

Establishing a Relationship Between Passive Soil Vapor and Grab Sample Techniques for Determining Volatile Organic Compounds

Alan D. Hewitt

September 1996

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Abstract: A passive soil vapor and an in-vial sample handling and analysis method were compared for estimating volatile organic compound (VOC) contamination in the near-surface vadose zone. These two methods of VOC site characterization, although very different operationally, established very similar trends for trichloroethylene (TCE) contamination. The correlation ($r^2 = 0.944$) of the results from these two methods shows a much better agreement than what has been reported between comparisons of in-vial methods (or solvent

immersion) and conventional soil sample collection and handling methods often used for site characterization activities. The strong correlation between these two methods and from grab samples taken 15 cm apart indicates that this analyte is homogeneously distributed as compared to metals and semivolatile organic compounds. For contaminants such as TCE, soil vapor measurement technologies offer a promising means of estimating subsurface concentrations in locations where grab samples cannot be easily obtained.

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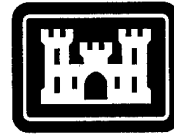
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PREFACE

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 (CRREL), Hanover, New Hampshire. Funding for this work was provided by the U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, through Environmental Quality Technology Project AF25, Ann B. Strong, Project Monitor.

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Establishing a Relationship Between Passive Soil Vapor and Grab Sample Techniques for Determining Volatile Organic Compounds

ALAN D. HEWITT

INTRODUCTION

Traditionally, passive soil vapor techniques have been used to establish the presence and relative distribution of volatile organic compounds (VOCs) in the near-surface vadose zone. These methods of screening are often used during the initial phase of a site investigation to provide insight for the placement of monitoring wells and to delineate areas for intensive sampling. In contrast, discrete soil sample ("grab samples") techniques are used for risk assessment, to establish both the horizontal and vertical profiles of contamination in areas of concern and to assess the progress of remediation.

To date, we are unaware of a study showing a strong relationship between the results from a passive soil vapor survey and soil VOC concentrations resulting from grab sample collection and analysis. The task of establishing a relationship between these two VOC assessment technologies is confounded by both environmental and operational variables. Among environmental variables, temperature, soil moisture, organic carbon content, grain size, mineralogy, texture, and barometric pressure all influence VOC concentrations in both the soil gas and sorbed phases (Conant et al. 1996). Among operational variables, these two approaches to VOC characterization have very little in common. Passive soil gas survey methods require a long-term exposure (several days to a couple of weeks) to establish an in-situ, time-integrated amount for a unknown volume of soil. Furthermore, because this application is usually designated for screening purposes, concentration determinations are not rigorous (i.e., single point calibration). Grab samples on the other hand represent a single point in time and are obtained in an intrusive fashion, by collecting a discrete quan-

tity of soil. Analysis of grab samples is performed using a specified laboratory procedure, which is usually validated by accompanying quality assurance (QA) and quality control (QC) data.

VOCs in an unsaturated porous medium partly exist in a gaseous state due to their high vapor pressures. Indeed, it is this physical characteristic of VOCs that has led to the success of both passive and active soil vapor techniques. On the other hand, because a portion of the contaminant VOC is present in the gaseous phase, intrusive sampling protocols have to be rapid and minimize disruption of the soil structure to prevent losses. Hewitt and Lukash (1996) have shown that in less than 40 minutes, more than 90% of the low boiling point VOCs (i.e., trichloroethylene [TCE]) can be lost from an intact soil stored in an uncovered core liner. Moreover, procedures that require multiple handling operations often result in underestimating soil VOC concentrations by one to three orders of magnitude (Urban et al. 1989, Hewitt 1994a, Hewitt et al. 1995).

In recognition of the problems with past intrusive soil sample collection, handling and analysis techniques, in-vial methodologies are now being promulgated. The U.S. Environmental Protection Agency is currently proposing two in-vial methods, 5021 and 5035, for the third update of the *Test Methods for Evaluating Solid Waste, SW-846* (U.S. EPA 1986). Using an in-vial approach requires that a discrete soil sample be collected and transferred directly to a vial with hermetic seals, that then has to be punctured by a needle in order to perform a VOC analysis. Furthermore, Hewitt and Lukash (1996) recommend that these soil samples be collected within a few minutes of exposing a fresh surface and transferred to the collection/analysis vial with minimal disruption to the native soil structure.

