

Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds

Alan D. Hewitt and Nicole J.E. Lukash

February 1996

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Abstract

The ability to retain volatile organic compounds (VOCs) while collecting and transferring intact soils for in-vial analysis was evaluated with field and laboratory samples. Experiments were designed to assess if VOC concentrations are maintained in an intact soil sample when 1) held for under an hour in a metal core liner, 2) held for days in a metal core liner sealed with TFE-fluorocarbon sheets or aluminum foil (ASTM D4547-91), 3) held for less than 2 minutes in a plastic bag after extruding from a sampling device, and 4) immediately transferred to an empty vial to which a solvent was added later. Results indicate that these procedures are all highly susceptible to volatilization losses. To maintain site-representative VOC concentrations, collection of soil samples for in-vial analysis should occur within minutes of exposing a fresh surface by using a device that limits soil structure disruption and exposure.

For conversion of SI units to non-SI units of measurement consult ASTM Standard E380-93, *Standard Practice for Use of the International System of Units*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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Engineering Laboratory

Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, and Nicole Lukash, Physical Science Aid, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

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Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds

ALAN D. HEWITT AND NICOLE J.E. LUKASH

INTRODUCTION

An in-vial method of preparing and analyzing soils for volatile organic compounds (VOCs) requires soil to be transferred directly to a vessel with hermetic seals. This approach differs from those often used under the guidelines of Method 5030 of the SW-846 (U.S. EPA 1986) by using only a single transfer process and a vessel that is compatible with the instrumentation on which the analysis will be performed. In-vial soil sample preparation and analysis methods address much of the past criticism regarding the volatilization losses of VOCs caused by repeated exposures and uncontrolled disturbance of soil samples when transferred to and from receptacles of various shapes and sizes (Urban et al. 1989, Seigris and Jenssen 1990, Hewitt et al. 1993, Illias 1993, Voice and Kolb 1993, Lewis et al. 1994).

The U.S. Environmental Protection Agency has proposed Methods 5021 and 5035, two in-vial preparation and analysis procedures for the third update of the *Test Methods for Evaluating Solid Waste*, SW-846. The first is designed for low level (<1- μ g VOC/g) analysis by purge-and-trap, gas chromatography/mass spectrometry (Method 8240 or 8260). The second is an equilibrium headspace (HS) approach to analysis that can be used in conjunction with Methods 8015, 8021, or 8260. Both of these methods use volatile organic analysis (VOA) vials (22 and 44 mL), which rely on a Teflon-faced septum with bonded silicon or rubber backing, compressed by a rigid plastic or aluminum cap, to form a hermetic seal with a glass rim. This septum also forms a vapor-tight seal around the needles used to remove VOCs from the vial during sample analysis.

In addition to using the in-vial preparation and analysis methods described in Methods 5021 and

5035, attention must also be given to how the sample is obtained and transferred prior to this treatment. The necessity to limit disruption and exposure of the unsaturated soil sample, while it is being transferred to an analysis vial, is imperative because the analytes of concern have high vapor pressures, allowing them to either partly or largely exist as gases under environmental conditions. For instance, to avoid the volatilization losses incurred by using utensils that allow the soil to randomly fracture and expose an uncontrolled amount of surface area (stainless steel spoons, spatulas, garden trowels, etc.), small coring tools have been used. Examples of such devices are common laboratory plastic syringes with their tips removed (Griffith et al. 1988) and specially designed stainless steel samplers (Associated Design and Manufacturing Co., EN CHEM, Inc.). The use of these coring tools is addressed in the current draft of Method 5021, and the inclusion of these devices is anticipated for the final version of Method 5035. The merit of using a limited-disruption single-transfer and in-vial approach to soil sample collection, handling and analysis is to achieve more representative estimates of the in-situ environmental VOC concentrations than possible using previous approaches.

The purpose of this study is to look closely at some collection and transfer procedures that may be used with in-vial methods of analysis. Experiments were designed to assess if VOC concentrations are maintained in an intact soil sample when 1) held for less than an hour in a metal core liner, 2) held for days in a metal core liner sealed with TFE-fluorocarbon sheets or aluminum foil (ASTM D4547-91), 3) held for less than 2 minutes in a plastic bag after extruding from a sampling device, and 4) immediately transferred to an empty vial to which a solvent was added later.

EXPERIMENTAL

All of the field samples used during the following experiments were obtained from rectangular holes approximately 25×25 cm and extending to depths between 20 and 46 cm below the ground surface. At the site where the holes were excavated, trichloroethylene (TCE) contamination has been present for about 25 years. The soil at this location (Hanover, N.H.) is characterized as a cohesive silty-clay with an organic carbon content of less than 0.5% (Hach method 8097), ranging in moisture from 13 to 16% (ASTM D2216-66).

