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# Sampling and On-Site Analytical Methods for Volatiles in Soil and Groundwater

## Field Guidance Manual

Alan D. Hewitt and Karen F. Myers

November 1999

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**Abstract:** Volatile organic compounds (VOCs) are among the most frequently identified contaminants in soil and groundwater samples obtained during the investigation of suspected hazardous waste sites. Because some VOCs and their degradation products are potentially mutagenic, carcinogenic, or teratogenic, their concentrations in these two matrices are key factors in the risk assessment process. Furthermore, when risk-based corrective actions are deemed necessary, the subsequent selection and implementation of the appropriate remediation technologies rely heavily upon the VOC concentrations established during site characterization activities. This report briefly addresses procedures, equipment, and logistics for the collection and timely (less than 48 hr) on-site analysis of VOCs in discrete soil and groundwater samples. The collection, preservation, and preparation procedures presented strive to acquire and maintain analyte concentrations that are representative of the location and medium from which the sample was removed.

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OFFICE OF THE CHIEF OF ENGINEERS

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## PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, Cold Regions Research and Engineering Laboratory (CRREL), U.S. Army Engineer Research and Development Center (ERDC), Hanover, New Hampshire, and by Karen F. Myers, Environmental Laboratory, ERDC, Vicksburg, Mississippi. Funding was provided by the U.S. Army Corps of Engineers Advanced Site Monitoring Systems AF-25 programs, Dr. James Brannon, Project Monitor.

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# Sampling and On-Site Analytical Methods for Volatiles in Soil and Groundwater

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ALAN D. HEWITT AND KAREN F. MYERS

## INTRODUCTION

In soil and groundwater, volatile organic compounds (VOCs) coexist in equilibrium among two to three physical phases, i.e., liquid, solid (sorbed), and gaseous (Minnich 1993, Lewis 1994). The fairly rapid shifts in equilibrium among these phases have often confounded efforts to establish representative environmental concentrations. For instance, when performing the collection, handling, or storage of soil samples prior to analysis, uncontrolled losses of VOC can easily bias the quantitative estimates by one or more orders of magnitude (Siegrist and Jenssen 1990, Urban et al. 1989, Illias and Jeager 1993, Hewitt et al. 1995, Liikala et al. 1996, Smith 1996). In extreme cases, losses from poor collection and handling techniques with respect to a porous medium can result in false negatives, e.g., the failure to identify VOCs when they are present. In general, the greatest sources of indeterminate error associated with the characterization of VOC concentrations are volatilization, and to a lesser extent, biodegradation.

Volatilization losses occur whenever gaseous molecules, which have diffusion coefficients up to four orders of magnitude greater than liquid diffusion coefficients, are allowed to move freely. The extent to which VOCs can be lost by this mechanism depends on the vapor phase concentration (analyte vapor pressure), duration and extent (surface area) of exposure, and the matrix porosity (Siegrist and Jenssen 1990). Siegrist and Jenssen (1990) and Hewitt and Lukash (1996) have shown that significant volatilization losses often occur on a time scale measured in minutes. Biodegradation losses are also a function of several variables, e.g., indigenous microbiological population, chemical properties of contaminant analytes, temperature, and length of sample storage prior to analysis (Hewitt 1995). The potential for biodegradation losses is not as great as that for volatilization losses, because they are not as rapid. Indeed, most experimental evidence has shown that it often takes at least a couple of days before losses solely caused by biodegradation are significant.

## SAMPLING

### Soil sampling

Soil sample collection and on-site preparation and analysis require a timely and well-orchestrated protocol for both surface and subsurface characterization activities. For example, subsurface investigations require that an intact bulk sample be brought to the surface so that subsamples can be transferred to prepared container(s) for the chosen method(s) of chemical and geotechnical analysis. With respect to VOC characterization, the two most common methods for preparing discrete soil subsamples for instrumental analysis are methanol extraction and direct vapor partitioning (i.e., purge and trap or headspace). Choosing which (or both) methods of subsample preparation should be used depends on the data quality objectives and instrumentation used for analysis (e.g., site-specific action levels and detection limits for the sample preparation

and analysis procedure must meet the project objectives). All of the issues concerning how to handle and prepare samples must be resolved before the sampling activity. The following sections discuss in greater detail the various steps and some of the criteria for selecting a method of subsample preparation and on-site analysis. Subsurface bulk sample collection is discussed prior to discrete sampling activities, since this is the logical sequence of events when characterizing the vadose zone. The procedures presented for the collection of subsurface bulk samples and for obtaining and processing discrete samples are consistent with the latest revision of the ASTM D4547 (American Society for Testing and Materials 1998), and with the EPA SW846 Methods 5021 and 5035 (U.S. EPA 1997a, 1997c).

*Subsurface bulk soil sample collection*

There are at least two steps involved in performing subsurface soil sampling: the retrieval of a bulk sample from the depth of interest, and the subsequent transfer of subsamples to volatile organic analysis (VOA) vials. To obtain subsurface bulk samples, usually a hollow tube designed to obtain an intact cylindrical core of material is used. Coring tubes typically range in size from 1.5 to 4 in. (3.8 to 10 cm) in diameter, and one to several feet (meters) in length. Coring tubes are filled by being hydraulically pushed (i.e., geoprobe and penetrometer), hammered, or vibrated in a previously undisturbed formation. For sampling activities within the first 6 m, manually operated coring devices can often be used, while equipment mounted in a pickup truck (small vehicle) can often reach up to 15 m in many geological formations. When sampling at depths below 15 m, often it is necessary to use larger and less mobile equipment, for instance, a drilling rig equipped for hollow stem augering or a 20-ton or larger cone penetrometer truck.