If in-vial sample handling and analysis methods work as intended, then VOCs present as vapor, sorbed, or liquid (pure product or mixture) should be included in the measurement. Therefore, using in-vial sample handling and analysis procedures should increase the chances of establishing a relationship with a vapor survey method. To test this hypothesis, soil mass concentrations established using an in-vial handling and analysis method were compared to soil vapor analyte amounts obtained with a passive collector, Gore-Sorber modules. Use of Gore-Sorber modules is a relatively new method of performing a passive soil gas survey for VOCs and some semivolatile organic compounds (Wrigley 1995). The sorbent present in the modules used in this study was Tenax-TA, a material that has strong affinity for a broad range of organic compounds, independent of sample moisture. Experimentally, comparisons between the Gore-Sorber modules and well-established grab sample VOC measurement methods were performed with both laboratory-fortified and field-contaminated soils.

MATERIAL

Each Gore-Sorber module consists of long (≈ 120 -cm) hollow Gore-Tex membrane cord that allows for installation and retrieval, and contains three separate granular Tenax-TA sorbent packs (40 mg) positioned at one end. The Gore-Tex membrane, which also serves as a wrapping for each pack, is an expanded polytetrafluoroethylene (ePTFE), transparent to gases while preventing direct contact of the sorbent with solid or aqueous matrices. Thus, during deployment in the field, the sorbent module is both wrapped and sheathed in an inert, hydrophobic, microporous membrane, allowing only for the penetration of vapors.

EXPERIMENTAL

Laboratory-fortified soil

The capabilities of the Gore-Sorber module, headspace gas chromatography (HS/GC), and

Table 1. VOC concentrations ($\mu\text{g/g}$) established for vapor-fortified QA soil samples.

Analyte*	Aqueous	Methanol	Tenax-TA TD/GC/MS***		
	extraction HS/GC ($\mu\text{g/g}$)	extraction PT/GC/MS ($\mu\text{g/g}$)	1 d [†]	9 d	15 d
TDCE	5.5 \pm 0.6**	5.8 \pm 0.55	0.73	1.81	1.68
CDCE	51 \pm 0.9	51.7 \pm 1.21	8.1	15.6	14.5
CF	89 \pm 5.0	85.3 \pm 1.58	17.4	30.2	30.0
C-tet	ND ^{††}	44.3 \pm 1.01	11.7	18.4	18.2
Ben	63 \pm 0.4	61.7 \pm 1.49	14.2	26.4	24.2
TCE	8.0 \pm 0.3	8.3 \pm 0.44	3.24	4.56	3.99
1,1,2 TCA	ND	6.3 \pm 0.31	2.74	3.54	3.44
Tol	56 \pm 0.6	49.7 \pm 1.76	22.4	30.8	27.5
PCE	91 \pm 3.0	74.2 \pm 0.96	57.6	70.1	47.6
E-Ben	13 \pm 0.1	11.7 \pm 0.31	7.10	9.00	8.64
p-Xyl	26 \pm 0.4	22.7 \pm 0.32	13.5	16.9	15.6
o-Xyl	41 \pm 0.7	36.9 \pm 0.85	22.5	27.2	22.8
1,4 DCB	10 \pm 0.1	12.4 \pm 0.31	9.45	11.5	9.85
Napht	12 \pm 1.0	9.3 \pm 0.76	4.24	7.69	7.01

* TDCE, trans-1,2-dichloroethylene; CDCE, cis-1,2-dichloroethylene; CF, chloroform; C-tet, carbon tetrachloride; Ben, benzene; TCE, trichloroethylene; 1,1,2 TCA, 1,1,2 trichloroethane; Tol, toluene; PCE, tetrachloroethylene; E-Ben, ethylbenzene; p-Xyl, para Xylene; o-Xyl, ortho Xylene; 1,4 DCB, 1,4 dichlorobenzene; Napht, naphthalene

** Mean and standard deviation of sample triplicates

[†] Equilibration period (days)

^{††} Not detectable by instrumental configuration.

*** Thermal desorption gas chromatography mass spectrometry.

purge-and-trap gas chromatography mass spectrometry (PT/GC/MS) Method 8260 (U.S. EPA 1986) were initially compared using vapor fortified soil samples. These secondary quality assurance (QA) standards were fortified with 14 VOCs, ranging in concentration from 5 to 100 $\mu\text{g/g}$ (Table 1). Briefly, vapor fortification involves exposing a desiccated soil held in small (1-mL) glass ampoule to vapors emanating from an organic solution, inside of a sealed chamber (Hewitt 1994b). This method of producing performance evaluation samples is precise, mimics an environmental pollution pathway, and uses a 1-week or longer exposure period. Furthermore, once fortification has been completed and the ampoules heat sealed, analyte concentration remain stable for up to 6 months.