Each experiment was performed as rapidly as possible after exposing a smooth flat surface in the native substrate. Except where noted, samples taken for analysis were obtained and transferred to VOA vials using 3-, 5-, or 10-cm³ plastic syringes with their injection tip and rubber plunger-cap removed. The open end of these corers were pushed approximately 2.5 cm into the exposed surface, resulting in soil plugs of approximately 2, 4, and 6 g. When transferring the soil sample, care was taken to remove soil adhering to the exterior of the corer before inserting it into the mouth of a collection vial, so that the sealing surfaces would not be compromised. The mass of the collected sample was obtained by the weight difference of the collection vial before and after adding the sample. Samples collected with either the 3- or 5-cm³ syringe were transferred to 22-mL auto sampler vial (Wheaton), containing either 10 or 15 mL of Type 1 water, and capped with a Teflon-faced gray butyl septum and aluminum crimp top. Samples obtained with the 10-cm³ syringe were transferred to 44-mL VOA vials (Eagle Picher) containing 30 mL of Type 1 water and capped with a Teflon-faced silicone septum and plastic screw top. Soil samples, collected immediately after exposing a fresh surface and transferred as described above, served as the reference samples to which others were compared.

Core liner experiments

Field samples

In all, four separate field experiments were performed using 3.6-cm-i.d. \times 5.1-cm brass core liners (Environmental Instruments). Uncovered intact soils obtained in these core liners have an exposed surface area/sample mass ratio of approximately 0.27 cm²/g. In each experiment, six core liners were inserted vertically into the bottom of the hole, creating a 3×2 array. A wooden block

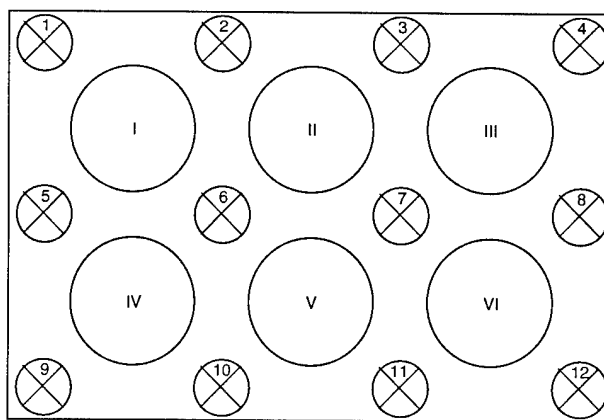


Figure 1. Sampling pattern for core liner experiments. Circles with crosses show location of samples taken exterior to core liners.

and hammer were used to push each core liner to a 5.1-cm depth. These core liners were numbered I-VI, denoting their position and orientation. Once positioned, 12 reference soil samples were taken in a pattern, so that four sampling locations surrounded each of the core liners (Fig. 1).

In the first experiment, samples were sequentially collected by inserting a 5-cm³ syringe into the freshly exposed surface 1.2 cm, removing and discarding the soil, followed by a second insertion into the same sampling hole, 2.5 cm beyond the first insertion, and removing a plug of intact soil. This subsurface sample was immediately transferred to a VOA vial containing water. After all the reference samples (exterior to the core liners) were taken, the core liners were removed from the hole and, without covering, placed in a large plastic bag. Each core liner was then sequentially subsampled in the same manner, after periods of 1, 10, 20, 30, 40 and 60 minutes (one sample/core liner).

The second experiment followed the same format as the first, except four of the core liners were individually covered and stored. Once the samples exterior to the core liners had been collected, the core liner in the lower right-hand corner (VI) was removed with the soil intact and sampled as described for the before-mentioned reference samples. The next four core liners were then removed, one at a time, going from right to left. Once removed their exteriors and rims (top and bottom) were wiped clean with a paper towel, both ends were then covered with either a single 7.6-cm-wide sheet of TFE (Environmental Instruments) or heavy duty aluminum foil, followed by press fitting plastic end caps. The last core liner (I) was

removed and immediately sampled as described for core liner VI. Shortly thereafter, the core liners covered with aluminum foil were wrapped with PVC tape, sealing both the edges of the foil and plastic cap to the core liners' exterior walls.

The third and fourth experiments used the same general format as the second, except that the reference samples and those taken from the core liners were collected without discarding the top 1.2 cm of soil. The last experiment used 18, 3-cm³ syringes: 12 were positioned exterior to the core liners, and 3 each into core liners I and VI. Once they all were in position (pushed 2.5 cm into the exposed soil surface) they were sequentially removed and the plug of soil obtained in each syringe was transferred to a prepared VOA vial.

For all of these field experiments the entire sampling operation, from the point of inserting the core liners until the last sample was collected, took approximately 15 minutes. Covered core liners were stored in a refrigerator (4°C) for either 5 or 10 days before being sampled in the laboratory using the same procedure that had been used in the field.

