



Soil-Vapor Versus Discrete Soil Sample Measurements for VOCs in the Near-Surface Vadose Zone

Feasibility Study

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June 1998

Abstract: Soil vapor samples were taken from 1 m beneath the ground surface at 16 different locations. Measured trichloroethene (TCE) in these samples was compared to that obtained for a collocated sample of the soil matrix. The linear slope (0.806) and strong correlation ($r^2 = 0.950$) obtained for this comparison of soil vapor (mg TCE/L) to soil mass (mg TCE/kg) concentrations are in good agreement with recent theoretical and empirical models for this volatile organic compound (VOC) in a low organic carbon

soil matrix. This strong relationship suggests that active soil-vapor measurements could be used as an alternative to collecting and analyzing discrete soil samples for establishing both the presence and concentration of VOCs during site characterization and monitoring. Moreover, the techniques and instruments described here are robust, simple to use, and designed to enhance the reliability of soil-gas surveys to characterize vadose zone VOC contamination.

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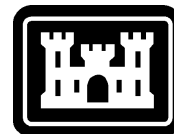
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Special Report 98-7



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Prepared for
U.S. ARMY CORPS OF ENGINEERS
WATERWAYS EXPERIMENT STATION

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory.

Funding for this work was provided by the U.S. Army Waterways Experiment Station, Vicksburg, Mississippi, Ann B. Strong, Project Monitor. The author thanks Marianne Walsh and Nicole J.E. Lukash for critical review of the text.

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ALAN D. HEWITT

INTRODUCTION

Using a soil-gas survey to investigate subsurface volatile organic compound (VOC) contamination has been a common practice for well over a decade. Traditionally, this technique establishes the presence and relative distribution of VOCs in the near-surface vadose zone on temporal and spatial scales. To make this method of site characterization even more attractive, it is often coupled with an on-site method of analysis, allowing data acquisition to approach real time. Indeed, the low cost and speed of soil-gas surveys are often touted as their greatest advantages.

However, the data only qualify for screening because a relationship between concentrations obtained from discrete grab samples and those from soil-gas surveys has yet to be established, despite numerous attempts (e.g., Smith et al. 1990, Sextro 1996, Minnich et al. 1997). Even with this handicap, soil-vapor surveys have excelled for locating hot spots of groundwater contamination (Marrin and Thompson 1987, Marrin and Kerfoot 1988) or residual product in the overburden (Spittler et al. 1985). In both cases, the soil-vapor measurements provide guidance for placing monitoring wells or obtaining soil borings, or both. Thereafter, the collection and analysis of discrete aqueous or soil samples are used to aid risk assessment decisions, to establish both the horizontal and vertical profiles of contamination, and to monitor the progress of remediation.

More recently, soil-gas sampling has been applied to the study of the fate and transport of VOCs in the vadose zone. One of the major concerns of this effort was to establish whether or not vapors originating from a residual contamination source could affect water quality in the

adjacent saturated zone (Hughes et al. 1992, Conant et al. 1996). In their experiments, Hughes et al. (1992) gave special attention to the soil-gas sampling system to minimize its effect on the in-situ conditions during installation and soil vapor removal. This has not been one of the top priorities for the soil-gas surveys used to detect VOCs leaking from underground storage tanks or to delineate concentration gradients above groundwater plumes. The soil-vapor sampling probe developed by Hughes et al. (1992) had internal volumes of 5–30 mL, whereas most conventional systems usually exceed 100 mL. The intent behind designing a probe with a smaller dead volume was to allow discrete locations in the subsurface to be measured instead of taking samples that are averaged over large, unspecified areas and times. Using the approach taken by Hughes et al. (1992), this study developed a soil-vapor probe with a micro (1.2 mL) internal volume.

To compare soil-vapor and discrete soil matrix samples, however, also requires that the grab samples collected for analysis be representative of the in-situ conditions. Several studies have shown that procedures requiring multiple handling operations often result in underestimating soil VOC concentration by one to three orders of magnitude (e.g., Urban et al. 1989, Illias and Jaeger 1993, Hewitt et al. 1995, Liikala et al. 1996). As an example of how fast the VOC concentration can change, a bulk sample (in a 7.5-cm-long \times 7.5-cm-wide core barrel liner), consisting of a silty-sand matrix experiencing minimal disruption, can lose greater than 90% of these analytes in less than 40 minutes (Hewitt and Lukash 1996).

In recognition of the problems with past sam-

ple collection, handling, and analysis techniques, the U.S. Environmental Protection Agency has now adopted new methodologies (Method 5021 and Method 5035) (third update to the Test Methods for Evaluating Solid Waste, SW-846, [U.S. EPA 1986]). To help maintain representative VOC concentrations, both methods 5021 and 5035 recommend that samples be collected with a coring tool and be either immediately transferred to prepared collection-analysis vials or stored for less than 48 hours in En Core samplers. Samples transferred to a prepared vial are typically either analyzed directly (vapor being removed by puncturing a Teflon-lined septum cap with a needle), as would be the case for headspace and purge-and-trap analysis, or the VOCs of interest are extracted into methanol, to be analyzed later. The En Core sampler is a coring tool with a chamber that can be hermetically sealed, thus allowing discrete samples to be taken to a laboratory before the preparation steps necessary for later instrumental analysis are begun (Hewitt 1997).