To analyze the VOCs present in one of these vapor-fortified samples, the entire ampoule is placed inside of a container (usually a volatile organic analysis [VOA] vial or equivalent vessel) with the appropriate solvent or sorbent for the chosen method of analysis. For this study Type 1 water was used for HS/GC, methanol for Method 8260 (U.S. EPA 1986), and a single Tenax-TA sorbent pack for the Gore-Sorber module. Once the VOA vial or vessel has been capped, the soil is dispersed for extraction/equilibration, by hand

shaking, causing only the glass ampoule to break. For this study three separate secondary standards were supplied to W.L. Gore & Associates. To test the VOC affinity of the Tenax-TA sorbent pack with these QA samples, one was allowed to equilibrate for 1 day, while the other two were allowed to equilibrate for 9 and 15 days.

Field samples

Discrete grab and passive soil vapor samples were collected at 18 separate locations, at the CRREL (Fig. 1). This site has previously been characterized as having TCE contamination in both the vadose zone and groundwater, ranging in concentration from <0.001 to >100 ppm ($\mu\text{g/g}$ or mg/L, Hewitt 1994b, Hewitt and Shoop 1994). Consequently, the locations chosen for this comparison study took full advantage of this feature. In general, the soils typical of this site are silty-sands with a moisture content of around 10% and an organic carbon content of $<1.0\%$. However, the substrate was dominated by either silty-clays or sand at a couple of the sampling locations.

The near-surface holes, from which grab samples were collected and then the Gore-Sorber modules were placed, were made using a Veihmeyer tube. A Veihmeyer tube uses a sliding bar hammer to push its hollow stem into the soil subsurface, and, once removed, a 3.2-cm-i.d. open channel remains from the ground surface to the depth of interest. Grab samples were collected and the Gore-Sorber modules were initially exposed (installed) on 4 December 1995. For the purpose of this report, all of the samples taken from a single location (Fig. 1) will be referred to as colocated. These sampling locations were created, 42 grab samples collected, and 18 Gore-Sorber modules installed in approximately 4 hours by two people.

For in-vial sample handling and HS/GC analysis, two grab samples (≈ 3 g each) were taken from each location (hole), one at 76 cm and a second at 91 cm. In addition, at six locations grab samples from a depth of 84 cm were collected and placed directly into jars with a Gore-Sorber module. The vessels, used for shipping and storage of the sorber modules, were 125-mL

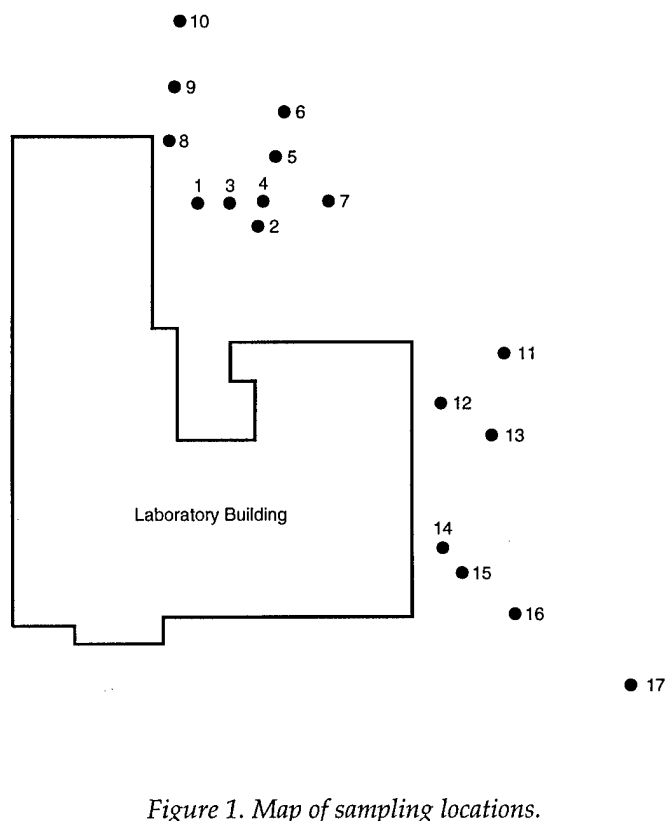


Figure 1. Map of sampling locations.

glass jars with Teflon-faced cushioned lids, which formed a hermetic seal upon capping. Prior to adding the grab samples to these jars, the ePTFE cord was shortened to eliminate unnecessary weight.