Laboratory experiment

Three laboratory experiments were performed with modified core liners (3.6-cm-i.d. × 3.4 cm high) made by soldering a brass cap onto one end, making a cup. The matrix used was a sandy soil desiccated with CaSO₄ or moistened with water to 1% or 10%. In each case 50 g of the soil was packed (1.4 g/cm³) into 12 brass cups, leaving <2 mm of space between the soil surface and rim. Uncovered, the surface area to sample mass ratio was approximately 0.20 cm²/g. Handling one sample at a time, we then spiked each of the 12 replicates by inserting the needle (gauge 26s) of a 10-μL syringe to the bottom of a soil-filled cup and injecting 5 μL of a methanol (MeOH) standard containing trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben) and toluene (Tol). Upon removing the needle, the soil was tamped down filling the injection channel. These experiments were performed in conjunction with others not reported here; thus, for convenience, different methanol standard solution was used for the 10% moisture experiment than was used for the desiccated and 1% moisture experiments. Of the 12 replicates, five were covered with two sheets of TFE, and five were covered with aluminum foil, then capped and taped as described previously. The remaining two samples were immediately taken for analysis, by submersing the entire cup into 300

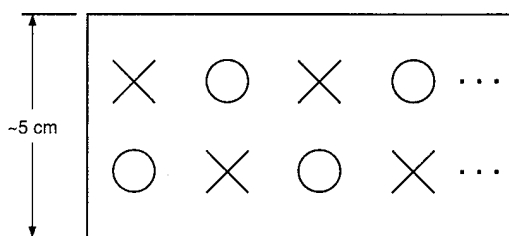


Figure 2. Sample collection pattern for extruded soil cores.

mL of water contained in a 500-mL jar and capped with a Teflon-backed silicone septum top. These jars have a special opening in the cap to allow for syringe penetration. All covered samples were stored at 4°C until the day of analysis, whereupon the caps and coverings were removed and the cups quickly submersed into 300 mL of water contained in 500-mL jars.

Extruded soil cores

This study initially compared soil samples obtained with 10- and 3-cm³ syringes and extruded directly into 44- or 22-mL VOA vials containing water, respectively. Samples for this initial comparison were collected at a depth of 33 cm after inserting five of each size of the syringes into the bottom of the hole. The syringes were positioned in a tight array (12 × 5 cm) in two rows (Fig. 2). A second experiment, performed in the same hole at a depth of 38 cm, collected two separate arrays of eight soil samples, using first the 10-cm³ then the 3-cm³ syringes. Again all eight syringes were positioned, prior to being sequentially removed, placing alternating soil plugs into VOA vials containing water, or into small (7.5-cm × 5-cm) plastic Ziploc bags and sealing. Those transferred to the Ziploc bags were held for 1 to 2 minutes; then the bags were cut open with scissors so that the plugs of soil could be easily transferred (Ziploc bags have a lip that interfered with the sliding of a plug of soil). Special care was taken for those plugs extruded into the plastic bags so that they would remain intact until immersed in the water present in the VOA vials. Once extruded into the plastic bags the soil samples had a surface area/mass exposure ratio of approximately 2.0 and 3.6 cm²/g for the 10- and 3-cm³ syringes, respectively.

Collection vessel preparation

This experiment assesses the effect of introducing a solvent to a sample after it has been transferred to an empty VOA vial compared to samples transferred to VOA vials with water present. Six-

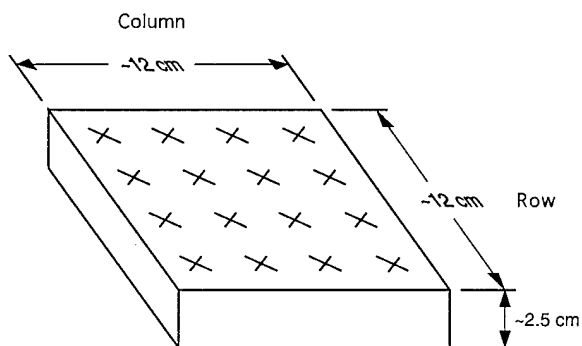


Figure 3. Sampling pattern for composite samples.

teen, 3-cm³ tipless syringes were inserted vertically in a 4 × 4 array (Fig. 3) into the bottom of a 38-cm hole. Once all the syringes had been positioned, one from each row and column of the 4 × 4 array was randomly removed and its contents quickly composited (4 separate plugs) into either a VOA vial containing 10 mL of water or empty VOA that was then covered with Parafilm. For the vials covered with Parafilm, this temporary covering was removed after a 2-minute period and 10 mL of water was added. The 4 × 4 sampling array allowed for duplicates of the composited samples to be compared. This series of steps was repeated in the same hole at depths of 40, 43, and 46 cm. At the next two depths (40 and 43 cm) the vials without water were sealed with Teflon-faced gray butyl rubber septa and aluminum crimp tops, and they were opened after 20 or 200 minutes to add 10 mL of water and then recapped. At the depth of 46 cm, 10 mL of water was added immediately after the last soil plug of four being composited had been transferred to the empty VOA vial. In all cases, the plugs of soil remained intact during collection process; i.e., they remained in the cylindrical shape created by the coring tool even after they were transferred to the analysis vials.