Two of the more commonly used coring devices for subsurface sample collection and retrieval are the split-spoon corer and core barrel liners. Once filled and returned to the surface, the ends of the split-spoon corer and one side of the core barrel are removed, so that one-half of the surface area of the bulk sample can be exposed for subsampling. The split-spoon corer and many other types of hollow coring devices can also be equipped with a core barrel liner. Core barrel liners fit snugly within a corer and come in a variety of lengths and materials (stainless steel, brass, Teflon, rigid plastics, etc.). When core barrel liners are used, subsamples can be removed through the open ends, or if constructed of a plastic material, they can be cut at any point to allow access. Subsurface materials taken for VOC characterization should be brought to the surface as quickly as possible and remain undisturbed until they are subsampled. This subsampling operation should be performed without delay (within several minutes) to limit losses of VOCs through the open ends of the coring tube. Temporarily capping the ends of the core barrel liner is not recommended, since sheets of Teflon or aluminum foil are not adequate VOC vapor barriers (Hewitt and Lukash 1996). The number of bulk samples that can be brought to the surface in 8-hour period ranges anywhere from 10 to 100, depending on the sampling depth, sampling intervals, type of geological formation, and the equipment used.

A study comparing subsurface sampling equipment, which meets the guidelines provided here for subsampling and rapid on-site analysis (within 48 hr), was recently completed by the U.S. EPA's Environmental Technology Verification Program (U.S. EPA 1998a, b, c, and d). The main purpose of this effort was to compare different subsurface sampling technologies. The technologies compared were (1) a conventional hollow stem auguring and split spoon sampler, (2) Large-Bore Soil Sampler (Geoprobe Systems), (3) JMC Environmentalist's Subsurface Probe (Clements Associates, Inc.), (4) Dual Tube Liner Sampler (Art's Manufacturing & Supply, Inc.), and (5) the Simulprobe sampler. The following criteria were used to compare these bulk soil sampling systems: sample recovery (i.e., volume obtained), contaminant concentration, sample integrity (e.g., cross-contamination between sampling locations), reliability, rate of sample collection, and cost.

Two sites were selected for this study, one being characterized as having clay soils and the other as a sandy soil. At both sites, cis-1,2-dichloroethene, trichloroethene, and tetrachloroethene were present, while 1,1,1-trichloroethane was present at only one of the sites. Samples were collected from discrete locations in the subsurface between a depth of 1 to 12 m that had been previously identified as having high or low levels of contamination present (i.e., greater than or less than 0.2 mg/kg). Samples were obtained at seven randomly selected positions within a 3.2- × 3.2-m specified grid, at several different locations on each site, using each of five subsurface samplers listed above and the subsampling procedures cited below. Table 1 shows the average sampling rate for

**Table 1. Sampling rates for five different subsurface bulk sample retrieval technologies.**

| | *Clay soil** | *Sandy soil** |
|---|---|---|
| Hollow stem augering–split spoon sampler | 18 | 57 |
| Simulprobe™ Core Barrel Sampler† | 22 | 41 |
| JMC Environmentalist's Subsurface Probe** | 13 | 21 |
| AMS Dual Tube Liner†† | 29 | 44 |
| Geoprobe™ Large-Bore soil sampler*** | 17 | 31 |

*Average number of samples collected over an 8-hr period (i.e., time to set up equipment, collect a sample at one specified depth, grout hole, decon equipment, and move to next sampling location).
†Simulprobe, 150 Shoreline Highway, Bld E, Mill Valley, CA 94941.
**Clements Associates, Inc. (JMC Environmentalist's Subsurface Probe), 1992 Hunter Avenue, Newton, IA 50208.
††Art's Manufacturing & Supply, Inc. (Dual Tube Liner Sampler), 105 Harrison St., American Falls, ID 83211.
***Geoprobe Systems, 601 N. Broadway, Salina, KS 67401.

these five different bulk sampling systems. The other criteria evaluated during this program, while exposing some limitations and potential weaknesses, did not establish that any of these subsurface sampling systems would be inappropriate for site characterization.

*Discrete samples (i.e., subsamples taken for analysis)*

After a fresh surface is exposed to the atmosphere, whether it is a split-spoon, barrel liner, pit wall, or a surface location (e.g., manually dug hole), the subsampling process should be completed in a couple of minutes. If a surface has been exposed for more than a couple of minutes, it should no longer be considered fresh, and rough trimming of at least 2 cm from the surface with a clean spatula, scoop, knife, or shovel should be performed before subsample collection. To obtain and transfer a subsample, a hand-operated coring tool that acquires and holds a subsample of the appropriate size for analysis (e.g., 5 g or larger) should be used. Coring tools for the purpose of transferring a subsample can be made from disposable plastic syringes by cutting off the tapered front end and removing the rubber cap from the plunger (Fig. 1). Plastic coring tools are commercially available (U.S. Oil Co., Inc., Kimberly, Wisconsin) and also can be made from a small piece of pipe and solid rod. This type of subsampling device helps to maintain the structure of the materials being sampled during collection and transfer to a VOA vial or a larger bottle.