Grab samples were collected from the bottom of the open channel (hole) using a 116-cm-long, 1.9-cm-i.d. Plexiglas subcorer equipped with a plunger. This sampling device works in the same manner as a plastic syringe with its tip removed (Griffith et al. 1988). Discrete plugs of undisturbed soil were obtained immediately after removing the Veihmeyer tube, by inserting the open barrel of the Plexiglas subcorer approximately 2.5 cm beyond the hole's present depth. The plug of soil was then quickly transferred directly to either a prepared VOA vial or jar containing a Gore-Sorber module. These plugs of soil, transferred to jars containing sorbent modules, remained intact throughout the study (maintained the cylindrical shape created by the subcorer).

Soil samples taken for the in-vial collection and HS/GC analysis protocol were placed into pre-weighed 22-mL VOA vials containing 10 mL of Type 1 water. Before inserting a soil plug, a sheet of Parafilm "M," which had covered the vial to prevent spilling or evaporation, was removed. Immediately after the sample had been extruded directly into the VOA vial, it was sealed with a Teflon-faced septum and aluminum crimp top. Using this protocol, grab samples from the depth of interest were collected, transferred, and enclosed in a vessel with hermetic seals, within a minute of exposing a fresh surface.

The moist weight of each soil sample was obtained by weighing the collection/analysis VOA vial before and after sampling. Likewise the jars with Gore-Sorber modules, into which grab sample were placed, were also weighed before and after the sampling event to obtain the samples' moist weight. These jars were allowed to sit at room temperature (22°C) for 16 days after sample collection.

The Gore-Sorber modules were quickly positioned at the bottom of the 3.2-cm-i.d., 91-cm-deep hole by using an insertion tool to push the sorbent end of the cord into the exposed substrate. These modules that were left in the field were retrieved after 16 days, and placed into their individual shipping and storage jars. During the 16-day exposure period (4 to 20 December 1995) the holes into which the sorber had been placed were sealed with a cork stopper that was covered with a Styrofoam dish. Wooden stakes were also

used to locate each sampling hole. During the sampling period there was a continuous snow cover (≈ 30 cm at installation, ≈ 76 cm at retrieval) and a frost zone that penetrated 5 to 10 cm below the ground surface. The same day the sorbent modules were retrieved from the field, these sample jars and the ones into which grab samples had been placed were packed in a cooler with blue ice and shipped to W.L. Gore & Associates for analysis.

ANALYSIS

Grab samples placed in VOA vials containing water were analyzed the day after collection using a HS autosampler (Tekmar 7000) coupled to a GC (SRI, model 8610-0058) equipped with a 15-m, 0.53-mm diam. MXT-1 capillary column (Restex Corp.), and photo-ionization/flame ionization sequential detectors. This same system was also used to determine the VOCs in the vapor-fortified samples. Before placing the VOA vials that either contained field grab samples or vapor-fortified samples onto the HS auto sampler, they were shaken for 2 minutes to assist in attaining an equilibrium partition of VOCs among the phases present. In accordance with in-vial analysis protocols, a portion of the headspace VOC vapors were removed from these VOA vials by puncturing the septum with a needle.

Analyte concentrations were established relative to aqueous headspace standards prepared by adding small (<10 μL) quantities of a methanol (MeOH) stock solution to autosampler vials containing 10 mL of Type 1 water. This HS/GC method of analysis has a detection limit of approximately 0.001 $\mu\text{g TCE/g}$. Instrumental 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 1995).

The vapor-fortified soil samples were also analyzed by PT/GC/MS following Method 8260 (U.S. EPA 1986). Due the high concentrations of VOC present (5–100 $\mu\text{g/g}$) this sample was first extracted with MeOH. Once immersed in MeOH, VOCs associated with a soil matrix become dissolved in this solvent. Completeness and the rate of extraction is a function of both organic carbon content and macro/micropore structure inherent to the matrix (Pignatello and Xing 1996). After extraction into MeOH, VOC concentrations re-

