MEMORANDUM

Subject: New methods for Preservation of Volatile Organic Compounds in Soil

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To: All DHWM Personnel

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I. Implementation

Methods 5021 and 5035, outlined in this memorandum, are currently available for use by the regulated community. These methods are incorporated in the latest update to SW-846 which was finalized in June of 1997. Methods 5021 and 5035 mark a fundamental change in how soil samples are taken and analyzed for VOCs. Sampling for compliance, closure of hazardous waste sites, and RCRA corrective actions will be impacted by these changes in sampling methodology. It is therefore necessary that personnel understand the various options and procedural changes that these methods entail. Of the two methods addressed in this memorandum, method 5035 will have the widest applicability to the hazardous waste (RCRA, Subtitle C) program. Recommendations concerning implementation of this method are:

1. OEPA, DHWM recognizes the advantages in analyzing soils for VOC concentrations using Method 5035. The primary application for the RCRA program is in assessment and closure of RCRA units.

2. OEPA, DHWM recognizes that method 5035 is a major departure from the conventional methods for sampling soils and for analysis in a laboratory. Because the implementation of this method requires a large capital outlay from laboratories and training for consulting firms, OEPA, DHWM will not require the use of method 5035 until June 30, 1998. After this date, OEPA, DHWM expects that method 5035 will become an integral component of sampling and analysis plans and closure plans submitted for DHWM's review. This time frame will also allow environmental laboratories to acquire the proper equipment, train personnel, and perform method detection limit studies.

3. OEPA, DHWM will not require sampling and analysis plans and closure plans that were approved prior to June 30, 1998 to be modified to reflect the changes in soil sampling that is outlined in Method 5035.

II. Specific Options and Recommendations

Method 5035 allows a variety of options for the collection of soil samples. The need and use of each option must be based on the specific site requirements and data quality objectives. The type of option must also reflect the required risk-based standards and

other closure standards at a particular site (e.g., MDL would be less than 5 ppb for some constituents). The following list details several options that are available for use, based upon method 5035:

1. High Concentration VOC Option: (If the soil contains greater than 200 ppb VOCs):

a. Soil samples may be collected using the options stipulated in Method 5035. The use of the EnCoreTM Sampler is encouraged because of its ease of use.

b. If the data quality objectives can be satisfied with raised detection limits, one field VOA vial, or one EnCoreTM Sampler may be collected and preserved with methanol.

c. It is important to note that method 5035 allows the use of the "bulk" method for high concentrations (> 200 g/kg) of VOCs (see section 2.2.1, method 5035). Thus, screening and hazardous characteristics assessment CAN be accomplished using the present sampling procedures. For example, if the sample volume is sufficient, TCLP and Total VOC concentrations can be determined from one sample container.

d. Methanol extracts can be composited. In addition, there are distinct advantages to methanol preservation. Multiple analyses can be made on a single sample.

2. Low Concentration VOC Option: (If the soil contains less than 200 ppb)

a. Soil samples may be collected using either VOA vials or the EnCoreTM Sampler. The use of the EnCoreTM Sampler is encouraged because of it's ease of use.

b. If the EnCoreTM Sampler is used, two to three samplers may be required per sample location. If effervescence is not a problem, these samplers should be preserved with sodium bisulfate in the laboratory.

- An additional bulk sample must be taken for percent moisture determination and for screening of effervescence.
- If effervescence is a problem, the samples should not be preserved (i.e. distilled water will be used as the matrix modifying solution).
- The EnCoreTM Sampler is not appropriate for samples with high water (>30%), or organic carbon (>2%) content, where free product is present, or if soils are non-cohesive.

c. If pre-preserved VOA vials are to be used, two to three VOA vials may be collected per sample location. Two of these vials should be preserved with sodium bisulfate solution. If effervescence is a problem, a VOA vial containing distilled water should be used to collect the sample. An additional vial may also be required for QA/QC requirements.

- An additional bulk sample must be taken for percent moisture determination and for screening of effervescence.

- If effervescence is a problem, the sample should not be preserved (i.e. distilled water will be used as the matrix modifying solution). This would require prior knowledge of soil composition.
- A field analytical balance is required for this option.

3. Sampling unknown VOC concentrations in soil

a. If the concentrations of VOCs are not known, it is recommended that three EnCoreTM Samplers be used. One sampler will be designated for high level analysis (preserved with methanol) and the other two are for low level analysis (preserved with sodium bisulfate). The actual preservation of samples will take place in the laboratory.

- An additional bulk sample must be taken for percent moisture and for screening of effervescence.

b. If field preservation is used, at least three VOA vials must be collected per sample location. One will be preserved with methanol, and the other two with sodium bisulfate. An additional VOA vial containing distilled water should also be considered if the soils are highly calcareous. QA/QC requirements may require additional VOA vials.

- An bulk sample must be taken for percent moisture determination and for screening of effervescence.