ANALYSIS

All samples were analyzed by equilibrium headspace (HS) analysis. Samples transferred to 44-mL VOA vials or 500-mL jars were analyzed on a model 10S10 PhotoVac gas chromatograph (GC). Samples transferred to 22-mL VOA vials were analyzed on an automated system composed of a

HS auto sampler (Tekmar 7000) coupled to a GC (SRI, model 8610-0058). Additional information concerning sample analysis and the operating conditions used with these instruments can be found elsewhere (Hewitt et al. 1992, Hewitt 1995a).

Concentration estimates were established on moist weight basis relative to working standards, which were prepared by spiking analysis vials (jars) that contained the same amount of water as the samples with small volumes (<100 µL) of a methanol stock standard. The stock standards were prepared on a weight basis, then volumetrically diluted as necessary. Samples and standards were hand shaken for at least two minutes prior to analysis. This approach to the analysis establishes VOC concentration estimates that often are not significantly different than more rigorous purge-and-trap procedures when the soil matrix has a low (<1%) organic carbon content (Hewitt et al. 1992).

RESULTS

Core liners

A greater than 90% decrease in TCE concentration resulted in less than 40 minutes for the samples collected and stored in core liners, when compared to the mean of the four reference samples obtained around the liners' exterior (Table 1). In addition, the rate of TCE loss during the first 30 minutes was greater than the subsequent 30 minutes of exposure (Fig. 4). Therefore it is reasonable to assume that these samples, which had been removed from the middle of the core liners

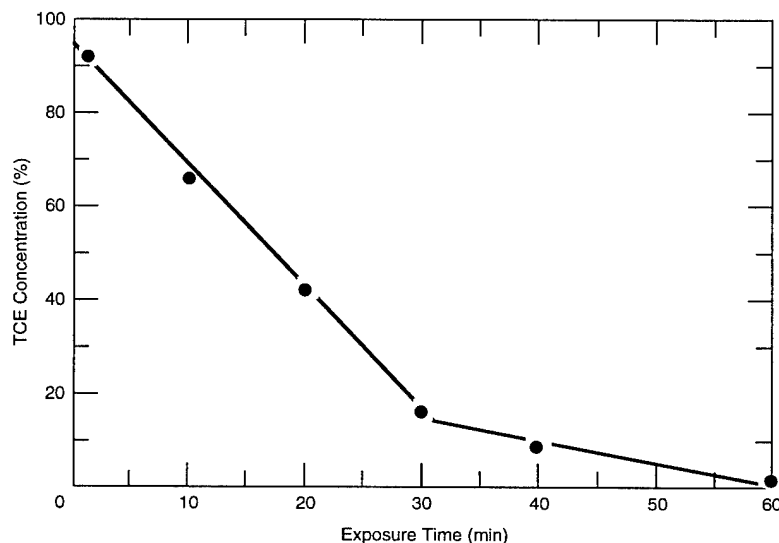


Figure 4. Concentrations of TCE established exterior to and within uncovered core liners.

Table 1. Concentration ($\mu\text{g/g}$) of TCE determined for soil samples collected around and within core liners.

Core liner/exposure period (min.)	Within core liner	Reference soil samples from around the core liner	
		Mean	Standard Deviation
I/60	0.27	9.7 \pm 1.0*	(1,2,5,6) [†]
II/40	0.99	11 \pm 0.7	(2,3,6,7)
III/30	2.1	12 \pm 1.0	(3,4,7,8)
IV/20	4.7	11 \pm 0.5	(5,6,8,10)
V/10	6.5	10 \pm 0.9	(6,7,10,11)
VI/1	11	12 \pm 1.0	(7,8,11,12)

* Mean and standard deviation, $n = 4$

[†] Sample positions exterior to core liner (Fig. 1)

(1.2 cm below/above the exposed surfaces), had experienced large volatilization losses, due to gaseous diffusion. The observed faster rate of desorption has been attributed to processes occurring at the mineral surfaces (macropores), whereas the slower rate may result from diffusion from intra-aggregate micropores (Sawhney and Gent 1990, Pavlostathis and Mathavan 1992).

Core liners are devices designed to prevent VOC volatilization losses from intact soil samples so that the soil can be shipped from the field to an off-site laboratory prior to sampling for analysis. During transportation and storage this device is covered with either sheets of TFE or aluminum foil (ASTM, D 4547-91). Ideally, when using core liners, sample exposure would be limited to two short periods: when the sample is first retrieved and covered, and when it is opened in the laboratory to prepare a sample for analysis. For this approach to be useful, VOC concentrations must be maintained for at least several days to allow time for samples to be shipped to the analytical laboratory.

Table 2 shows results of field samples stored in core liners and covered with either TFE or aluminum foil. As in Table 1, samples taken from core liners immediately after they were removed from the hole showed TCE concentration estimates comparable to the means obtained for adjacent samples. However, regardless of the covering or how the samples were collected, after five or more days of storage at 4°C, the TCE concentration esti-

Table 2. Concentration ($\mu\text{g/g}$) of TCE determined for soil samples collected around and within core liners. Core liners covered with either TFE sheets or aluminum foil were stored at 4°C.