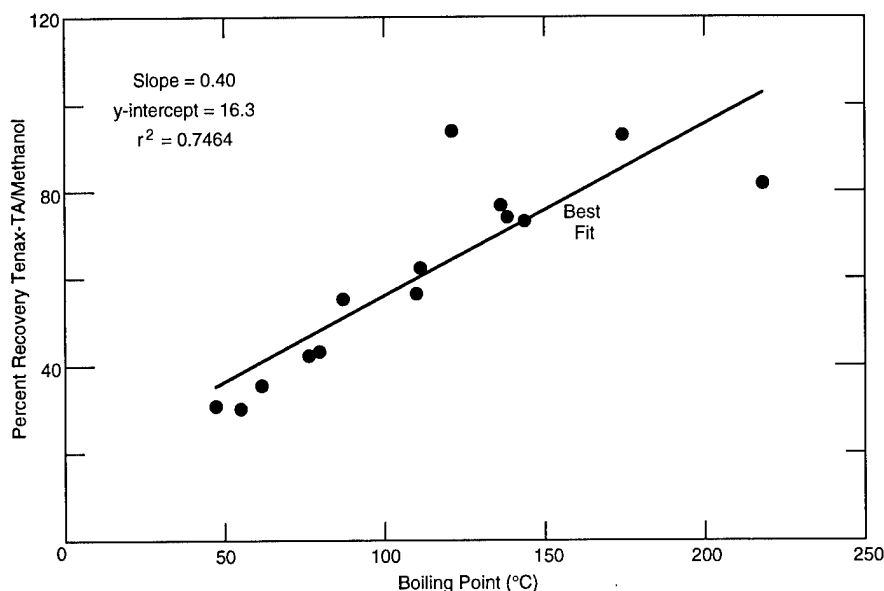


Figure 2. Percentage analyte recovery by the Tenax-TA sorbent relative to methanol extraction vs. boiling point.

main stable for extended periods (several months), and the vessel can be intermittently opened for aliquot removal without significant losses (Hewitt 1995b). Therefore, the immersion of a soil sample into an organic solvent also accomplishes the intent of in-vial handling and analysis protocols, relative to controlling volatilization losses.

Individual Tenax-TA packs from the Gore-Sorber modules were analyzed by thermal desorption gas chromatography mass spectrometry (TD/GC/MS), using a Level 1 screening procedure (W.L. Gore & Associates). This semiquantitative procedure establishes a compound mass, based on a single point calibration 5- μ g standard mass, and has a reported detection limit of 0.02 μ g for TCE.

RESULTS

Laboratory-fortified soil

Table 1 shows the VOC concentrations determined for the vapor fortified soil samples by HS/GC, PT/GC/MS (Method 8260) and by TD/GC/MS analysis of the Tenax-TA packs after three different exposure periods. All concentrations are expressed on a mass per mass basis since the amount of soil present was known. Quantitatively, both HS/GC and PT/GC/MS (Method 8260) established similar concentrations for 12 of the 14 analytes (two compounds were not determined by HS/GC analysis due to co-elution). Good agreement between these two methods of sample preparation and analysis has been established previ-

ously for soils with a low (<1%) organic carbon content (Hewitt et al. 1992).

In comparison, the sorbent pack TD/GC/MS analysis attained a maximum recovery after 9 days of exposure, showing analyte concentrations 30% to 93% of that established by MeOH extraction PT/GC/MS analysis. The analyte recoveries established by the Tenax-TA sorbent is a function of its affinity for the individual VOC vapors, and their release from the desiccated soil. By plotting the percentage recovery after 9 days of exposure for the Tenax-TA sorbent relative to the MeOH extraction results vs. the boiling points of the analytes, an direct relationship is established (Fig. 2). Clearly, this sorbent's ability to passively acquire VOCs from this matrix is dependent on the boiling point (i.e., vapor pressure).

Qualitatively, the TD/GC/MS analysis of the sorbent pack was able to rapidly (1-day exposure) identify all of the analytes present in the vapor fortified QA soil sample (Table 1). Thus, even under a desiccated condition where soils show a much greater capacity for the sorption of VOCs (Chiou and Shoup 1985) and analytes may be held to crystalline surfaces by physical forces, such as van de Waals (Sawheny and Gent 1990), this technology is effective on a relative basis.

Field samples

The results shown in Table 2 are for locations where a grab sample was collected at a depth of 85 cm and placed in a jar with the Gore-Sorber module. This table also includes results for collocated grab samples collected some 7 cm above

Table 2. Soil sample concentrations established for discrete grab samples by the Gore-Sorber module and by in-vial sample collection and HS/GC analysis.