III. Other Considerations

- The person responsible for reviewing sampling and analysis plans, or closure plans MUST be aware of specific data quality objectives of the site being investigated. This person MUST be aware that detection limits will be raised for methanol preserved samples. Sodium bisulfate preserved samples may also have raised detection limits. The responsible party is encouraged to seek confirmation from their contract laboratory that it can meet the method detection limit requirements for closure PRIOR to initiation of sampling.
- Method 5035 allows the compositing of soil samples taken for VOC determination. Soil samples are not actually composited - only the methanol extracts.
    - The reason for compositing samples must be clearly spelled out and how the data
      will be used.
    - The number of individual aliquots must be specified
- Methanol is a hazardous substance and proper safe-handling practices should be considered. In addition, methanol preserved samples may require the use of a separate transportation carrier because of hazardous substance shipping restrictions. Assurances from the laboratory must be obtained on how it will handle samples as a regulated substance.

- Volatile Organic Compounds (VOCs) are ubiquitous contaminants found at hazardous waste sites. VOCs generally have boiling points less than 200 C and are relatively insoluble in water. They do partition into the soil atmosphere, sorb onto soil particles and, to a limited extent, solubilize into pore water. This multi-phase partitioning enhances the migration of VOCs from their source. The migration of VOCs is a particular concern because many of these compounds are carcinogens.

  The volatility of VOCs are a problem because field procedures and sub-sampling in the laboratory can effectively diminish the concentration of VOCs in soil samples prior to analysis. This negative concentration bias has long been recognized by organizations such as the U.S. EPA, and ASTM. To over come volatilization from sample handling, U.S. EPA adopted new procedures that are contained in SW-846, Update III, 5000 series methods. These methods establish new sample handling procedures, preservation methods, and sample introduction methods for soil and waste samples. The benefits of sample preservation, an outline of SW-846 5000 series method procedures, and recommendations from Ohio EPA, DHWM will now be presented.

IV. Background Information

Field sampling for volatile components usually involves taking soil from a core; soil profile, such as a trench wall; or from surficial materials. Soil is spooned into a 4-, 6-, or 8-ounce jar and packed tightly until there is no head space. The jar's outer surface is wiped and then quickly capped with a Teflon-lined lid. The sample container is placed on ice and delivered to the laboratory for analysis. Once in the laboratory, a sub-sample is removed from the jar, placed in a VOA vial, where distilled water, internal standards, and surrogate compounds were added. This sample is usually analyzed by a purge and trap technique (method 5030). The various practices that are used to prepare the sample for analysis presents many opportunities for volatile compounds to escape.

Investigations concerning sampling procedures conducted by U.S. EPA have concluded that loss of volatile compounds from soil samples is due to a combination of physical and biological processes. Primarily, volatile loss occurs with field activities that tend to increase the surface area of the soil. These activities include removal of soil from the sampling device, sub-sampling the soil, and desegregating the soil to fit into the sample bottles. Other losses can occur when small soil particles prevent the lid from being tightly capped. One study illustrating volatile loss from improper sealing techniques showed that approximately 40 percent of the volatile compounds were lost in 5 days. Transportation of sample containers may also have an effect on volatile loss. For example, air transport may enhance volatilization because of the rapid fluctuations in pressure and temperature. Sample preparation in the laboratory can also lead to VOC loss. Volatization develops in a number of different ways. Mandatory laboratory practice, such as opening the jar for sub-sampling, will result in loss of VOCs. Furthermore, investigations have shown that a major mode of loss occurs when the sample aliquot is removed from the jar and weighed. This practice acts to break apart the soil leading to

an increase in surface area and volatilization. In addition, accurate weighing takes time which would promote volatile loss. Therefore, sub-sampling practices in the laboratory tend to intensify volatile loss from soil, especially if it is coarse-grained and dry.

Biodegradation of certain volatile compounds (especially BTEX compounds) can also occur prior to sample analysis. The usual method of soil preservation, cooling the sample to 4 C, may be inadequate where soil micro-flora is abundant and active. For example, Hewitt et al. (1995) performed experiments on soil samples with spiked aliquots of benzene and toluene. These soil samples were held in hermetically sealed vials, and cooled to 4 C. The only expected loss of VOCs from these samples would be from biological mineralization. The initial concentration of these compounds were 13.0+0.2 ppb and 33+0.5 ppb, respectively. At the end of 14 days, the normal holding time for VOC analysis, the concentrations decreased to non-detectable levels for benzene and to 10+2.5 for toluene. Control samples showed no loss of these compounds over this period. Therefore, biological activity can result in major losses of VOCs over short spans of time.

V. Introduction to Modified Sampling Techniques and Preservation

If volatilization is promoted by field and laboratory practices, how can these effects be overcome? Research at U.S. EPA and other research groups have lead to the promulgation of procedures that are part of the latest update to SW-846 method series 5000 (preparatory techniques for volatile analysis). These procedures try to avoid volatilization by limiting sample handling and/or preserving soil samples with solvents.