Core liner no. covering	Storage period**			Reference soil samples from around the core liner
	Day 0	Day 5	Day 10	
Second experiment				
I/None	2.9			3.2 \pm 0.4 [†] (1,2,5,6)
II/Aluminum		0.15		3.4 \pm 0.7 (2,3,6,7)
III/TFE		0.18		3.6 \pm 0.5 (3,4,7,8)
IV/TFE			0.049	3.4 \pm 0.8 (5,6,8,10)
V/Aluminum			0.16	3.3 \pm 0.6 (6,7,10,11)
VI/None	2.5			3.5 \pm 0.4 (7,8,11,12)
Third experiment				
I/None	0.63			0.79 \pm 0.17 (1,2,5,6)
II/Aluminum		0.018		0.70 \pm 0.28 (2,3,6,7)
III/TFE		0.018		2.4 \pm 2.5 (3,4,7,8)
IV/Aluminum			0.017	0.62 \pm 0.25 (5,6,8,10)
V/TFE			0.006	0.70 \pm 0.33 (6,7,10,11)
VI/None	0.82			1.2 \pm 0.7 (7,8,11,12)
Fourth experiment				
I/None	0.86 \pm 0.01*			1.2 \pm 0.4 (1,2,5,6)
II/Aluminum		0.14 \pm 0.08		1.6 \pm 0.8 (2,3,6,7)
III/TFE		0.069 \pm 0.014		1.6 \pm 0.8 (3,4,7,8)
IV/TFE		0.059 \pm 0.016	0.86 \pm 0.18	(5,6,8,10)
V/Aluminum		0.072 \pm 0.001	1.4 \pm 0.9	(6,7,10,11)
VI/None	0.64 \pm 0.21		1.4 \pm 0.9	(7,8,11,12)

* Mean and standard deviation, $n = 3$

[†] Mean and standard deviation, $n = 4$

** Samples taken from within core liner.

mates were consistently lower than the mean of the adjacent samples by more than 90%. In addition, all of the samples covered with aluminum foil and wrapped with PVC tape showed concentrations of Tol ranging from 0.1 to 0.3 $\mu\text{g/g}$ after five days of storage. Since Tol was not observed in any of the other field samples collected for this study, its source was most likely the adhesive used in the PVC tape. This assumption was confirmed by the analysis of this material.

The results of the laboratory experiments performed with modified core liners are shown in Table 3. These samples differed from those obtained in the field by being laboratory fortified, held in a brass cup (smaller exposed surface/mass ratio), and using two layers of TFE for the samples

covered with this material. Two trends established by these experiments were 1) analyte concentration stability was markedly better for the desiccated condition and 2) aluminum foil was superior to TFE as a barrier for the prevention of volatilization losses. The first trend can be explained by a dry mineral surface's greater affinity for the sorption of VOCs (Chiou and Shoup 1985, Smith et al. 1990). This is a condition under which physical processes, perhaps involving van de Waals forces, help retain the VOCs (Sawhney and Gent 1990). The stability of the analytes on the desiccated soil can, therefore, be attributed to the condition of grain surfaces prior to treatment. The second trend can be explained by the observation that sheets of pliable TFE, used for covering ends of

Table 3. Analyte concentrations ($\mu\text{g/g}$) in modified core liners laboratory experiments, before and after covering with TFE sheets or aluminum foil and storing at 4°C.

Condition/covering/ analyte	Storage period					
	Day 0	Day 1	Day 2	Day 3	Day 7	Day 14
Desiccated/TFE/						
TDCE	3.1/3.1	1.9	1.5	1.3	0.56	ND*
Ben	4.4/4.3	4.4	4.2	4.3	4.0	2.9
TCE	7.1/7.0	7.3	6.3	6.3	5.3	2.4
Tol	6.7/6.6	7.0	6.8	7.0	6.4	6.1
Desiccated/aluminum/						
TDCE	3.1/3.1	3.0	0.92	0.97	2.2	1.5
Ben	4.4/4.3	4.4	4.2	4.3	4.3	4.4
TCE	7.1/7.0	7.3	6.2	6.8	6.9	6.4
Tol	6.7/6.6	7.0	6.9	7.0	6.8	7.1
10% Moisture/TFE/						
TDCE	1.8/1.8	0.074	0.028 [†]	0.010	ND	
Ben	7.9/8.1	0.45	0.20	0.10	0.040	
TCE	5.1/5.2	0.24	0.12	0.071	0.032	
Tol	7.2/7.2	0.31	0.26	0.13	0.056	
10% Moisture/aluminum/						
TDCE	1.8/1.8	0.41	0.21/0.21	0.24	0.053	
Ben	7.9/8.1	2.5	1.1/1.1	1.5	0.37	
TCE	5.1/5.2	1.1	0.35/0.36	0.65	0.14	
Tol	7.2/7.2	2.0	0.49/0.46	1.3	0.19	
1% Moisture/TFE/						
TDCE	3.0/3.1	0.064±0.02**				
Ben	4.5/4.3	0.17±0.5				
TCE	7.2/7.1	0.25±0.08				
Tol	6.7/6.7	0.39±0.08				
1% Moisture/aluminum/						
TDCE	3.0/3.1	0.50±0.11				
Ben	4.5/4.3	1.2±0.5				
TCE	7.2/7.1	1.4±0.3				
Tol	6.7/6.7	2.6±0.6				

