



FINAL POLICY

**PRESERVATION OF VOCs in
SOIL SAMPLES**

MARCH 2000

Soil Sampling for VOC Analysis Policy

1.0 INTRODUCTION

This New Hampshire Department of Environmental Services (DES) “Soil Sampling for VOC Analyses” guidance document contains recommendations for soil sampling protocols for all petroleum and hazardous waste sites. The protocols are applicable to all soil samples analyzed for volatile organic compounds (VOC). This guidance was developed in response to a preponderance of scientific evidence indicating the under-reporting of VOC concentrations due to VOC loss during sample collection and storage. The three main mechanisms responsible for the VOC loss are: 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.

The EPA has issued soil VOC sampling and analysis methodology [SW 846 Method 5035 (December 1996)]. ASTM has also adopted a standard for low VOC loss sampling [ASTM Standard D4547-98 (Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds)]. In these methods (see Appendix A), methanol is added immediately to the sample while in the field to preserve the soil sample. Region IV and a number of states, including Alaska, Massachusetts, Minnesota, New Jersey, New Mexico, Pennsylvania, South Carolina and Wisconsin, have adopted policies requiring methanol preservation of soil samples containing VOCs. In Massachusetts the methanol preservation requirement was established on October 31, 1997 for the Volatile Petroleum Hydrocarbon (VPH) analysis method and on March 5, 1999 for all soil samples subject to VOC analysis (Preservation Techniques for Volatile Organic Compound (VOC) Soil Sample Analyses: WSC #99-415). The Massachusetts Policy and a general article on VOC loss from samples are included in Appendix B.

DES believes that the availability of specialized soil VOC sample containers with pre-measured methanol and the recent development of alternative low VOC loss sample devices/containers minimizes the costs and logistical requirements for implementing this new sampling approach.

2.0 APPLICABILITY

Sampling protocols contained in this document are required for all soil samples that will be analyzed for VOCs by EPA SW 846 Methods 8015A, 8021B, 8260B or equivalent EPA Standard Methods procedures. The sampling protocols should also be used whenever VOC loss can significantly affect the accuracy of the results, such as the analysis of gasoline contaminated soil for TPH. The policy does not apply to onsite mobile laboratory analyses, when samples are collected and analyzed the same day. The policy also does not apply to field screening methodologies, such as PID/FID headspace screening, UV Fluorescence & Adsorption, Immunoassay Test Kits or portable GC units that are used on a real time basis. All other data obtained from a sampling methodology that does not follow this policy will be considered to be improperly preserved and not scientifically valid. DES may reject the results and require resampling when the soil sampling protocols in this policy are not properly followed. No phase-in of the policy is

recommended because of the general availability of the required sampling equipment, and the familiarity of the laboratories in the region with the required methodologies due to the similarity with Massachusetts' policy. This policy will become effective March 30, 2000.

3.0 PREVIOUSLY OBTAINED OR SUBMITTED DATA

The following table describes how unpreserved VOC soil data will be managed, based upon the sample collection and the report submission date.

Sample Collection Date	Data Submission Date	Comments
Before 3/30/2000	Before 3/30/2000	DES will not reopen sites that were closed based on previous sampling practices, unless new data or information becomes available. DES may require reevaluation of data at active sites, if evidence exists that may be significant health and environmental concerns. Factors that will be considered when making a decision to reevaluate existing data are listed below.
Before 3/30/2000	On or after 3/30/2000	Consultants and site owners should evaluate the data and site characterization to determine whether loss of VOCs is a significant issue. The report should discuss the sampling protocols that were used and recommend whether the soil should be resampled.
After 3/30/2000	On or after 3/30/2000	Proper preservation techniques must be used, or DES will not accept the data. The petroleum reimbursement funds will not reimburse for the cost of the analysis of samples that were collected improperly. Change orders for related costs can be submitted to the reimbursement program for work scopes submitted prior to implementation of the policy.

Data Evaluation Factors

1. VOC headspace and other screening data indicate significant levels of VOCs;
2. The type, toxicity and persistence of VOCs present (e.g., Chlorinated compounds and MtBE generally pose a greater long term threat to groundwater and the environment);
3. High and/or consistent levels of VOCs in groundwater indicate that VOCs in soil may be a continuing source; or
4. The presence of sensitive receptors or exposure pathways at or in the vicinity of the disposal site.

4.0 METHODOLOGY

The methodology in ASTM Standard D4547-98 or EPA Method 5035 should be followed for the collection of all VOC samples. These methods provide additional, valuable guidance on sampling protocols, for example, procedures necessary to successfully sample oily wastes. DES believes that in the vast majority

of cases samples can be collected using the following two soil preservation techniques discussed in ASTM D4547-98 and EPA Method 5035: 1) field preservation with methanol and 2) the use of a low VOC loss sampling system such as the EnCore™ sampler or equivalent. The DES requires that the laboratory report a minimum wet weight estimated quantitation limit of 100 µg/kg for these two methods.