This study determines VOCs with a headspace analysis of a discrete soil sample dispersed in water. Therefore, vials of known weight containing water were taken to the field so that samples could be transferred directly to them. Furthermore, to limit exposure, discrete soil samples were obtained with a coring tool that reached the depth of interest (1 m), obtaining and transferring the sample in a single step.

Along with comparing the two methods of characterizing VOC contamination in the vadose zone, this study also assessed the performance of the above-mentioned soil-vapor probe. In addition, other issues associated with the collection, handling, and storage of soil-vapor samples were examined.

PROBE DESIGN

The soil-vapor probe was made of a steel rod that was 1.3 m in length and 1.27 cm in diameter. Its soil-vapor transfer line was a spare part for a purge and trap instrument (Tekmar), consisting of a stainless steel tube, 0.16 cm o.d., 0.10 cm i.d., with a nickel-plated liner. The transfer line was attached to the rod via a 0.318-cm groove (wide \times deep) cut into the rod's exterior. The groove was 1 m long, running between 1.3 cm from the tip to 25 cm from the top. The tip of the rod was machined down to a 0.95-cm diam. \times 0.32-cm-deep post (see Fig. 1). In the middle of this post, a small (0.32-cm-diam. tapered to 0.20-cm) hole was drilled, which

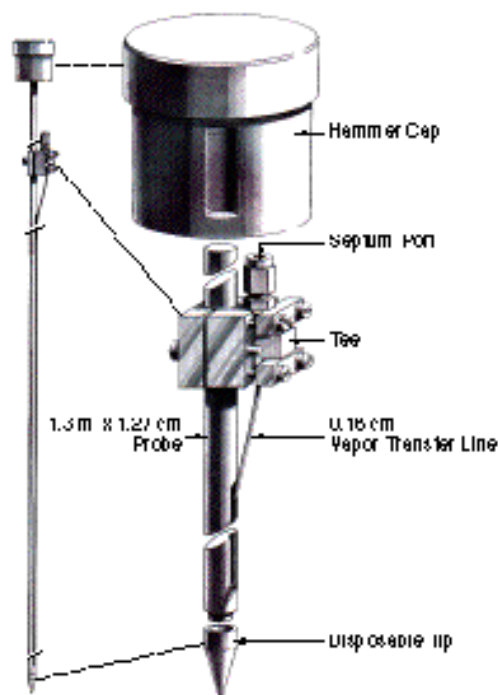


Figure 1. Soil-vapor probe.

connected to the groove on the outside of the rod. A 1.2-m-long section of the 0.16-cm-o.d. tubing, with a ferrule on the end, was threaded through the hole and epoxied into the groove, leaving only a 20-cm section not directly attached to the rod, at the top. After the epoxy had hardened, it was sanded, leaving a smooth surface over the groove. The tapered hole at the tip allowed the ferrule on the end of the stainless steel tube to be recessed, leaving the entrance to the transfer line flush with the bottom of the rod. At the top of the transfer line, a ferrule and nut assembly was used to connect the tube to a stainless steel Tee. The side port of the Tee was sealed with a cap, while a stainless steel reducing union (0.32 \times 0.16 cm), with a Teflon-lined septum, was used to seal the top. This Tee was firmly held to the rod by an aluminum block (see Fig. 1). The total dead volume for this soil-vapor transfer line was approximately 1.2 mL.

Two pieces that were not attached to the probe were a brass disposable tip (see Fig. 1) and a snug fitting hammer cap made out of steel. The tips had a sharp point, were 3 cm long, and had a recessed hole that allowed them to loosely fit over the post on the tip of the probe. The hammer cap was a cylindrical (7-cm-diam. \times 7-cm-long) solid piece of steel, with a 1.3-cm hole drilled 75% of the way through the middle, on one end.

EXPERIMENTAL METHODS

Initially, a laboratory experiment was conducted to see if VOC vapors could be quantitatively transferred from the probe's inlet to a syringe and then into a sealed VOA vial. A 22-mL VOA vial was attached to the tip of the probe using strips of Parafilm "M," and then VOCs were spiked into this empty chamber. The volume inside the VOA vial was estimated to be around 21 mL. Once the vial was securely attached, a 2- μ L volume of a methanol (MeOH) stock standard, containing trans-1,2-dichloroethene (TDCE), cis-1,2-dichloroethene (CDCE), and TCE, was injected into the vial using a 10- μ L syringe (26-gauge needle) that punctured the Parafilm "M" wrapping. After a 5-minute wait for the MeOH and analytes to evaporate, a 3.5-mL volume of vapor was purged through the transfer line of the soil-gas probe with a 3-mL Luer Lok syringe (actual volume 4 mL). Next, three consecutive 0.500-mL volumes were obtained with a gas-tight syringe (Hamilton) and each was transferred to a sealed VOA vial. For comparison, three working standards were similarly prepared in 22-mL VOA vials. A 0.500-mL volume was removed from each and transferred to a sealed VOA vial.