Location	In-vial HS/GC ($\mu\text{g TCE/g}$)			Gore-Sorber
	76 cm	91 cm	Mean	($\mu\text{g TCE/g}$) 85 cm
1	5.7	6.8	6.2	11.0
2	15	16	16	23.5
4	3.1	5.5	4.3	5.12
7	0.016	0.014	0.015	<0.02
13	1.5	1.6	1.6	2.19
14	2.1	5.2	3.6	2.31

and below, and analyzed by HS/GC. All values are reported on a mass per mass basis by accounting for the number of sorbent packs present (only one of the three replicate packets present during exposure was analyzed). A comparison between these two methods was evaluated by plotting the mean TCE concentration from the two grab samples analyzed by HS/GC vs. the concentration estimated from analysis of the Gore-Sorber module. This limited comparison (five out of the six locations) has a correlation coefficient (r^2) of 0.964, and slope of 1.62 (Fig. 3). Failure to detect TCE on the sorber module positioned at location no. 7 is consistent with the detection limit reported for this technology (0.02 $\mu\text{g TCE}$) and the concentrations established by the colocated grab samples taken for HS/GC analysis (Table 2).

Unlike the 57% recovery of TCE from the laboratory fortified soil as determined by TD/GC/MS analysis of the Tenax-TA sorbent (Table 1)

relative to HS/GC analysis, the correlation shown in Figure 3 suggests the opposite trend for recovery of this analyte from colocated field grab samples. That is, TD/GC/MS analysis of the Gore-Sorber module typically resulted in greater concentrations of TCE than established by HS/GC analysis. In reality too few comparison were made to offer an explanation for this observation. However, in the presence of moisture (i.e., ample water vapor), VOCs may not be as strongly retained as by a desiccated soil; thus under field conditions Tenax-TA may have a greater apparent affinity.

Table 3 shows the TCE results obtained from 18 locations (Fig. 1), for both the two grab samples taken for HS/GC analysis and the mass of TCE sorbed by the passive soil vapor GORE SORBER modules over the 16-day exposure period. In this table (Table 3) the GORE SORBER results are reported only as the total amount of TCE determined, since the mass of soil from which the vapors came is not known. Not included in Table 3 is a single detection of cis-1,2-dichloroethylene, and several for carbon tetrachloride and tetrachloroethylene, established by the analysis of the Gore-Sorber module. In every case where these other analytes were detected, the mass established for TCE was at least 20 times greater (more often >100x).

Looking first at the comparison between the colocated grab sample results, a strong linear relationship is shown, with a correlation coefficient of 0.957 (Fig. 4). This correlation and slope of 1.088 show that TCE was homogeneously distrib-

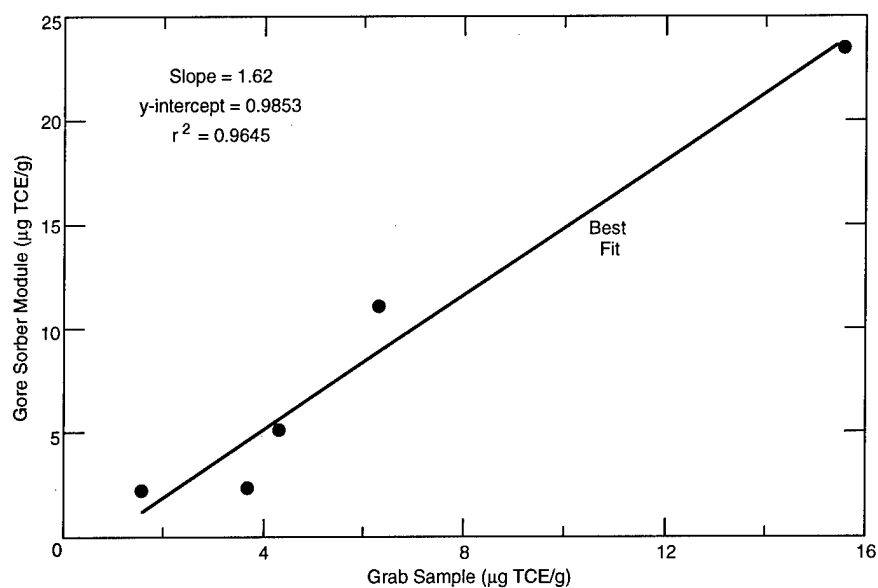


Figure 3. Comparison of the mean TCE concentrations ($\mu\text{g/g}$) in grab samples established by HS/GC and by Gore-Sorber modules.

Table 3. Soil vapor mass established by the Gore-Sorber module and concentrations established for grab samples taken for in-vial sample handling and HS/GC analysis.

