings from West Coast Conference on Hydrocarbon Contaminated Soils and Ground Water, Newport Beach, CA, February, 1990.

Schuring, J., et. al., "An alternative Technique for Sampling Soils Containing VOC's, Madison Waste Conference, 1991.

Siegrist, R., and Jenssen, P., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Environmental Science and Technology, Vol. 24, No. 9, September, 1990.

Siegrist, R., "Volatile Organic Compounds in Contaminated Soils: The Nature and Validity of the Measurement Process", Journal of Hazardous Materials, 29 (1992) 3-15, Elsevier Science Publishers B.V. Amsterdam.

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