During the field trials, active soil-vapor and discrete soil samples were collected from 16 separate locations at CRREL in Hanover, New Hampshire. This site has TCE contamination in the vadose zone, ranging from less than 0.001 mg/kg to more than 100 mg/kg, attributable to accidental spills more than 20 years ago (Hewitt 1994). The site's typical soils at 1 m depth are silty-sands, with a moisture content of around $21 \pm 7\%$ and an organic carbon content that is less than 0.5% (percent organic carbon anticipated on the basis of previous measurements of soils from this depth). At each location, soil-vapor samples were collected first and then a discrete soil sample was obtained.

The following is an outline for the sampling protocol used to collect both the soil-vapor and matrix samples. Before the soil-vapor probe was pushed into the soil, a 0.32-cm-diam. solid steel rod was manually pushed approximately 60 cm into the ground to check for interfering obstructions (rocks and cobble) close to the surface. After this small-diameter rod was removed, the active soil-gas probe, with its disposable tip, was pressed into the soil surface at the same penetration point. Once the probe was in place, the hammer cap was put on top and repeatedly hit with a 2.5-lb (approximately 1-kg) hammer until the

probe was driven to 1 m. After this depth was reached, the hammer cap was removed and locking pliers were clamped onto the top of the probe. Next the entire rod was rotated a half turn and raised approximately 2 cm. Lifting the probe separates it from its tip, creating approximately a 3-mL void in the subsurface.

Soil-vapor samples of 0.5 mL were obtained as follows. After 30 minutes was allowed for equilibration, the transfer line was flushed by pulling a 3.5-mL volume of soil gas through it via a 3-mL Luer Lok syringe fitted with a 22-gauge stainless steel needle (Becton Dickinson). Both longer and shorter equilibration periods were studied to see how long it takes for TCE vapor concentrations to stabilize and to see how they fluctuate with time. For this study, all soil-gas samples were collected in at least triplicates, using a 0.5-mL gas-tight syringe with a 22-gauge needle (Hamilton), and were immediately transferred to 22-mL VOA vials sealed with Teflon-lined butyl rubber septa and aluminum crimp tops (Wheaton). Furthermore, the probe's transfer line was always purged before soil-vapor samples were collected.

Before the soil-vapor sample was transferred to a VOA vial, a 22-gauge disposable needle was inserted through the septum to serve as a pressure vent for the sample container. When the sample was injected into the VOA vial, the tip of the pressure vent needle was positioned near the septum's Teflon face, while the tip of the sample needle was placed near the middle of the vial. All collections and transfers with these gas-tight syringes were done cautiously and slowly, so their seals would not be bypassed. Furthermore, because needles can easily become clogged by a piece of septum, they were frequently checked by making them blow bubbles through water. For example, samples of soil vapor were routinely taken by slightly over-filling the syringe, then pushing one or more bubbles out prior to setting the volume to 0.500 mL and transferring the soil-vapor sample into a VOA vial. This procedure was also used with the Luer Lok syringe, especially after a new septum was installed in the soil-gas probe.

When the soil-vapor samples were completely collected at a given location, the probe was pulled out of the ground using the locking pliers as a handle. If the probe could not be easily freed from the substrate, the locking pliers were tapped in an upwards direction with the 2.5-lb hammer. Once the probe was retrieved, a Veihmeyer tube was inserted into its channel to make a

3.2-cm-i.d. hole to the depth where the soil vapor was taken. However, since the disposable tips were never retrieved, this second channel was most likely offset slightly from the original. A Veihmeyer tube uses a sliding bar hammer to push its hollow stem into the soil subsurface, and leaves an open hole when removed.

Discrete soil samples were collected with a 116-cm-long, 1.9-cm-i.d. Plexiglas corer equipped with a plunger. This sampling device works in the same way as a plastic syringe with its tip removed (Griffith et al. 1988). A discrete plug of undisturbed soil was collected immediately after the Veihmeyer tube had been removed from the hole by pushing the open barrel of the Plexiglas corer approximately 2.5 cm beyond the hole's current depth. Each sample was quickly transferred to a 22-mL VOA vial that was prepared for headspace gas chromatography (HS/GC) analysis. More specifically, for these soil matrix samples, each VOA vial contained 10 mL of organic free water and had been weighed to the nearest 0.01 g in a laboratory prior to being taken to the field. While in the field, a small piece of Parafilm "M" was used to cover the top of the VOA vial to prevent the loss of water vapor. The sheet of Parafilm was removed just before a soil sample was put inside, then the vial was sealed with a Teflon-lined septum and aluminum crimp top. This vial was weighed again once it had been returned to the laboratory to establish the moist weight of the soil sample.

At the beginning of the field trials, samples were collected on two separate occasions to determine how long the equilibration period should be after the probe was installed. In addition, samples taken on these two occasions were used to assess fluctuations of TCE soil-gas concentrations with time. Multiple vapor samples were taken at these two locations, and at least a single set of triplicate soil-vapor samples was taken at 14 other locations. A collocated sample of the soil matrix was taken at all 16 locations. In addition, a final experiment assessed an alternative method for handling soil vapor to establish a procedure to extend holding times for some common aromatic and chlorinated compounds.

Multiple sets of triplicate soil-vapor samples were obtained on 2 days from three separate locations. On the first day, triplicate soil-vapor samples were taken 15, 30, 60, and 120 minutes after the probe was installed. Soil vapor collection started at 1005 hours on an overcast and sporadically rainy day. At a second location on the same

day, nine consecutive 0.500-mL soil-vapor samples were taken after the probe equilibrated for 30 minutes. The first, fifth, and ninth samples taken were analyzed within 2 hours of collection, while equal numbers of the remaining samples were stored for 3 days at 4 and -12°C before analysis.