The VOA vials or bottles used for sample collection should be made of glass, have a Teflon-lined septum, and a rigid cap that creates an airtight (hermetic) seal when screwed on. The thickness of the Teflon used for lining the septum should be at least 10 mil. The selection of a coring tool size depends on the following: size of the opening on the collection vial or bottle (tool should fit inside the mouth of the sample bottle), particle size of the solid materials (e.g., gravel-size particles would require larger samplers), and volume of sample required for analysis. To collect an undisturbed subsample, the barrel of the coring tool is pushed into a freshly exposed surface and removed once the desired volume has been ob-

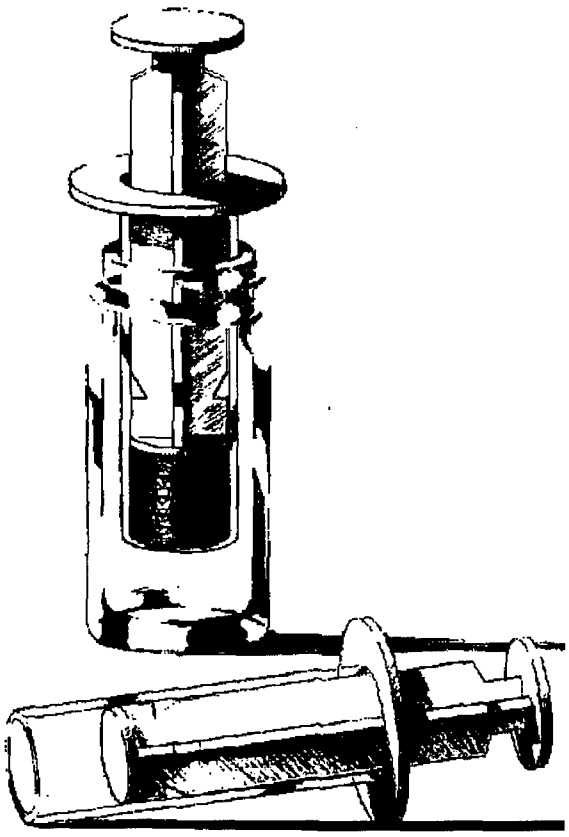

*Figure 1. Modified 10-mL syringe and empty VOA vial. The syringe was modified by removing the tip and rubber plunger cap.*

tained. After removing it from the substrate, the exterior of the barrel should be quickly wiped with a clean disposable towel, and then the subsample is extruded into a tared VOA vial. Transferring a sample and closing the sample vial should be done rapidly (<10 seconds) to limit volatilization losses.

Samples of hard or cementitious material may be obtained by fragmenting a larger portion of the material using a clean chisel to generate aggregate(s) of a size that can be placed into a VOA vial or bottle. When sampling gravel, or a mixture of gravel and fines that cannot be obtained or transferred using coring tools, a spatula or scoop can be used as a last resort. Caution should be taken in the interpretation of the data obtained from materials that fit either of these two descriptions. In the case of cementitious materials, losses of VOCs by using this procedure would depend on the location of the contaminant relative to the surface of the material being sampled. For gravel and loose fines, losses of VOCs are likely because of the nature of the sampling method and the noncohesive nature of the material (Hewitt et al. 1995).

**Groundwater**

Within the saturated zone VOCs exist principally as a dissolved or undissolved (sorbed or nonaqueous) state. The collection of a groundwater sample, while less susceptible than a porous medium to volatilization losses, still must be performed in a timely well-orchestrated fashion. With respect to groundwater characterization, a recent concern has been focused at how to obtain samples that are representative of the formation (ambient flow conditions at a given depth within the saturated zone). This concern has led to the development of a low stress (e.g., low flow, < 1 L/min.) or limited disruption approach to monitoring well purging and sampling that requires that stable water chemistry exists prior to initiating sample collection. Past groundwater sampling guidance often specified the removal of five or more well volumes of water prior to sample collection. This practice is no longer recommended since it is arbitrary relative to the chemistry of groundwater. For example, rapid purging tends to create a drawdown condition that heavily favors the chemistry related to the zone of greatest permeability (fastest recharge), which may or may not be representative of the formation over the screened interval. Furthermore, rapid purging also has a tendency to increase particulate loading (Puls and Paul 1995).

By convention most monitoring wells are installed in a vertical orientation and located so their screened interval, which is typically a 3-m-long section, intercepts the contaminant plume(s). However, the low-stress groundwater sampling procedure is not only limited to wells of this configuration; it can also be used in horizontal wells or ones were the screened interval extends from the top of the groundwater table to bedrock. When large screened intervals exist, this sampling procedure can also be used to determine if there is a vertical or horizontal concentration profile within the well. The sampling procedures presented in this report are consistent with revision 2 of "low stress (low flow) purging and sampling procedure for the collection of ground water samples from monitoring wells" (U.S. EPA Region I 1996a). Sample preservation and subsample preparation follows the recommended procedures in Method 5030B (U.S. EPA 1997b).