* ND not detected

[†] Sample replicate lost

** Mean and standard deviation, $n = 5$; 1-day storage.

core liners, can be permeated by many gases. This phenomenon has been established for oxygen (Barbeau et al. 1995), and although not yet documented, has been demonstrated using a vapor fortification process (Hewitt and Grant 1995) to treat a soil with TDCE, Ben, TCE, Tol, ethyl benzene, and para- and ortho-xylene, held in glass ampoules covered with TFE.

A closer look at the results in both Tables 2 and 3 shows a fairly continuous decreasing trend in analyte concentration with time for the TFE covered samples, but a more sporadic trend for aluminum foil. An explanation for this discrepancy between the coverings: while TFE allows for uniform rate of loss by penetration through the entire covered end of the core liner, vaporization losses occur only around the rim when aluminum foil is used. The tightness of the seal between these two metal surfaces was variable from sample to sample, resulting in variable rates of loss for individual samples.

The most important finding of these two experiments (Table 2 and 3) is that VOC volatilization losses are not prevented by covering the open ends of core liners with either of these two materials. The rate of VOC losses from intact soils held in a core liner thus would be more dependent on the rate of analyte diffusion in a given matrix. Therefore, grain size, soil type, moisture content, organic carbon content, transportation conditions, etc., would all be variables. Based on the experiments performed, unsaturated soils with low organic carbon and clay contents would be suspect after very short periods of storage, perhaps even less than a single day. In contrast to the poor performance of TFE sheets of <0.02 mm thickness, the formulation and ≥ 0.13 mm thickness of the material used to seal VOA vials serves as an adequate barrier for the prevention of VOC volatilization losses over a period of a couple of weeks (Hewitt 1995c). Indeed, solutions of several VOCs (TDCE, TCE, perchloroethylene, Ben, Tol, ethylbenzene, and para- and ortho-xylene) showed only a 5% to 15% reduction in concentrations when held in Teflon-lined gray butyl rubber-capped VOA vials for 28 days under similar conditions as the covered core liners.

Extruded samples

Table 4 presents TCE concentration variations for samples collected with different size plastic

Table 4. Extruded samples.

a. Comparison of samples collected with 3- and 10-cm³ syringes and transferred directly to VOA vials.

3-cm ³ syringe ($\mu\text{g TCE/g}$)	10-cm ³ syringe ($\mu\text{g TCE/g}$)
3.4 \pm 0.4*	4.0 \pm 0.4

* Average and standard deviation, $n = 5$

b. Comparison of samples collected with either 3- or 10-cm³ syringes, half of the samples being extruded directly into VOA vials, the other half extruded into a plastic bag, stored for 1- to 2-minute period and then transferred to a VOA vial.

3-cm ³ syringe		10-cm ³ syringe	
VOA vial ($\mu\text{g TCE/g}$)	plastic bag ($\mu\text{g TCE/g}$)	VOA vial ($\mu\text{g TCE/g}$)	Plastic bag ($\mu\text{g TCE/g}$)
1.6 \pm 0.4†	0.14 \pm 0.09	3.1 \pm 0.6	0.72 \pm 0.16

† Average and standard deviation, $n = 4$

syringes and as a function of whether samples were extruded directly into a vial or were temporarily stored in a plastic bag. The two samplers used in these experiments were 10- and 3-cm³ plastic syringes with 1.4- and 0.8-cm i.d., respectively. A statistical comparison of the mean TCE concentrations estimates for these samplers, when transferred immediately to VOA vials containing water, found a small but significant difference at the 95% confidence level. On the average the samples collected with the 3-cm³ syringe were 15% lower in estimated TCE concentration.

The second experiment looked at the effect of extruding an intact soil core into a plastic bag for temporary storage. When samples passed through this additional step were compared to samples transferred directly to prepared VOA vials, those extruded from a 3-cm³ syringe showed a loss of greater than 90% in TCE concentration, while those transferred with the 10-cm³ syringe showed a loss of 77%. Both of these experiments suggest that sample size (i.e., surface area to mass ratio) is an important variable, and that large volatilization losses are likely when an extruded soil sample is exposed for less than 2 minutes, even if placed inside a plastic bag. Based on these findings both the diameter of the soil collection device (i.e., Geoprobe, Veihmeyer tube, etc.), and the method by which an extruded sample is transferred to a prepared vial can significantly influence the VOC concentrations present.