On another day at a new location, triplicate soil-vapor samples were taken 0.083, 0.25, 0.5, 1, 2, 4, 7.5, 24, and 26 hours after the probe was installed. The sampling started at 0700 on a day that cleared up and became sunny (sunlight reached the sampling location at about 0730). The following day had very similar weather. During this longer time study, two sets of triplicate samples were obtained during the 2-hour collection period. One set was analyzed immediately while the other was held at room temperature for 24 hours prior to analysis. When all of the planned soil-vapor samples had been collected, a collocated soil matrix sample was obtained. At all of the 13 additional sampling locations, soil-vapor samples were always taken after at least a 30-minute equilibration period. Furthermore, except where noted, all of the samples taken during these experiments were analyzed within 4 hours of collection.

As mentioned, a final experiment looked at an alternative method of handling and storing vapor samples. For this alternative method, 0.5 mL of organic free water, acidified to a pH of 1.9 with NaHSO_4 (1 g NaHSO_4 in 40 mL of water), was placed into the 22-mL VOA vials prior to their being sealed with a Teflon-faced butyl rubber septum and aluminum crimp top cap. To each of the six vials prepared this way, a 2- μL volume of a MeOH working standard containing TDCE, CDEC, TCE, tetrachloroethene, benzene, toluene, ethyl-benzene, para-xylene, and ortho-xylene was added via a 10- μL syringe. In each case, the standard was added after two holes were punched into the septum with a 22-gauge needle. One of the holes was used when the standard was transferred onto the inner wall of the vessel with a smaller gauge needle syringe. Once the standard had been added, the vial was inverted so that the aqueous solution covered the two punctures made in the septum.

Triplicates of these working standards were held for 5 and 12 days at room temperature ($22 \pm 1^{\circ}\text{C}$). The responses of these working standards were compared to those of sets of triplicate working standards prepared from the same stock standard on the day of analysis. Two sets of working standards were prepared on the day of analysis. One set was made using one of two puncture

holes as the entrance to the VOA vial, while a second set was made by transferring the spike to an open vial, which was then quickly capped.

ANALYSIS

The soil-vapor samples and discrete soil matrix samples were analyzed using a headspace (HS) autosampler (model 7000, Tekmar-Dohrmann, Cincinnati, Ohio) coupled to a GC (model 8610-0058, SRI Instruments, Torrance, California) equipped with a 15-m, 0.53-mm-diam. MXT-1 capillary column (Restek Corp., Bellefonte, Pennsylvania) and photo-ionization-flame-ionization sequential detectors. Before the VOA vials containing an aqueous soil slurry were placed onto the HS autosampler, they were shaken for 2 minutes to completely disperse the soil and to help them attain equilibrium. Prior to analysis, the autosampler heated all of the samples to 40°C for 20 minutes.

Analyte concentrations for the soil matrix samples were established relative to aqueous headspace standards prepared by adding small (less than 10- μ L) quantities of a MeOH stock solution to autosampler (22-mL VOA) vials containing 10 mL of organic free water. Analyte concentrations for the soil-vapor samples were established relative to vapor working standards. The vapor working standards were prepared by transferring 4 μ L or less of a MeOH stock standard, consisting of weighed amounts of TDCE, CDEC, and TCE, to empty autosampler vials. This approach to instrumental calibration for soil-vapor samples is consistent with the works of Hughes et al. (1992). Instrument settings for the autosampler and gas chromatograph and information concerning the performance of this method for establishing VOC concentrations in soil have been previously documented (Hewitt et al. 1992, Hewitt 1998a). Values for both the soil-vapor concentrations and discrete soil are only reported with two significant figures, based on the uncertainty associated with sample handling, analysis, and analyte spatial variability.

The soil-vapor collection and handling method used in this study required the transfer of 0.500-mL of sample to a 22-mL container. With this approach, a detection limit of at least 2 ng/mL is anticipated for TCE. In general, this same detection limit also applies for many other VOCs that can be photoionized and would be even lower for those compounds that respond to electrolytic conductivity detectors.

RESULTS AND DISCUSSION

Table 1 shows the results of the laboratory performance study assessing the overall operation of the probe, including the handling and analysis of a vapor sample. The 91% or greater efficiency measured for this process suggests that this soil-vapor probe and the approach to sample handling are very likely to be quantitative. Furthermore, the precision of subsample collection is very good, as is shown by the less than 10% relative standard deviations for the triplicate VOC measurements.

Table 1. Comparison of analyte responses (PID peak area) taken from three separate working standards (VOA vials) and from the similarly prepared standard (VOA vial attached to end of soil vapor probe) sampled through the soil gas probe.

	Working standard	Soil vapor probe	Percent rsd*	Transfer efficiency (%)
TDCE	362 \pm 6.4	329 \pm 9.5 [†]	2.9	91
CDCE	326 \pm 10.4	305 \pm 12.7 [†]	4.2	94
TCE	280 \pm 4.4	254 \pm 17.0 [†]	6.7	91

* Relative standard deviation.