Prior to installing a pump for purging and sampling, synoptic water level and well depth measurements should be performed. If the well depth measurement is not made the day prior to the sampling event, this task should be performed after sample collection so as not to increase the particulate loading in the water column. A submersible pump capable of reduced flows of between 0.1 and 0.4 L/minute and able to push a column of water from the sampling depth to the surface (i.e., stainless steel centrifugal or bladder pumps) should be slowly lowered into the water column until the desired sampling zone is reached. Before starting the pump, the water level should be measured to establish the nonpumping elevation. Well purging is initiated by running the pump at its lowest speed and increasing slowly until water is discharged from the transfer tubing. While water is slowly being discharged from the well, the water level should be checked for drawdown. The pump speed should be set at a minimum, and if possible, should not cause more than a 9-cm drawdown from the prepumping level. Throughout purging, the flow rate and well level should be monitored at least every 5 minutes.

Once the flow rate and drawdown criteria have been meet, a transparent flow-through cell should be put in line capable of monitoring DO (dissolved oxygen), specific conductance, temperature, pH, and ORP/Eh (redox potential). In addition, the turbidity should also be monitored. Stable groundwater chemistry is achieved and sampling can start when (1) three consecutive readings taken at 3- to 5-minute intervals fall within the range given for

each of the following parameters: DO, 10%; specific conductance, 3%; temperature, 3%; pH, ±0.1 units; ORP/Eh, ±10 mV; and (2) the final purge water volume exceeds the drawdown volume and the volume of water necessary to fill the sample transfer tubing. When more than one flow-through cell is used, the first one that groundwater passes through should contain the DO probe to avoid potential influences due to leaks or from small bubbles of air being trapped in the system. Wells that have slow recharge rates may either require a special pump capable of lower pumping rates (e.g., bladder or peristaltic pumps), or if recharge is lower than the slowest pumping rate, the well should be purged dry and then sampled as soon as recharge allows.

Water samples taken for laboratory analysis must be collected before the groundwater has passed through a cell by either having a by-pass valve or disconnecting the tubing. Furthermore, the transfer tubing should remain filled so as to minimize contact with the atmosphere. Samples taken for VOC analysis should be collected first, followed by those taken for other constituents of concern. Samples should be collected in a 40- to 120-mL VOA vial that either already contains the appropriate amount of acid (sodium thiosulfate, $Na_2S_2O_3$, ascorbic acid, or 1:1 hydrochloric acid, HCl) to establish a pH below 2, or to which this amount of acid is added immediately after filling the vial. The appropriate amount of acid needed to meet this pH requirement should be established during well purging. When filling the sample vial, it should be initially tipped to allow the water to flow gently down the side, then turned vertical so that the water surface forms a crown above the bottle's rim (top edge). By slightly overfilling the collection bottle, little or no air is trapped when the cap is screwed on. Once sealed, VOA vials containing preserved samples should be stored at 4° ± 2°C until prepared for analysis.

## PREPARATION FOR ANALYSIS

### Soil preparation

The VOA vials or bottles used for sample preparation should already have its tared weight recorded to the nearest 0.01 g before a subsample is transferred. Furthermore, the sample collection vial may also already contain a solution and stirring bar, depending on the anticipated concentrations of analytes, method of analysis, or to inhibit biological activity.

When methanol extraction is the chosen method of sample preparation, the appropriate volume of analytical-grade methanol (high performance liquid chromatography or spectrographic) is added to the container in a laboratory setting. This task can be performed prior to or after sample collection (Hewitt 1999). If methanol is added to a soil sample after it has been enclosed in a VOA vial, this addition must be performed using a syringe by puncturing the septum with a 23 or smaller gauge needle. For example, a Luer Lok needle (B-D) attached to a 5.00-mL glass syringe (SGE) with a Luer connector could be used. After introducing the methanol, the soil sample should be completely dispersed and the inner glass surfaces rinsed. Caution should be taken if aliquots are removed after different extraction periods since grit on the Teflon-lined septum may prevent a hermetic seal from forming when closing the VOA vial.

Once methanol has been placed in a container, it should be opened only to add the subsamples and to remove aliquots for analysis. The ratio of sample to methanol is based on a sample weight in grams that is equivalent to or less than the volume (mL) of methanol (i.e., ≤ 1:1, grams of soil to milliliters of methanol). Sample volume can be used instead of weight once the matrix density has been established. The ratio used between these two constituents should allow for the formation of a clear layer of methanol over the sample after thoroughly mixing and allowing the suspended particles to settle. When a sample that was placed into a VOA vial containing methanol fails to allow a clear supernatant layer to form, an additional volume of methanol can be added through the septum after the samples weight is established. The difference in weight of the container, measured before and after the sample is introduced, is used to establish the sample's wet weight. Samples immersed in methanol should not be stored for more than a couple days in VOA vials that have punctured septa. When methanol is introduced through the septum via a needle, the septum should be replaced if the sample is archived. Lastly, when samples are immersed in methanol, both organic analytes and water (i.e., soil moisture) are extracted from the sample. Because water is miscible in methanol, they form a single solution that for all practical purposes is volumetrically additive. Since an aliquot is removed from this solution, the dilution effect must be accounted for when calculating the sample's analyte concentration. Similarly, this correction factor applies to surrogates if

they are present in the sample/methanol slurry. The correction factor is the total liquid volume of the sample (methanol plus water) divided by the original volume of the methanol added to the sample vial. Therefore the correction factor is greater than or equal to 1.