Collection vessel experiment

From the data in the last table (Table 5) we can assess the effect of adding a soil sample to a VOA vial containing water vs. adding soil to an empty vial and then adding water. These experiments used composited samples to minimize effects of spatial variability. The results of these experiments show that even if the water is added immediately after the soil sample, measurable TCE was lost. When the period between addition of soil and water was increased, and temporary covers were used, greater than 60% loss of TCE resulted. Similar findings have also been reported for laboratory experiments comparing treated and field-contaminated soils transferred to vials with and without solvent (Jenkins and Schumacher 1987, Hewitt et al. 1995). Therefore, vials into which soils are transferred for in-vial handling and analysis methods cannot have their hermetic seals broken to introduce a solvent, or for any other reason, without significant VOC loss. An exception to this statement is when the soil sample is immersed into a solvent in which the VOCs are highly soluble (i.e., methanol, etc.), then the VOA vial can be repeatedly opened and aliquots withdrawn without significant VOC losses (Hewitt 1995b).

The results in Table 5 also show that the amount of TCE lost did not appear to change when the addition of water was varied between 2 to 200 minutes. One explanation for this is that the TCE in the soil plugs rapidly achieved an equilibrium condition with the air inside the vial. Therefore, when the water was introduced, TCE was lost due to displacement (10 mL of water/10 cm³ of air) and other air exchange processes. The rapid attainment of equilibration for these soil plugs (3.6 cm²/g, surface area to mass ratio) agrees with the previous experiment, showing that 90% of the TCE was lost in less than 2 minutes when similar plugs of soil were temporarily stored in plastic bags.

DISCUSSION

Once in-vial methods are used for site investigations, samples with VOC concentration more representative of their environment will be handled and analyzed by off-site laboratories. Reducing volatilization losses by using in-vial methods, samples that better represent the site conditions will often equate to higher concentrations. Therefore, laboratories will have to be better informed of the site conditions and the sampling and analysis plan. The reason for increased awareness

Table 5. Comparison of pairs of composited samples added to VOA vials with and without solvent present.

<i>Time (min.) lapse before addition of water/temporary cap/depth (cm) of samples collected</i>	<i>Immersed (µg TCE/g)</i>	<i>Solvent added (µg TCE/g)</i>
0.1/None/45	1.7/1.6	1.3/1.1
2/Parafilm/38	1.7/1.6	0.50/0.50
20/VOA septum/40	1.7/1.5	0.53/0.69
200/VOA septum/43	1.9/2.1	0.60/0.59

Note: Four samples collected at a depth of 35 cm with a 5-cm³ syringe established mean and standard deviation of 2.0±0.4 µg TCE/g.

is to avoid the potential problem that could occur when samples that require purge and trap gas chromatography mass spectrometry (PT/GC/MS) analysis have concentrations of 1 ppm or greater, as that would damage the detection system. Samples with these high VOC concentrations will become a common occurrence on those sites where VOCs can be easily detected (smelled) by field personnel. To address this issue, Methods 5021 and 5035 recommend that two or more colocated samples be collected, thus allowing for a screening analysis to be performed prior to PT/GC/MS. One logical solution would be to always collect one colocated sample for equilibrium HS analysis (Hewitt et al. 1995). The concentrations established by HS would inform the analyst how to prepare a colocated sample, or which colocated sample should be then taken for PT/GC/MS analysis. However, as pointed out earlier, the sample is likely to be compromised with regard to VOC concentration, unless a nondisruptive and limited exposure transfer is made to a VOA vial that is either prepared for in-vial handling and analysis or that contains an appropriate solvent.

If PT/GC/MS analysis is required, VOC concentrations exceed 1 ppm, and an organic solvent such as methanol cannot be used on-site. At present there is no effective way of storing an intact soil sample so that it can be placed in a solvent off-site, without allowing for uncontrolled volatilization losses. Collection of samples in core liners that are then covered with either sheets of TFE or aluminum foil fail to maintain a VOC concentration representative of the field condition, as would VOA vials requiring their hermetic seal be broken so as to introduce a solvent after sample collection.

However, a device is under development that shows promise for allowing colocated samples to

be held for a couple of days without altering the VOC concentration present (Turriff et al. 1995). This sampling tool maintains the soil structure during collection, storage and transfer as would a plastic syringe; however, it is made out of either stainless steel and proprietary composite material, and uses Viton O-rings for hermetic seals. These materials are believed to rival that of the currently accepted VOA vial with regard to inertness and preventing volatilization losses. In its current design, once an undisturbed soil core has been obtained by pushing the core barrel into an exposed surface and removing it, a gas tight cap is used to seal the opening. After estimating the concentration of VOC present for a colocated sample, the soil can then be extruded after moving the cap from this temporary holding chamber, and transferred directly into an appropriately prepared VOA vial.