[†] Corrected by a factor of 1.27, because of both a smaller vessel (21 vs. 22 mL) and subsequent dilution of analyte caused by purging with approximately 4 mL room air prior to and while collecting the triplicate vapor samples.

Table 2 assesses the waiting period necessary after the probe is installed to obtain a soil-vapor sample that is in quasi-equilibrium with the in-situ concentration of TCE. Review of these data suggests that between 15 and 30 minutes is appropriate. However, it should be noted that, after a wait of only 5 minutes, greater than 80% of the maximum TCE concentration was obtained. Therefore, a reasonable estimate of the soil-vapor concentration could have been obtained without delay. Caution, however, should be taken when dealing with analytes of lower vapor pressures than TCE, and when dealing with fine-textured or very moist substrates (e.g., clays).

The concentrations of TCE in the soil vapor appeared to be somewhat influenced by the time of day that the sample was collected. To better understand this phenomenon, more attention should be given to meteorological parameters (e.g., ambient temperature and barometric pressure) in the future. The intent of this experiment, however, was not to quantify the potential influence of meteorological variables, but to see if

Table 2. TCE soil vapor equilibration and temporal variations.

Time	Triplicate values (mg/L)	Average and standard deviation (mg/L)
First probe installation at 1005, 21 July 1997		
1020	2.0, 2.1, 2.2	2.1 ± 0.10
1025	1.9, 2.1, 2.2	2.1 ± 0.15
1155	2.0, 1.9, 1.8	1.9 ± 0.10
1255	2.2, 2.1, 2.1	2.1 ± 0.06
Second probe Installation at 0700, 29 July 1997		
<i>Day 1</i>		
0705	20, 22, 22	21 ± 1.2
0715	23, 23, 24	23 ± 0.58
0730	25, 27, 26	26 ± 1.0
0800	25, 25, 26	25 ± 0.58
0900*	24, 28, 26	26 ± 2.0
1300	28, 23, 27	26 ± 2.6
1430	20, 23, 23	22 ± 1.7
<i>Day 2</i>		
0700	14, 14, 20	16 ± 3.5
0900	21, 22, 25	23 ± 2.1

* Triplicate soil vapor samples taken for holding time study.

there were large changes in soil-vapor TCE concentrations over the course of a day. As a result of these temporal trends, all subsequent samples were obtained between 0800 and 1400 to limit the influence of this potential variable.

Table 3. Initial hold time for soil vapor samples.

Time and condition	Triplicate values* (mg/L)	Average and standard deviation (mg/L)		Percent relative difference
		Stored	Time 0	
1 day at 22°C	22, 22, 25	23 ± 1.7	26.0 ± 2.0	12
3 days at 4°C	13, 12, 11	12 ± 1.0	15 ± 1.2	20
3 days at -12°C	11, 11, 12	11 ± 0.58	15 ± 1.2	27

* Triplicate values of stored vapor samples.

Table 3 shows the results for soil-vapor samples that were held under different conditions for periods of 1 to 3 days. These findings suggest that, regardless of storage temperature, TCE can be quickly lost from the sample vessels. Vapor losses are most likely attributable to the two holes in the Teflon-lined septum.

To reduce the approximately 10% loss of analyte per day of storage, as seen in these initial experiments, an alternative sample handling procedure, using a water barrier to cover the holes in the septum, was assessed (Table 4). Including 0.5 mL of water in the sample collection and analysis VOA vial caused less than a 5% reduction in sensitivity. This small disadvantage was offset, however, since the water present in the sample vial was useful for visually confirming that a vapor sample was being introduced by syringe during the transfer step. More specifically, the sample vessel was tipped so that the tip of the needle

Table 4. Average responses (peak area) and standard deviations (values in parentheses) for VOC vapor samples prepared in VOA vials with 0.5 mL of acidified water covering the septum puncture holes.

	TDCE	CDCE	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl*
First set									
Fresh standard	452	476	1307	409	1857	419	1617	1837	1723
No puncture	(4.5)	(3.6)	(38)	(0.6)	(32)	(4.6)	(12)	(23)	(29)
Fresh standard	440	468	1277	401	1837	413	1650	1770	1693
Punctured	(5.9)	(8.0)	(29)	(6.0)	(55)	(8.1)	(17)	(20)	(15)
5-day-old standard	411	448	1223	364	1643	346	1387	1417	1423
Punctured	(8.5)	(5.1)	(15)	(4.0)	(32)	(4.7)	(50)	(57)	(49)
Second set									
Fresh standard	447	475	1287	405	1830	416	1640	1793	1720
No puncture	(3.5)	(2.3)	(5.8)	(3.1)	(46)	(3.2)	(50)	(21)	(27)
Fresh standard	444	473	1288	405	1847	413	1640	1770	1713
Punctured	(1.0)	(4.6)	(15)	(3.8)	(42)	(0.58)	(36)	(72)	(25)
12-day-old standard	383	427	1167	340	1543	319	1253	1240	1253
Punctured	(14)	(9.5)	(31)	(9.1)	(67)	(7.4)	(31)	(62)	(23)
Average daily rate	1.2	0.83	0.80	1.6	1.8	2.6	2.6	3.4	2.7
of percent loss	(0.1)	(0.03)	(0.07)	(0.4)	(0.5)	(0.9)	(0.9)	(1.2)	(0.7)

* Trans-1,2-dichloroethene (TDCE), cis-1,2-dichloroethene (CDEC), benzene (Ben), trichloroethene (TCE), toluene (Tol), tetrachloroethene (PCE), ethyl-benzene (E-Ben), para-xylene (p-Xyl), and ortho-xylene (o-Xyl).

touched the water when the soil-gas sample was added; thus, the formation of bubbles confirmed that a vapor sample was being transferred.