When a vapor partitioning (i.e., purge-and-trap or headspace) method is the analytical method of choice, the sample is placed into a tared VOA vial from which the vapor is removed for analysis without the container being opened. Water that contains no detectable levels of VOCs can either be present in the VOA vial prior to introducing the sample, or it can be added via a needle as described above for methanol, after a sample has been obtained. However, in the case of purge-and-trap analysis, a Teflon-coated stir bar should be present prior to the sample introduction step. Furthermore, since elevated temperatures and some form of mechanical mixing are recommended during or before the removal of vapors, special automated equipment is often necessary. The current automated equipment for purge-and-trap and headspace systems use 44- (or 40-) and 22-mL VOA vials, respectively (U.S. EPA 1996a and 1996c). The volume of water used for these two different systems is typically 10 mL or less. The difference in weight of the container, measured before and after the sample is added, is used to determine the sample's wet weight.

If aromatic compounds are of concern and the sample has been taken from an area receiving treatment to increase its biological activity, then some form of preservation besides refrigerated (4°C) storage should be implemented soon (within a couple of hours) after collection. If a sample is placed into an empty VOA vial or one that contains only a Teflon-coated stirring bar and a limited amount of water (vessel less than 1/3 filled) the sample can be preserved by placing in a freezer (–12° ± 3°C) (Hewitt 1999). When methanol is present in the VOA vial, no additional preservation measures are necessary other than 4° ± 2°C storage. For vapor partitioning methods of analysis, preservation can also be achieved by making this solution acidic (e.g., a pH of 2 or less with either sodium bisulfate or hydrochloric acid), when carbonates are not present. Frozen storage should be used when carbonates are present and low level concentrations of aromatic compounds are of interest.

Because the subsample is placed directly into a tared container for both of these procedures (methanol extraction and vapor partitioning), a separate collocated sample should be collected if the analyte concentration needs to be expressed on a dry weight basis. This sample should be collected within a couple of centimeters and from the same stratum as the subsample taken for VOC analysis. Likewise, the location adjacent to where the subsample for VOC analysis was removed should be inspected visually and its characteristics logged. In addition, the adjacent material can be retained for determining other relevant properties, such as the presence of oils, other visible signs of contamination, grain-size distribution, organic carbon content, etc. Collection of these ancillary samples should be performed after subsamples for VOC analysis have been collected.

When a subsample is prepared by methanol extraction, an aliquot of the extract is transferred to a VOA vial containing water for either purge-and-trap or headspace analysis. Before an aliquot of the extract is transferred, the sample should be completely dispersed in methanol, and then allowed to settle so that an aliquot of clear supernatant can be removed for analysis. However, since studies have shown that extraction kinetics can be slow, it may be advisable to assist extraction with heat (40°C) and vibrational energy (sonication for 30 minutes) when a total recovery is necessary (Askari et al. 1996, Ball et al. 1997, Hewitt 1998). Ensuring the completeness of analyte extraction from a given matrix requires an analysis of additional aliquots after further treatment. For purge-and-trap analysis, methanol aliquot volumes of 0.1 mL or less are typically transferred, while for headspace analysis, methanol aliquot volumes as large as 1.0 mL can be transferred, depending on the detector and analytes of concern.

Vapor partitioning involves the direct analysis of a sample by either a purge-and-trap or a headspace method. In both cases, the sample is placed into a tared VOA vial from which the vapor is removed for analysis without the container being opened. Water is usually used to assist with the partitioning of the VOCs from the sample. Before being placed on the autosampler carousel, the sampled materials should be completely dispersed in water, if possible (vortex mixing or sonication can be used). This mixing of the solid material with the aqueous solution not only helps prevent the plugging of the sparging needle used by purge-and-trap systems, but the mixing also assists in attaining an equilibrium state by completely exposing the sample to the partitioning solution.

Vapor partitioning methods of sample preparation for analysis are much more likely to be af-

fected by soil matrix variables than methanol extraction. For example, when using direct vapor partitioning, it has been shown that as the organic carbon content of the matrix increases the recovery of VOCs with higher octanol-water partitioning coefficients tends to decrease (Hewitt 1998). Similar discrepancies between these two methods of sample preparation have also been attributed to the type and amount of clay present (Ball et al. 1997, Minnich et al. 1996). Therefore, methanol extraction and direct vapor partitioning should not be considered as equivalent methods of sample preparation for analysis.

### Groundwater

For the analysis of VOCs in groundwater either a 5- or 25-mL aliquot can be used. The removal of these sample volumes from the sample containers can either be performed manually or by an autosampler. In either case, the sample should be allowed to warm to room temperature before an aliquot is removed. If performed manually, the top of the collection bottle is removed and the appropriate size glass syringe is slowly filled to near capacity after removing the plunger and attaching a closed syringe valve. Once filled, the plunger is replaced and the contents of the syringe compressed slightly, the syringe valve is opened so that the trapped air can be expelled and the liquid volume adjusted to 5.00 or 25.00 mL. When samples require additional dilution prior to analysis a volumetric flask can be used. This is achieved by adding the appropriate volume of groundwater to a flask that contains organic-free water, then bringing to volume and inverting three times to mix the aqueous solutions before taking an aliquot for analysis as previously described. Autosamplers do not require that the cap be removed since they use a needle to puncture the septum of the VOA vial, and once positioned, the autosamplers withdraw the appropriate volume of groundwater through the tip of the needle while allowing a gas to fill the void created, near the vial's cap.