A third methodology can potentially be used to achieve a lower VOC detection limit (<100 µg/kg). This method is known as the low level or sodium bisulfate preservation technique. DES notes that only the following twelve VOC contaminants have S-1 soil cleanup standards equal to or below the <100 µg/kg detection limits achievable by methanol preservation: acrylonitrile, bromodichloromethane, bromoform, chloroform, dibromochloromethane, dibromochloropropane, 1,2-dichloroethane, 1,2-dichloropropane, ethylene dibromide, methylene chloride, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane. All of the S-1 soil standards for these compounds were based on a potential threat to groundwater, not direct contact risk. As a result, it is not necessary to achieve the lower detection limit using the sodium bisulfate preservation technique, if data exists indicating that groundwater impacts have not occurred. It should be noted that the bisulfate method has the following shortcomings: a) special equipment is required at the laboratory, b) the sodium bisulfate may react with humic compounds to generate acetone and 2-butanone, c) the sample will effervesce when carbonates are present and d) more complex field protocols are required. DES, as a result, does not recommend the use of the sodium bisulfate preservation technique, unless the lower detection limit is absolutely necessary to identify groundwater contamination source areas containing one of the twelve contaminants with S-1 standards less than or equal to 100 µg/kg.

DES will consider other low VOC loss sampling protocols beyond the three discussed in this document on a case-by-case or site-specific basis. DES approval is required prior to sample collection for any other low VOC loss protocol that is not specifically discussed in this policy.

4.1 Methanol Preservation

The methanol preservation technique must be performed in the field and involves the following key steps:

- Collection of 5 to 25 grams of soil. Typically the lab will mark a level on the bottle that indicates the volume that should result after the addition of the soil to the methanol. A duplicate sample should be collected, in case the sample analysis must be rerun. Additional samples may need to be collected based on site-specific QA/QC requirements (i.e., matrix spike, matrix spike duplicate, etc.)
- Addition of “purge and trap” grade or equivalent methanol to the sample vial at a desired ratio of 1:1 (grams soil/mL methanol). The tolerance for this ratio is +/- 25%. Ratios outside of this range may be acceptable, depending on data quality objectives. Soil samples must be completely immersed in methanol.
- It is not necessary to weigh the sampled soil in the field as long as the weight of the soil can be calculated and the soil weight/volume ratio is +/- 25% of the acceptable 1:1 ratio. There are a number of soil sample collection devices available to facilitate accurate collection of the required

volume of sample.

- An additional unpreserved sample must be collected to allow for a determination of moisture content. Without the additional sample, the laboratory cannot report the results on a dry-weight basis. Moisture effects may become significant at moisture contents greater than 25%. When moisture content is greater than 25%, data reports should discuss the implications of sample dilution resulting from the high moisture content.
- The sample must be analyzed by an EPA or New Hampshire accredited laboratory.

DES prefers the use of sampling bottles obtained from the laboratory with pre-measured quantities of methanol. This will ensure that appropriate purity methanol is used and minimizes handling of methanol by field personnel. DES also recommends using a volumetric sampling device to collect the soil sample. This minimizes the loss of VOCs during sample collection and eliminates the need to weigh samples in the field. Sample containers should not remain open for long periods of time to minimize the potential for cross contamination of the sample and the loss of methanol. Please refer to ASTM D4547-98 and EPA Method 5035 for additional information about proper sampling technique and the sodium bisulfate method (if site specific circumstances warrant its use).

4.2 Alternate Sampling Methods

An EnCore™ sampler or similar DES approved device with proven effectiveness may be used to obtain samples in the field without preservation, provided that the sample is extruded into methanol or extracted by a laboratory within 48 hours of sample collection. The sampler must follow the manufacturer's directions for the sampling device used and all other appropriate sample preservation protocols, such as keeping samples at or below 4° C. Information on the use of EnCore™ samplers is included in ASTM 4547-98 in Appendix A.

5.0 SAMPLE COMPOSITING

Composite samples can be collected using the methanol method of sampling. To accomplish this, grab samples would be collected in accordance with the methodology discussed in section 4.1 of this policy. The laboratory then prepares the composite sample by using a syringe to collect equal amounts of the methanol preserved sample from each of the vials. The subsamples are then combined to yield the required composite sample volume.

An alternate approach to collecting composite samples that does not require compositing of the samples at the laboratory is to use a large VOC vial with septum lid. Methanol is added to the VOC vial in proportion with the number of samples that will be composited to ensure that the desired ratio of 1:1 (grams soil/mL methanol) is maintained. For example, 25 ml of methanol would be added to composite five, 5 gram soil samples. All of the soil samples that are to be composited are then added to the VOC vial containing the methanol with care exercised to prevent methanol from splashing out of the vial.

Soils that are proposed for reuse onsite must be analyzed using a low VOC loss composite sampling methodology such as this, or by representative low VOC loss grab sampling. DES does not require that this policy be used for the purposes of characterizing soil for an offsite disposal facility. It is necessary to use the sampling approach discussed in this policy, however, if the data will be used for both offsite site disposal facility purposes and remedial decision making on whether the soil can remain onsite.

Appendix A
ASTM D 4547-98 and EPA Method 5035

Appendix B
Massachusetts [Policy](#) and Article