Table 4 shows that the rates of loss for several analytes were only about 2% per day of storage. Furthermore, the rate of loss was fairly constant, thus a correction factor could be used to restore values to day 1 concentrations. Perhaps even slower rates of vapor loss would have been established if the sample vials were refrigerated, frozen ($-12 \pm 3^\circ\text{C}$), or treated with an acidified solution saturated with sodium chloride. Furthermore, the presence of two holes had no effect because working standards prepared with and without two holes in the septum frequently gave the same response.

In general, this storage and handling system works better than Tedlar bags (Wang et al. 1996) but not as well as passivated Summa canisters (Wang and Clifford 1991). However, neither of these other methods of storing VOC vapors is well suited for soil-gas studies of in-situ concentrations in discrete locations because of the volume of sample that is required.

The data in Table 5 also show that soil-vapor TCE concentrations did not appear to become diluted after as many as nine sequential samples were taken at a single place (location 14; the subsamples in Table 5 were the first, fifth and ninth taken). This indicates that a longer probe, with a larger dead volume, would also be effective, thus allowing even greater depths to be sampled.

The comparison between TCE concentrations in soil-vapor samples and collocated moist soil matrix samples appears in Table 5 and Figure 2. The precision of this sample collection, handling, and analysis method was very good. Frequently (14 out of 16 times), a relative standard deviation of less than 10% was obtained for the triplicate measurements. The linear and highly significant correlation ($r^2 = 0.950$) established between these two methods of characterizing vadose zone VOC contamination is consistent with both theoretical

(Rong 1996) and empirical (Hewitt 1998b) models.

Table 6 shows the conversion coefficients (CO) between soil-vapor and soil matrix concentrations for TCE that have been established in this study and previously. The value for this field study agrees well with the mean value based on a theoretical model (Rong 1996) and is bracketed by those based on a laboratory study (Hewitt 1998b). Indeed, the value of 0.806 established for this study fits between those established in the laboratory study for soil from the same site,

Table 5. Soil vapor and collocated soil matrix concentrations.

Sample number	Soil sample (mg TCE/kg)	Triplicate values (mg TCE/L)			Average soil vapor (mg TCE/L)*
1	0.021	0.018	0.020	0.018	0.019 \pm 0.0012 (6.1%)
2	0.057	0.030	0.030	0.030	0.030 \pm 0.0 (0.0%)
3	0.051	0.041	0.043	0.044	0.043 \pm 0.0015 (3.6%)
4	0.18	0.13	0.15	0.15	0.14 \pm 0.012 (8.2%)
5	0.28	0.46	0.40	0.42	0.43 \pm 0.031 (7.1%)
6†	1.7	1.9	2.1	2.3	2.1 \pm 0.20 (9.5%)
7	3.6	3.4	3.9	3.8	3.7 \pm 0.26 (7.2%)
8	8.1	5.6	4.4	4.5	4.8 \pm 0.67 (14%)
9	11	11	13	NA	12 \pm 1.4 (12%)
10	12	7.1	8.6	7.8	7.8 \pm 0.75 (9.6%)
11	14	7.2	7.6	7.2	7.3 \pm 0.23 (3.2%)
12	16	12	12	13	12 \pm 0.53 (4.8%)
13	16	15	15	15	15 \pm 0.0 (0.0%)
14**	19	14	16	14	15 \pm 1.2 (7.7%)
15††	28	25	27	26	26 \pm 1.0 (3.8%)
16	32	22	24	26	24 \pm 2.0 (8.3%)

* Average, standard deviation, and relative standard deviation.

† First equilibrium-temporal study.

** Nine replicate soil-vapor samples collected at this location.

†† Second equilibrium-temporal study.

NA Sample lost.

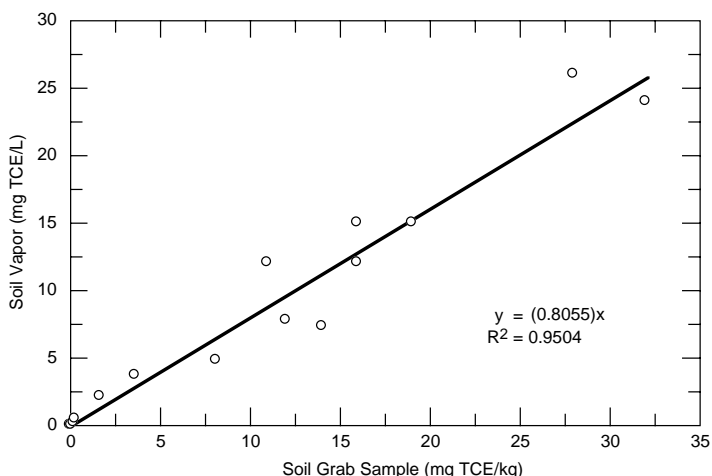


Figure 2. Correlation between mean soil-vapor TCE concentrations and soil matrix TCE concentrations.