## ANALYSIS

### Soil samples

On-site analysis of samples by purge-and-trap (Method 5035) or headspace (Method 5021) can be coupled with any of the following accepted methods of analyte detection (Methods 8260B, 8015B, or 8021B). All of these methods rely on gas chromatography to separate the analytes prior to detection. The instrumentation and quality assurance associated with these analyses require the use of a laboratory with relatively stable indoor temperature. In addition, the weighing of sample containers before and after adding samples to them would require an enclosed area with a stable benchtop so that measurements of $0.01 \pm 0.01$ could be performed.

Method 8260B, which uses gas chromatography/mass spectrometry (GC/MS) for analyte separation and detection, offers absolute qualification for all VOCs, but has a limited range of operation and an even smaller linear dynamic range, i.e., less than three orders of magnitude. The upper threshold of analyte detection with this type of instrumentation is around $1.0 \times 10^{-6}$ g for a single analyte in a discrete sample. To cope with this limitation, 5-g subsamples with analyte concentrations greater than 0.2 mg/kg are first extracted with methanol, and then only a 0.1-mL volume of the extract is transferred into 5 mL of water for analysis. This extraction and aliquot removal step accounts for at least a 50-fold dilution in analyte concentration. Greater dilution of analyte concentration can be achieved by taking a smaller aliquot volume, or further diluting the sample with methanol. Samples with concentrations below 0.2 mg/kg can be run directly. The lower level of analyte detection for this system being between 0.1 to $1 \times 10^{-9}$ g of an analyte per sample.

To assist in deciding how samples should be prepared for instrumental analysis, a simple total VOC screening procedure has been developed using a hand-held photoionization detector and site-specific working standards (Hewitt and Stutz 1998). The main purpose of this screening method is to provide a decision tool during the sampling activity to help establish whether samples taken for laboratory analysis should be prepared by a low-level, or high-level procedure, or by both procedures. This method, which is currently being promulgated as Method 3815 "screening solid samples for volatile organics," is scheduled to be added to the SW-846, as part of the 4th update. An outline of this screening procedure is provided in Appendix A.

Method 8015B uses a gas chromatograph/flame ionization (GC/FID) analyte separation and detection system. The flame ionization detector is well suited for the analysis of petroleum hydrocarbons, including gasoline range organics (C6 to C10, boiling point range from 60° to 170°C), and nonhalogenated organics. The FID has wide dynamic range of operation extended from $1 \times 10^{-7}$

to $1 \times 10^{-2}$ g of an analyte per sample. Method 8021 uses a gas chromatograph/photoionization and/or electrolytic conductivity (GC/PID/ECLD) analyte separation and detection system. These detection system can be used for many VOCs and has a lower limit of detection around $1 \times 10^{-10}$ g of an analyte per sample. However, like the MS detection system, these detectors have a limited range of linear response, often less than two orders of magnitude.

**Groundwater**

On-site analysis of groundwater samples by purge-and-trap (i.e., Method 5030) can also be coupled with any of the following accepted methods of analyte detection, Methods 8260B, 8015B, or 8021B. See the *Soil Sample* section for a brief description of these methods. As with soil analysis a stable laboratory temperature must be maintained to meet the quality assurance requirements. Since this system can be equipped to handle a 25-mL aliquot, detection limits can be increased by about a factor of five, as compared to those of the soil samples.

## LOGISTICS

On-site analysis has been greatly facilitated by the increase in field portable analytical instrumentation and methodologies. The quality of data obtained from on-site activities, whether centered around a mobile laboratory or a permanent on-site laboratory, can be greatly increased through careful planning and by taking a few precautions.

**Location and climate control**

In many cases, a mobile laboratory can be driven directly to the sampling site. When parking, try to orient the door so that the prevailing wind does not blow exhaust fumes from operations into the laboratory and possibly compromise the quality of the samples, the analysis, or the water supply. Also, try to level the laboratory as much as possible or have leveling benches. Because of the nature of GC analysis, temperature swings of 5 or 10 degrees over the course of the working day can have an effect on identification and quantitation results. For this reason stable climate control is a necessity. Any operations that must be performed outside should take place in a sheltered area away from the prevailing wind and direct sunlight. Small, portable folding tables can improve working conditions dramatically.

**Power supply**

GCs require a stable, continuous power supply, especially if an autosampler is used to continue the analytical sequence overnight. Instruments powered down each night will require time during the next morning to warm up before calibration can be performed. This will cut into the work day. Power can be supplied by portable generators, either gasoline or diesel, or by heavy duty electrical cords tied into existing site power. When using generators, it is important to size the generator to the power requirements of the laboratory. If the fuel reservoir is too small, it may need refilling during the middle of the night to keep the instruments running. Be aware that in heavily grassed, dry areas, there is always the danger of causing a fire from the use of gasoline generators. Check with site personnel during the planning stage to identify site specific hazards or regulations.

**Laboratory supplies**

Because water for VOC analysis can easily be contaminated by gasoline and diesel fumes, the water supply should be checked frequently. When an on-site source of distilled water is not available, a water supply can be acquired through the purchase of commercial bottled water. Several local brands of distilled water may have to be purchased and tested to find a suitable water source. Bottled distilled water treated by ozonation frequently will be the best choice.