Map location	In-vial HS/GC ($\mu\text{g TCE/g}$)			Gore-Sorber module ($\mu\text{g TCE}$)
	76 cm	91 cm	Mean	
1	5.7	6.8	6.2	892.28
2	15	16	16	1012.03
3	4.3	4.6	4.4	827.25
4	3.1	5.5	4.3	923.29
5	0.11	0.11	0.11	88.34
6	0.017	0.023	0.020	82.92
7	0.016	0.014	0.015	33.82
8	0.010	0.014	0.012	109.29
9	0.013	0.0046	0.0088	43.15
10	0.0066	0.0077	0.0072	58.70
11	0.095	0.10	0.098	273.50
12	0.11	0.088	0.099	239.27
13	1.5	1.6	1.6	648.18
14	2.1	5.2	3.6	724.12
15	0.39	0.32	0.36	390.55
16	<0.001	<0.001		0.10
17	<0.001	<0.001		0.00
18	<0.001	<0.001		0.00

uted at the majority of sampling locations, on at least a scale of 15 cm. This degree of homogeneity for TCE in collocated samples is consistent with several other studies performed at this site (Hewitt et al. 1992, Hewitt et al. 1995, Hewitt and Lukash 1996). With the exception of samples collected within the first 30 cm of the surface, or when two distinctly different types of soil substrate are encountered, collocated samples have often been

found to agreed within a factor of 30%. Once in-vial methods or in-field solvent extraction methods become a common practice, collocated soil samples will offer a powerful tool for QA purposes.

In terms of contaminant distribution both the soil vapor survey and grab sample analysis methods established very similar trends for TCE in the near surface vadose zone. Moreover, a strong relationship was established between the mean of the collocated grab samples analyzed by HS/GC and the soil vapor Gore-Sorber results ($r^2 = 0.944$, Fig. 5). The correlation coefficient was only slightly less significant than that of the two collocated grab samples (Fig. 4). The semilog relationship found between the two methods could be a function of the TD/GC/MS detector response or a change in the Tenax-TA sorbent affinity with increasing loading of analyte. Even with this degree of nonlinearity, the TCE concentration (mass/mass) in the soil at discrete locations on this site could be adequately predicted over a range of 0.010 to 16 $\mu\text{g/g}$, based on passive soil gas measurements and the relationship shown in Figure 5. The worst case value (passive soil vapor amount established for location no. 5) for this comparison shows only a discrepancy of 5.5 \times between the predicted and measured TCE soil concentration. This discrepancy is not nearly as misrepresentative as the random 10 \times to 1000 \times range of disagreement reported for comparisons between collocated soil samples collected and analyzed using in-vial protocols vs. those collected and analyzed using common regulatory agency approved procedures (fill-

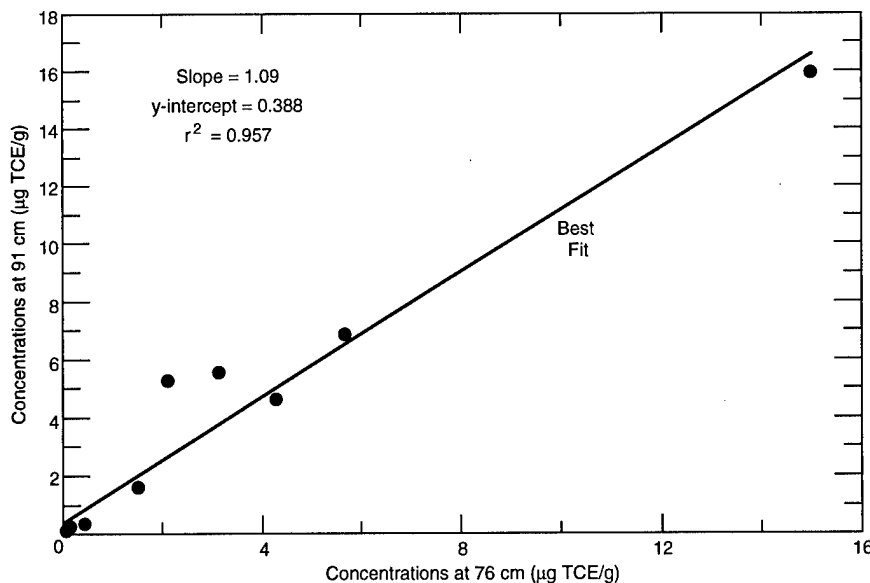


Figure 4. Comparison of TCE concentrations ($\mu\text{g/g}$) established for collocated grab samples taken for HS/GC analysis.