Table 6. Conversion coefficients for soil vapor (mg/L) to soil matrix (mg/kg) concentrations for trichloroethylene.

Soil type	kg/L	Percent organic carbon	Study
55 soils	1.16	0.14	Rong (1997)
CRREL silty-sand	0.386	0.88	Hewitt (1998b)
CRREL sandy-silt	1.36	0.10	
Wisconsin sand	1.09	0.17	
Silty-sand	0.806	<0.5*	This study

* Estimate of organic carbon content based on soils previously taken at this site from a depth below 30 cm.

except the samples were obtained both closer to the surface (20 ± 10 cm) and from a much greater depth (greater than 30 m). Because these soils were obtained from three different depths in the vadose zone, they have different levels of organic carbon associated with them, which most likely accounts for the discrepancies in the CO values (Hewitt 1998b).

These studies all support the concept that soil-vapor VOC measurements can not only establish spatial and temporal distributions, but, if done properly, can also accurately predict the concentration present in the soil matrix. To further develop this relationship, more rigorous studies involving other soils and VOCs are necessary.

SUMMARY

This study has established a soil-vapor collection, handling, and analysis protocol that is not only very precise but, when compared to collocated soil matrix concentrations for the measurement of TCE, resulted in a linear and highly significant correlation. Furthermore, the conversion coefficient established for the measurement of TCE in these two media was consistent with recent theoretical and empirical models. Clearly, the next logical step is to determine if this type of relationship exists for other VOCs in other types of soils. However, because there are two independent sources of information, it is very likely that soil-vapor surveys, accompanied by a sufficient number (5 to 20%) of confirmatory discrete soil matrix analyses, will become an alternative method for future site investigations for VOC contamination in the vadose zone.

The handling and analysis protocols presented show that soil-vapor samples could either be measured on-site, making data acquisition approach real time, or off-site, within 1 or 2 weeks. In either case, if the bulk of site was characterized using a proper soil-vapor survey method, the cost

and length of the field activity could be reduced by as much as an order of magnitude.

When the quantitative performance of a soil-vapor survey technique is assessed, special attention should be given to the collection and handling of both soil-vapor and matrix samples. It is imperative that the dead volume of soil-vapor samplers be small, perhaps on the order of a few milliliters. Although they were not presented here, several experimental findings indicated that it is important to create a small void from which to remove the subsurface soil vapors. In principle, this void serves as a chamber, which, with time, becomes filled with a vapor phase VOC concentration that is in quasi-equilibrium with the in-situ soil matrix. Moreover, when comparing soil-vapor VOC concentration to soil matrix concentrations, it is important to use an in-field sample preparation and perhaps preservation method that limits VOC losses. This does not necessarily preclude the use of the En Core sampler, since it could be attached to a long rod to obtain a sample of soil matrix at the bottom of a narrow channel. Furthermore, since, currently, there is no rigorous evaluation of how well subsurface sample retrieval systems (e.g., geoprobes, hollow stem augers, cone penetrometer, Veihmeyer tubes, etc.) retain representative VOC concentrations in bulk samples, it is recommended that these comparisons be initially made in the near-surface region.

LITERATURE CITED

- Conant, B.H., R.W. Gillham, and C.A. Mendoza (1996) Vapor transport of trichloroethylene in the unsaturated zone: Field and numerical modeling investigations. *Water Resources Research*, **32**: 9-22.
- Griffith, T.J., G.A. Robbins, and T.M. Spittler (1988) A new method for field analysis of soils contaminated with aromatic hydrocarbon compounds. In *FOCUS Conference on Eastern Regional Water Issues, September, Stamford, Connecticut*. National Water Well Association, p. 223-248.
- Hewitt, A.D. (1994) Comparison of methods for sampling vadose zone soils for the determination of trichloroethylene. *Journal of the Association of Analytical Chemistry*, **77**: 735-737.
- Hewitt, A.D. (1997) A tool for the collection and storage of soil samples for volatile organic compound analysis. *American Environmental Laboratory*, **9**: 14-16.
- Hewitt, A.D. (1998a) Comparison of sample preparation methods for the analysis of volatile organic compounds in soil samples: Solvent extrac-