To avoid costly delays, bring extra quantities of all supplies needed, including sampling vials, purge and trap grade methanol, vials of standards, gas-tight and Luer Lok syringes, and spare parts for analytical instrumentation. Even in an area with a local source, you could spend several hours obtaining the needed supplies.

During the planning stage locate a supplier of gases of the proper purity. Welding supply stores are usually a good source. Make arrangements ahead of time to ensure the gas you need is available. When inquiring, discuss price. A transient customer could be charged two or three times the price a regular customer is charged. In some cases, for short-term projects, you might consider bringing your own cylinders. In any case, always have extra in case of purity problems or leaks.

**Sample storage**

To avoid compromise, samples and standard solutions should be stored separately. If a reliable, continuous power supply is available, small refrigerators or freezers are ideal. Another choice is

a thermoelectric cooler / warmer ice chest. These chests are relatively inexpensive and can be powered by battery or electricity with the proper adapter; they cool down to 40°F (approx. 22°C) below ambient temperature. In an air conditioned environment of about 80°F (27°C) in the summer, these devices can lower the temperature to about 5°C. Be aware that the orientation of the plug into the jack on the chest will change the chest from a cooler to a warmer. If continuous power supply is not available, ice will have to be supplied daily.

**Waste removal**

During the planning stage, check with site personnel to determine the best way to handle disposal of any waste generated by sampling and analysis operations.

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## APPENDIX A: ESTIMATING THE TOTAL CONCENTRATION OF VOCS IN SOIL

### STATEMENT OF PURPOSE

This is a method for estimating the total concentration of volatile organic compounds (VOCs) in soil relative to a site-specific 0.2-mg/kg working standard. The reason for using this method is to provide a decision tool for field personnel, so that they can implement the appropriate soil sample preparation procedure necessary for the selected method of instrumental analysis. Coupling a rapid method for estimating the total VOC concentration with sample collection, handling, and preparation procedures that limit substrate dissaggregation and exposure complements efforts to achieve site-representative estimates for vadose zone contamination.

### MATERIALS

- Modified VOA vials (40, or 44 mL), Teflon-lined septa with 5- to 6-mm holes punched through the middle and 3- × 3-cm squares of light gauge aluminum foil for temporary covers (Fig. A1).

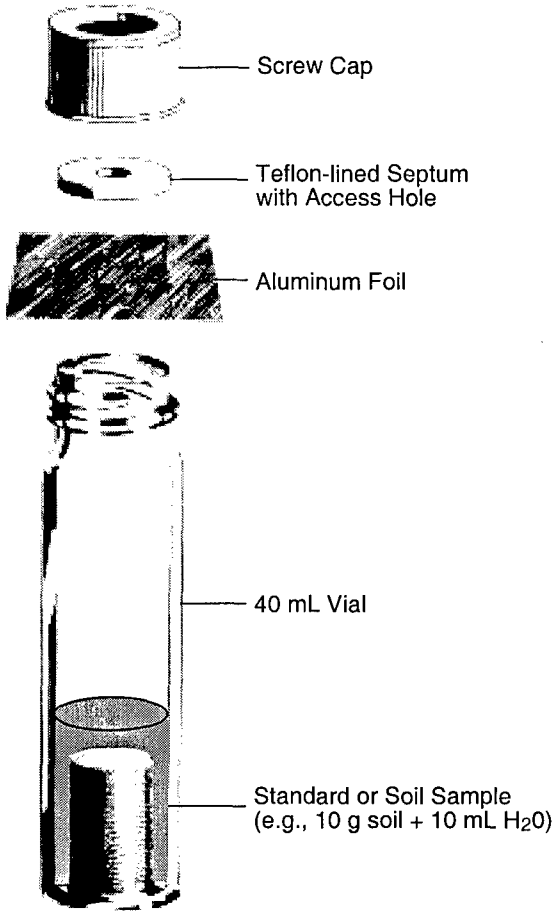


*Figure A1. Modified vial used for holding soil and water samples.*

- Coring tool for the collection and transfer of discrete soil samples, e.g., disposable 10-mL plastic syringes with the Luer Lok tip and rubber plunger cap removed or an equivalent metal tube and plunger.
- A portable photoionization detector (PID) analyzer with a 10.6-eV or greater electrode discharge tube, digital display, inlet flow rate of greater than 300 mL/min., and sample inlet tube of 3- to 4-mm o.d., at least 3 cm in length.
- A 10-μL syringe.
- Reagent grade, water, i.e., water with no detectable VOCs, polypropylene glycol (PPG) and principal VOC(s) of site interest.
- A cylinder of calibration gas for the PID, e.g., 100 ppm of isobutylene.

## STANDARDS

A stock standard is prepared by transferring the VOC of interest into PPG. The stock standard concentration should be based on the density of the analyte of interest, so that a 1- to 3-μL volume transferred to a 40-mL VOA vial containing 10 mL of reagent water and 10 g of the site specific soil matrix results in a 0.2-mg VOC/kg working standard.

*Example:*
Stock standard: 1.34* g/mL × 2.0 μL/ 2.5 mL = 1.1 mg TCE/mL
Working standard: 1.1 mg TCE/mL × 1.8 μL/ 10 g soil = 0.2 mg TCE/kg.