Another topic that this study addressed was sample size. Subsurface sample collection is both a very costly and time-consuming activity. Efforts to minimize the impact of these two factors has led to use of smaller and more rapid sampling systems. The results of this study show that as the surface area/mass ratio increases for intact soil cores, time of exposure needs to decrease in order to maintain VOC concentrations representative of the in-situ conditions. When samples are retrieved from intact core liners or from recently excavated pits, samples should be collected and transferred within a few minutes. However, if subsurface soils are retrieved in the barrel of a device with a diameter of less than 1.5 cm, and the soil has to be extruded prior to subsampling, the subsequent collection and transfer most likely cannot be performed without substantial volatilization losses. In general, as the diameter and cohesiveness of the matrix decreases and vapor pressure of the analyte increases, the ability to obtain samples that are representative of the in-situ conditions diminishes. Furthermore, with time playing such a critical variable for small diameter extruded soil cores, it becomes unlikely that even sequentially collected colocated samples, would be representative of one another.

CONCLUSIONS

Soil samples retained in core liners covered with either sheets of TFE-fluorocarbon or aluminum foil are subject to volatilization losses. Uncontrollable volatilization losses occur within seconds of ex-

posure for samples with a large surface/mass ratio. Thus, soils obtained in small diameter coring devices should be extruded directly into appropriately prepared analysis vials. Sample vials that do not contain an organic solvent before soil sample collection cannot have their hermetic seals broken without incurring volatilization losses. To maintain site-representative VOC concentrations in soil samples, any collections and transfers for in-vial analysis must occur rapidly with limited structure disruption and exposure.

LITERATURE CITED

- Barbeau, D.S., T.G. Ellis and C.P.L. Grady Jr.** (1995) Oxygen leakage during respirometric measurement: A caution on the use of PTFE tape. *Water Research*, **29**(4): 1211-1212.
- Chiou, C.T. and T.D. Shoup** (1985) Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. *Environmental Science and Technology*, **19**: 1196-1200.
- 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, National Water Well Association, September, Stamford, Connecticut*, p. 223-248.
- Hewitt, A.D.** (1995a) Determining volatile organic compound concentration stability in soil. In *Proceedings of 11th annual Waste Testing and Quality Assurance Symposium, 23-28 July, Washington, D.C., 1995*.
- Hewitt, A.D.** (1995b) Preservation of volatile organic compounds in soil subsamples. *American Environmental Laboratory*, 16-18 August.
- Hewitt, A.D.** (1995c) Enhanced preservation of volatile organic compounds in soil with sodium bisulfate. *USA Cold Regions Research and Engineering Laboratory, Special Report 95-26*.
- Hewitt, A.D. and C.L. Grant** (1995) Round-robin study of performance evaluation soils vapor-fortified with volatile organic compounds. *Environmental Science and Technology*, **29**: 769-774.
- 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*, January-February.
- Hewitt, A.D., P.H. Miyares and R.S. Sletten** (1993) Determination of two chlorinated volatile organic compounds in soil by headspace gas chromatography and purge-and-trap gas chromatography

- mass spectrometry. *Hydrocarbon Contaminated Soils*, 3: 135-145. Chelsea, Michigan: Lewis Publishers.
- 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: 1932-8.
- Illias, A.M. and C. Jaeger** (1993) Evaluation of sampling techniques for the analysis of volatile and total recoverable petroleum hydrocarbons (TRPH) by IR, GC, and GC/MS methods. *Hydrocarbon Contaminated Soils*, 3: 147-165. Chelsea, Michigan: Lewis Publishers.
- Jenkins, T.F. and P.W. Schumacher** (1987) Comparison of methanol and tetraglyme as extraction solvents for the determination of volatile organics in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 87-22.
- Lewis, T.E., A.B. Crockett, R.L. Siegrist and K. Zarrabi** (1994) Soil sampling and analysis for volatile organic compounds. *Environmental Monitoring and Assessment*, 30: 213-246.
- Pavlostathis, S.G. and G.N. Mathavan** (1992) Desorptive behavior of trichloroethylene in contaminated soil. *Environmental Science and Technology*, 26: 532-79.
- Sawhney, B.L. and M.P.N. Gent** (1990) Hydrophobicity of clay surfaces: Sorption of 1,2-dibromoethane and trichloroethylene. *Clays and Minerals*, 38: 14-20.
- Siegrist, R.L. and P.D. Jenssen** (1990) Evaluation of sampling method effects on volatile organic compounds measurements in contaminated soils. *Environmental Science and Technology*, 24: 1387-1392.
- Smith, J.A., C.T. Chiou, J.A. Kammer and D.E. Kile** (1990) Effects of soil moisture on the sorption of trichloroethylene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. *Environmental Science and Technology*, 24: 676-683.
- Turriff, D., C. Reitmeyer, L. Jacobs and N. Melberg** (1995) Comparison of alternatives for sampling and storage of VOCs in soil. In *Proceedings of 11th Annual Waste Testing and Quality Assurance Symposium*, 23-28 July, 1995, Washington, D.C., p. 51-58.
- U.S. Environmental Protection Agency** (1986) Test methods for evaluating solid waste. Vol. 1B. SW-846.
- 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*, U.S. Environmental Protection Agency, Washington, D.C., p. II-87-II-101.
- Voice, T.C. and B. Kolb** (1993) Static and dynamic headspace analysis of volatile organic compounds in soils. *Environmental Science and Technology*, 27: 709-713.

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