- tion vs. vapor partitioning. *Environmental Science and Technology*, **32**: 143–149.
- Hewitt, A.D.** (1998b) Laboratory study of VOC partitioning: Vapor/aqueous/soil. USA Cold Regions Research and Engineering Laboratory, Special Report 98-3.
- Hewitt, A.D., and N.J.E. Lukash** (1996) Sampling for in-vial analysis of volatile organic compounds in soil. *American Environmental Laboratory*, **7**(8): 15–19.
- Hewitt, A.D., and N.J.E. Lukash** (1997) Estimating the total concentration of volatile organic compounds in soil: A decision tool for sample handling. USA Cold Regions Research and Engineering Laboratory, Special Report 97-12.
- Hewitt, A.D., P.H. Miyares, D.C. Leggett, and T.F. Jenkins** (1992) Comparison of analytical methods for determination of volatile organic compounds. *Environmental Science and Technology*, **26**: 1932–1938.
- Hewitt, A.D., T.F. Jenkins, and C.L. Grant** (1995) Collection, handling, and storage: Keys to improved data quality for volatile organic compounds in soil. *American Environmental Laboratory*, **7**(1): 25–28.
- Hughes, B.M., R.D. McClellan, and R.W. Gillham** (1992) Application of soil-gas sampling technology to studies of trichloroethylene vapor transport in the unsaturated zone. In *Groundwater Contamination and Analysis at Hazardous Wastes Sites* (S. Lesarge and R.E. Jackson, Ed.). New York: Marcel Dekker, Inc.
- Illias, A.M., and C. Jaeger** (1993) Evaluation of sampling techniques for the analysis of volatile and total petroleum hydrocarbons (TRPH) by IR, GC, and GC/MS methods. In *Hydrocarbon Contaminated Soils*. Vol. 3. Chelsea, Michigan: Lewis Publishers, p. 147–165.
- Liikala, T.L., K.B. Olsen, S.S. Teel, and D.C. Lanigan** (1996) Volatile organic compounds: Comparison of two sample collection and preservation methods. *Environmental Science and Technology*, **30**: 3441–3447.
- Marrin, D.L., and G.M. Thompson** (1987) Gaseous behavior of TCE overlying a contaminated aquifer. *Ground Water*, **25**: 21–27.
- Marrin, D.L., and H.B. Kerfoot** (1988) Soil-gas surveying techniques. *Environmental Science and Technology*, **22**: 740–745.
- Minnich, M.M., B.A. Schumacher, and J.H. Zimmerman** (1997) Comparison of soil VOCs measured by soil gas, heated headspace, and methanol extraction techniques. *Journal of Soil Contamination*, **2**: 187–203.
- Rong, Y.** (1996) How to relate soil matrix to soil gas samples. *Soils and Groundwater Cleanup*, June–July.
- Sextro, R.K.** (1996) Estimation of volatile organic compound concentrations in the vadose zone: A case study using soil gas and soil sample results. In *Sampling Environmental Media*. ASTM STP 1282 (J.H. Morgan, Ed.). American Society for Testing and Materials.
- Smith, J.A., C.T. Chiou, J.A. Kammer, and D.E. Kile** (1990) Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. *Environmental Science and Technology*, **24**: 676–684.
- Spittler, T.M., L. Fitch, and S. Clifford** (1985) A new method for detection of organic vapors in the vadose zone. In *Proceedings of the Annual Symposium on Characterization and Monitoring of the Vadose Zone*. National Water Well Association: Worthington, Ohio, p. 295–305.
- U.S. Environmental Protection Agency** (1986) Test methods for evaluating solid waste. 3rd Update, June 1997. U.S. Environmental Protection Agency, SW-846, Washington, D.C.
- Urban, M.J., J.S. Smith, E.K. Schultz, and R.K. Dickinson** (1989) Volatile organic analysis for a soil, sediment or waste sample. In *5th Annual Waste Testing and Quality Assurance Symposium, Washington, D.C.* U.S. Environmental Protection Agency, p. II-87–II-101.
- Wang, H., and W.S. Clifford** (1991) Aqueous headspace air standards vs. Summa canister air standards for volatile organic compound field screening. In *Proceedings, Field Screening Methods for Hazardous Waste and Toxic Chemicals, 12–14 February, Las Vegas, Nevada*, p. 415–422.
- Wang, Y., T.S. Raihala, and R. St. John** (1996) Use of tedlar bags in OVC testing and storage: Evidence of significant VOC losses. *Environmental Science and Technology*, **30**: 3115–3117.

REPORT DOCUMENTATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1998	3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE Soil-Vapor Versus Discrete Soil Sample Measurements for VOCS in the Near-Surface Vadose Zone: Feasibility Study			5. FUNDING NUMBERS	
6. AUTHORS Alan D. Hewitt				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, New Hampshire 03755-1290			8. PERFORMING ORGANIZATION REPORT NUMBER Special Report 98-7	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Corps of Engineers Waterways Experiment Station Vicksburg, Mississippi			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES For conversion of SI units to non-SI units of measurement consult <i>Standard Practice for Use of the International System of Units (SI)</i> , ASTM Standard E380-93, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. Available from NTIS, Springfield, Virginia 22161.			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) Soil vapor samples were taken from 1 m beneath the ground surface at 16 different locations. Measured trichloroethene (TCE) in these samples was compared to that obtained for a collocated sample of the soil matrix. The linear slope (0.806) and strong correlation ($r^2 = 0.950$) obtained for this comparison of soil vapor (mg TCE/L) to soil mass (mg TCE/kg) concentrations are in good agreement with recent theoretical and empirical models for this volatile organic compound (VOC) in a low organic carbon soil matrix. This strong relationship suggests that active soil-vapor measurements could be used as an alternative to collecting and analyzing discrete soil samples for establishing both the presence and concentration of VOCs during site characterization and monitoring. Moreover, the techniques and instruments described here are robust, simple to use, and designed to enhance the reliability of soil-gas surveys to characterize vadose zone VOC contamination.				
14. SUBJECT TERMS Active probe Pollution Soil vapor Volatile organic compounds			15. NUMBER OF PAGES 13	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	