Immediately after spiking, these working standard vials are covered with a single sheet of aluminum foil, which is tightly held in position with a septum with a hole punched in the middle and a screw cap (Fig. A1). The vial contents of the working standards should be thoroughly mixed by hand shaking, then transported to the location of the sampling activity, stored out of direct sunlight, and allowed to equilibrate for 1 hr prior to use. Working standards should be prepared daily. The PID response to the working standard should be at least ×10 greater than its response to a blank (reagent water, contamination-free site-specific matrix, and appropriate volume of PPG).

## SAMPLE COLLECTION AND ANALYSIS

Prior to the field sampling episode, 10 mL of reagent water is added to the modified VOA vials. Once prepared, the VOA vials for screening samples should be transported to the sampling location and stored with the working standards until they are used. The location of samples taken for both screening purposes and laboratory analysis should be as close as possible to each other (generally within 10-cm radius), and from the same stratum. Prior to preparing (or exposing) a fresh sampling surface, for instance opening a split spoon or scraping away the top layer of a material, the cap and aluminum foil should be removed from the screening VOA vial. After retrieving a discrete sample with a coring tool, the barrel should be inserted into the mouth of the screening VOA vial and the sample extruded. Once the sample has been extruded, the aluminum foil and cap should immediately be replaced on the vial. If 10 g cannot easily be obtained in a single transfer, more than one corer can be used, or two transfers with a single corer can be made. This collection and transfer process should take less than 10 seconds, and the sample weight only has to approximate 10 g plus or minus 2 g.

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*Density of TCE.

Before the analysis of a working standard or sample, the VOA vial should be hand shaken for 10 to 15 seconds. Cohesive materials, such as silts and clays, do not break apart rapidly upon shaking and may require more than 15 seconds for complete dispersion. The vial is then visually checked for both the complete dispersion of the sample matrix and for particles adhering to the aluminum foil cap liner (knock large particles off the aluminum foil if present). Then the inlet tube of the PID is pushed through the foil liner, to a set position about 3 cm below the rim. A maximum response will be achieved within 2 to 3 seconds of punching through the foil liner. The maximum response for each sample screened and for the analysis of each working standard should be recorded.

## DAILY OPERATING PROCEDURE FOR VOC SCREENING

The PID should be initially calibrated with a cylinder of standard gas (e.g., 100 ppm of isobutylene) at the beginning of each day. This task can be performed prior to going to the sampling location. However, the analysis of both site-specific working standards and the screening of a sampling location should be performed under the same conditions, thereby normalizing meteorological influences on the performance of the PID. Site-specific working standards should be prepared daily, and in sufficient quantity to satisfy the study's objectives. At a minimum, one working standard should be analyzed for every hour of site activity.

Collection of samples for VOC analysis should always be the first operation performed after a surface to be sampled has been exposed to the atmosphere. This includes both samples for screening and for laboratory analysis. To establish how to handle and prepare the discrete sample for laboratory analysis (low, high, or both procedures), a total VOC screening analysis should be performed at each sampling location. Therefore, before opening a split spoon, scraping a fresh surface on a pit wall, removing surface vegetation and the appropriate amount of top soil for a surface grid location, or removing the first several inches of some other type of waste material, the PID of choice should be operating. Furthermore, if a working standard is being utilized to verify performance of the PID for the sampling location, the analysis of a working standard should be completed before exposing a fresh sampling surface.

Once a fresh surface has been exposed, a sample should be quickly obtained, transferred to a screening VOA vial, dispersed, and analyzed. If the maximum response is greater than the working standard (or the running average), the sample or samples taken for laboratory analysis should be prepared using the high-level procedure (i.e., MeOH extraction). If the maximum response is below the working standard, the laboratory sample(s) should be prepared using a low-level procedure. The total elapsed time between exposing a fresh surface, screening a sample and obtaining samples for laboratory analysis should be less that 2 minutes. As a precaution against false positive and false negative screening estimates relative to the decision point, the working standard response should have samples prepared by both high and low level procedures locations where screening results are between 0.5 and 2×.

## METHOD LIMITATIONS

For this method of sample location screening to work, the VOC(s) of interest must be detectable by photoionization. If more than one analyte is of interest, and there are large discrepancies (greater than a factor of two) in photoionization potentials, then the range around the decision point where samples are prepared by

both high and low level procedures should be increased proportionally. However, this often will not be a problem for sites contaminated with common chlorinated and aromatic compounds, because they have similar photoionization potentials. This approach would also not be effective is for sample matrices that are not readily dispersed in water (e.g., some clays and cementitious materials).

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**14. ABSTRACT**

Volatile organic compounds (VOCs) are among the most frequently identified contaminants in soil and groundwater samples obtained during the investigation of suspected hazardous waste sites. Because some VOCs and their degradation products are potentially mutagenic, carcinogenic, or teratogenic, their concentrations in these two matrices are key factors in the risk assessment process. Furthermore, when risk-based corrective actions are deemed necessary, the subsequent selection and implementation of the appropriate remediation technologies rely heavily upon the VOC concentrations established during site characterization activities. This report briefly addresses procedures, equipment, and logistics for the collection and timely (less than 48 hr) on-site analysis of VOCs in discrete soil and groundwater samples. The collection, preservation, and preparation procedures presented strive to acquire and maintain analyte concentrations that are representative of the location and medium from which the sample was removed.

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