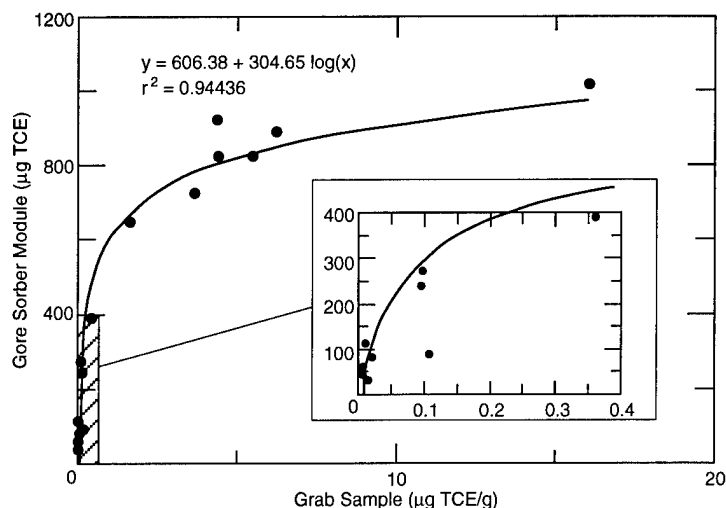


Figure 5. Comparison of TCE measurements established by mean of colocated grab samples analyzed by HS/GC and passive soil vapor established by the Gore-Sorber modules.

ing a collection bottle to capacity then shipping to an off-site laboratory for subsampling and analysis [Urban et al. 1989, Illias and Jaeger 1993, Hewitt 1994b, Hewitt et al. 1995]).

DISCUSSION

The most significant finding of this study is that strong relationships are very likely between passive soil vapor VOC measurements and VOC concentration established by grab samples. Secondly, TCE contamination in the vadose zone is largely caused by vapor transfer, because a homogeneous distribution of analytes is unlikely if they were principally to exist as separate liquid or solid phases. This characteristic of TCE contaminant transport was recently demonstrated experimentally and modeled for the unsaturated zone (Conant et al. 1996). Their study showed that in an unconsolidated subsurface zone, a vapor plume will radiate out from a point where a separate phase or residual source exists, forming gradient contours of contamination.

However, to accurately establish the relationship between soil vapor survey methods, passive or active, and grab samples requires that extreme precautions are taken to minimize VOC losses. With regard to volatilization, grab sample collection must be performed using a rapid non-disruptive transfer method, coupled with either in-vial handling and analysis or solvent-immersion. An additional concern not covered in this report is that if aromatic compounds are involved, grab sample analysis should occur within 2 days of collection if measures (i.e., solvent-immersion,

acidification, mercuric chloride, etc.) are not taken to prevent biological degradation (Hewitt 1995a,b).

At present, comparisons between soil vapor survey methods and grab samples are perhaps best suited for near-surface locations. Soil samples retrieved from depths beyond 6 m often take 15 minutes or longer before they can be subsampled. Intact soil cores held in open tubes may or may not retain representative VOC concentrations over this time period (Hewitt and Lukash 1996). In addition to the time concern, many down-hole sampling systems pull a vacuum on the soil core during retrieval, or require the sample be extruded from a sample chamber prior to subsampling. Therefore, many present sampling systems facilitate or allow volatilization losses even before discrete grab samples can be collected. However, once relationships have been established for near surface sampling locations, soil vapor technologies would provide means of estimating VOC concentrations in unsaturated subsurface regions that cannot be easily or quickly accessed for grab sample collection.

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13. ABSTRACT (Maximum 200 words) A passive soil vapor and an in-vial sample handling and analysis method were compared for estimating volatile organic compound (VOC) contamination in the near-surface vadose zone. These two methods of VOC site characterization, although very different operationally, established very similar trends for trichloroethylene (TCE) contamination. The correlation ($r^2 = 0.944$) of the results from these two methods shows a much better agreement than what has been reported between comparisons of in-vial methods (or solvent immersion) and conventional soil sample collection and handling methods often used for site characterization activities. The strong correlation between these two methods and from grab samples taken 15 cm apart indicates that this analyte is homogeneously distributed as compared to metals and semivolatile organic compounds. For contaminants such as TCE, soil vapor measurement technologies offer a promising means of estimating subsurface concentrations in locations where grab samples cannot be easily obtained.				
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