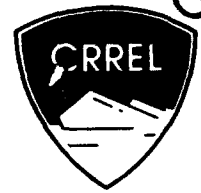


AD-A280 972



Losses of Trichloroethylene from Soil During Sample Collection, Storage and Laboratory Handling

Alan D. Hewitt

April 1994

**DTIC
ELECTE
JUL 01 1994
S B D**

DTIC QUALITY INSPECTED 2

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

94-20235



1388

94 7 1 038

Abstract

The losses of trichloroethylene (TCE) from soil samples transferred to and from a storage bottle were evaluated by comparing them to values obtained using a method that limits sample disruption and exposure and prevents vapor losses from a subsample after a single transfer step. The results strongly suggest that volatile organic compounds (VOCs) are readily lost from contaminated soils when care is not taken to limit surface area exposure and prevent vapor loss. For this site investigation and others using similar sample handling protocols, VOC losses are most abundant during field collection operations and storage. The magnitude of the VOC losses during these two steps far exceeds those anticipated when a subsample is transferred from these storage bottles prior to off-site laboratory analysis.

For conversion of SI metric units to U.S./British customary units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-89a, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

This report is printed on paper that contains a minimum of 50% recycled material.

Special Report 94-8



**US Army Corps
of Engineers**

**Cold Regions Research &
Engineering Laboratory**

Losses of Trichloroethylene from Soil During Sample Collection, Storage and Laboratory Handling

Alan D. Hewitt

April 1994

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
SFIM-AEC-TS-CR-94033

Approved for public release; distribution is unlimited.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

PREFACE

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

Funding for this work was provided by the U.S. Army Environmental Center, Martin Stutz, Project Monitor. The author thanks Dr. Thomas M. Spittler for providing the information concerning headspace gas chromatography and the method for collecting undisturbed soil subsamples, and Dr. Clarence L. Grant and Lawrence Perry for critical reviews of the text.

This publication reflects the views of the authors and does not suggest or reflect policy, practices, programs, or doctrine of the U.S. Army or the Government of the United States. The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

Losses of Trichloroethylene from Soil During Sample Collection, Storage and Laboratory Handling

ALAN D. HEWITT

INTRODUCTION

This site investigation was undertaken soon after high (ppm) levels of trichloroethylene (TCE) were found in industrial service wells located at the Cold Regions Research and Engineering Laboratory in Hanover, N.H. The main objective of the subsequent field studies was to identify point sources and the extent of subsurface contamination. Phase I of this site investigation was performed during the winter of 1991-92 and Phase II during the summer of 1993. Under the supervision of the U.S. Army Environmental Center (USAEC), numerous vadose-zone soil samples originating from the same drill core (co-located) were taken during Phase I and II field sampling exercises. Coupling research with site investigation activities authorized by government agencies (USAEC, the U.S. Environmental Protection Agency and the State of New Hampshire) has allowed us to study alternative sampling and analysis procedures. This report covers some of the findings for Phase II. Reports covering the research efforts associated with Phase I can be found elsewhere (Hewitt 1992, 1993; Hewitt et al. 1993; Hewitt, in press; Hewitt and Shoop, in prep.).

The Phase II work plan specified that 14 boreholes be drilled to depths of at least 15 m (50 ft). These vertical holes were drilled using conventional hollow-stem auguring, and subsurface soil samples were taken every 1.5 m (5 ft) from split spoons. Of the ten or more samples collected during the drilling of each borehole, only four were shipped off site for laboratory analysis. Many of the remaining soil sample storage bottles filled by the site investigator were available for on-site anal-

ysis. In addition to these subsamples a large quantity of co-located subsamples were collected using a limited disruption and exposure method. Samples collected by both of these methods were obtained simultaneously, immediately after a split spoon was opened.

The collection of soil samples by the site investigators followed the commonly accepted practice of filling a bottle to near capacity for shipping and storage. Protocols that require the soil to be handled twice and stored in a bottle with little headspace are suspect (Urban et al. 1989, Hewitt 1992).^{*} Often the utensils (i.e., spoons, paint scrapers, trowels, spatulas and wooden tongue depressors) used during the transfer of soil to and from the storage bottle fail to maintain the sample's structure. This process allows the soil to fracture and exposes a random amount of surface area, which facilitates the release of weakly sorbed and physically trapped volatile organic compounds (VOCs). In addition, filling a bottle to near capacity inevitably soils the sealing surfaces, making leaks possible. During Phase I of this site investigation this transfer to and from storage bottles was shown to cause TCE concentration losses that averaged 95% compared to concentrations found in co-located subsamples obtained by a limited disruption and exposure method (Hewitt 1992, in press). In our earlier study, subsampling variability (within a split spoon), holding time for samples held in vapor-tight vessels, instrumental calibration and method of analysis were ruled out as the principal reasons for this large discrepancy.

^{*} Also personal communication, T.M. Spittler, U.S. Environmental Protection Agency, 1989.

The intent of the Phase II study is to closely evaluate the losses of TCE that occur when following the site investigator's sample-handling protocols. This study specifically addressed the extent to which TCE is lost when the site investigators collect soil samples in the field, while the samples are stored and when subsamples are transferred and weighed in preparation for off-site laboratory analysis. This evaluation highlights the TCE concentration discrepancies that exist when samples collected by this currently accepted procedure are compared to values obtained by using a limited disruption and exposure method. The findings of this study apply to most hazardous waste site investigations that use the commonly accepted practice of transferring soil to and from a storage bottle prior to the determination of VOC concentrations.