- Method 5021: An automatic headspace method for soils and other similar solids. This method requires that a soil sample be placed in a pre-weighed septum-sealed vial at the time of sampling. A device must be used to obtain the correct amount of soil (e.g. 2 to 10 grams). In addition, the method recommends that 3 to 4 vials of soil be collected per sample. These separate vials provide for screening samples for high concentrations of VOCs (high concentrations are greater than 200 g/kg) and for the determination of moisture content. If high concentrations of VOCs exist, samples may be preserved by the addition of reagent grade methanol to the sample through the septum.
- Method 5021 provides for three variations in sample collection. The first procedure is to add soil to a pre-weighed VOA vial without addition of a matrix modifying solution or standards. The second method calls for the addition of matrix modifying solution to the soil sample in the field. The third method calls for the addition of soil to a VOA vial that contains 10 ml of reagent grade water. In addition, preservation of the sample by methanol may be added to sampling protocol.
- After the sample is collected and sent to the laboratory, the sample vial is then heated to 85 C and mixed by mechanical agitation. A measured aliquot of headspace gas is sampled automatically and introduced into a gas chromatograph (GC) and mass spectrometer (MS) for analysis.

- Method 5035: This method is a closed-system purge and trap method for soils and other similar solids. This method deviates from method 5030, the present purge and trap method, in that a soil sample is placed into a pre-weighed vial with a matrix modifying solution at the time of sampling. This method therefore reduces volatilization by sample handling and manipulation. The sample remains sealed throughout the analysis process. Standards, surrogates and a matrix modifying solution are added by the purge and trap system. Method 5035 also allows for the addition of methanol to a sample as a preservative.
- The samples are purged directly from the sampling vial using helium carrier gas for 11 minutes. The purged gases are trapped on an adsorbent column and then heated to desorb the volatile compounds into the GC system.
- Methanol Preservation: Both of these methods allow the investigator to preserve samples with methanol. The addition of methanol effectively reduces volatilization and microbial decomposition of VOCs. However, SW-846 cautions that methanol preservation should be used only if the soil contains greater than 200 g/kg of a volatile constituent. Since the concentration of constituents of concern are not known in most sampling situations, SW-846 recommends that an additional VOA vial of soil be collected at every location and preserved with methanol.
- EnCoreTM Sampler
- The procedures outlined above usually call for a fixed weight of sample to be added to the sample vial. SW-846 recommends several procedures to accomplish this task, but most of these procedures require weighing the sample in the field. Accurate weighing is essential because the final concentration is determined based on the weight of the sample. Weighing samples in the field are complicated by wearing gloves and other personnel protective equipment. In short, the problems associated with weighing samples may outweigh the advantages of these new methods. U.S. EPA recognized this problem and has recently recommended the use of a commercial device called the EnCoreTM Sampler. This device consists of a barrel capable of being capped, a T-handle, and a push rod.
- The EnCoreTM Sampler is used by thrusting it into the soil until it is full. The sampler is wiped, sealed, preserved with ice, and sent to the laboratory for analysis. Alternately, the sampler can be used to add soil to VOA vials for headspace (method 5021) or sealed purge and trap methods (method 5035). Matrix modifying solutions or methanol are added in the laboratory. The EnCoreTM Sampler was evaluated by it's manufacturer and found to have no significant loss of volatiles in unpreserved soil samples for as long as 48 hours after sampling. In addition, if the soil was extracted into methanol, sample concentrations were found to be 2 to 3 orders of magnitude higher than the bulk purge and trap method (method 5030).

A summary of options is presented in the following table.

Summary Table for Field Collection of Soil Samples				
SAMPLE COLLECTION STRATEGY		SAMPLE PREPARATION		ANALYSIS STRATEGY
TECHNIQUE	PROTOCOL	LOW LEVEL	HIGH LEVEL	PROTOCOL
EnCore Sampler:	1.Collect up to 3 EnCore Samplers per sample. 2. Collect soil in container for dry weight determination.	Tare VOA vials with sodium bisulfate. Extrude soil from EnCore Samplers. (48- hour holding time)	5 ml of Methanol added to sample either in the field or the laboratory. Methanol extracts can be composited	Up to three analyses can be run per sample (two low and one high). One sample may be archived (methanol). QA/QC samples would require a 25 ml EnCore Sampler.
VOA Vials:	1. Field scale needed for weighing. (+ 0.01g accuracy) 2. Need 3 tared VOA vials per sample with sodium bisulfate. 3.Methanol preservation is required for high level analysis.	Reweigh VOA vials in lab. Reject if proper weight is not found.	5 ml of methanol added to VOA vials. Methanol can be added to the VOAs before being sent or added in the field. Methanol extracts can be composited	Up to three analyses can be run per sample (two low and one high). One sample may be archived (methanol). QA/QC samples would require at least an additional VOA vial.