SAMPLING METHODS

Borehole drilling

Conventional hollow-stem auguring and split-spoon (60- $\times$ 4.4-cm) coring was used to obtain subsurface soils to profile VOC and total petroleum hydrocarbon (TPH) concentrations. The Phase II work plan required that these boreholes be drilled to a depth of at least 15 m (50 ft), and beyond if VOCs were detected. Field screening for VOCs was performed by partially filling a glass bottle, covering it with aluminum foil, shaking it and then poking a hole in the cap and sampling the headspace with a handheld instrument (PhotoVac). When photoionizable compounds were detected in the bottle's headspace, the borehole was continued to a depth where either VOCs were not detected or the hole was within 3 m (10 ft) of the water table. Upon completion of a borehole, subsamples from only four of the ten or more split spoons sampled were selected for off-site laboratory analysis.

Sample collection

Upon the retrieval of a split spoon, the site investigators completely filled two identical 4-oz wide-mouth (3-cm-diameter) bottles equipped with Teflon-lined lids, one each for the analyses of VOCs and TPH. In addition to the wide-mouth, 4-oz bottles, two wide-mouth, 8-oz glass bottles were partially filled, one for geological characterization and the other for VOC screening. All bottles were labeled ahead of time, and the VOC sample bottle was filled first or simultaneously with the TPH bottle, depending on the number of site investigators.

The soil was transferred to these bottles using

either a stainless steel paint scraper or a garden trowel. Neither of these utensils fit inside the mouth of the storage bottles, so the site investigators often had to push the soil into the container using their fingers, which were covered with plastic gloves. During the process of cutting into the soil core and transferring the sample, the native soil structure easily fractured into randomly sized aggregates, and the storage bottle's neck and brim became soiled. After filling the storage bottle, the investigators tried to wipe the closure surfaces clean with either a gloved hand or paper towel. With this collection method a storage bottle was usually filled and capped in less than 30 seconds. Once split-spoon subsampling was completed, the two soil-filled 4-oz bottles were placed in a cooler with ice until the borehole was completed and a decision was made regarding which samples would be sent for off-site laboratory analysis.

Limited disruptive and exposure sampling method

Obtaining subsamples using a single, less-disruptive soil subsample transfer and immediate on-site isolation from vapor losses is known as the limited disruption and exposure (LDE) method. A 10-cm³ tipless plastic syringe (1.6-cm o.d.) was used to transfer the material with minimal structure disaggregation and exposure (Lewis et al. 1991, Hewitt 1992).^{*} This device removes an intact plug of soil from a freshly exposed surface and fits into the mouth (1.8-cm i.d.) of a 40-mL volatile organic compound analysis (VOA) bottle. Before the syringe is pushed into the split-spoon soil core, the plunger is set, allowing the cylindrical barrel to be filled with 2-3 cm³ of material. After a subsample is extracted from the split spoon core, the external surface of the syringe is wiped with a clean paper towel, then the plug of soil is dispensed into a VOA vial by depressing the plunger. Frequently the plugs of soil remained intact during this transfer operation. To isolate the subsamples upon collection, this study used preweighed VOA vials equipped with Teflon-lined silicone septum caps and containing 30 mL of Type 1 water (Milli Q, Millipore Corp.). These bottles were then reweighed to obtain the actual soil sample weight. Subsamples prepared in this fashion were ready for headspace gas chromatography (HS/GC) analysis. Subsample collection was coincident with the site investigators' subsample collection and took about 5 seconds to perform.

^{*} Also personal communication, T.M. Spittler, U.S. Environmental Protection Agency, 1989.

EXPERIMENTAL DESIGN

Several different evaluations were performed to assess the extent of TCE losses that could be attributed to each of the three main handling steps (field collection, storage and laboratory subsample transfer) that transpire before soil subsample analysis by an off-site laboratory. All evaluations used the sample storage bottles that had been filled by the site investigators. When these samples were compared to co-located samples collected by the LDE method, subsamples removed from the storage bottles were visually classified as wet, clumped or fractured, and the storage period was recorded. The subsamples were classified as wet if there was standing water, as clumped if there were large soil aggregates (>1 cm) or as fractured if there were no soil aggregates (the sample conformed to container's internal volume).

The first evaluation compared the TCE concentrations in subsamples removed from the storage bottles to those of co-located subsamples collected with the LDE method. Single subsamples were removed from the site investigators' storage bottles that were classified as clumped or fractured. Three subsamples were periodically removed over an 11-day period from those classified as wet. The transfer of subsamples from these bottles was performed using a tipless 10-cm³ syringe and the same procedure used in the field for the LDE method. This comparison assumes that the concentration of TCE in a split spoon when it was first opened was fairly homogeneous. During Phase I, multiple subsamples were taken from several split spoons to establish the variability for this site. These subsamples collected with the LDE method showed TCE variations of less than a factor of three (Hewitt 1992, in press).

In another evaluation, six randomly chosen storage bottles were emptied of their soil contents. Three were completely washed, removing all visible soil from the bottle and cap, while the others were only partially washed, removing only the soil from the bottle's interior surface. These bottles, which each have a total capacity of 135 mL, were then filled with 125 mL of water, then spiked with a 1.00-mL solution containing four VOCs (trans-1,2-dichloroethylene, trichloroethylene, benzene and toluene) and tightly capped. After five days of storage at 4°C, the bottles were opened one at a time and a 5.00-mL aliquot was transferred to a VOA vial containing 25 mL of Type 1 water for HS/GC analysis. These first three experiments were performed to assess the extent of TCE reduction caused by the collection procedure and the subsequent storage conditions.

To assess the extent of VOC losses that might occur when subsamples are removed for laboratory analysis, ten subsamples were removed from two storage bottles containing clumped soils. The bottle for borehole B at 15–17 feet was subsampled three days after collection, and the bottle for borehole G at 45–47 feet was subsampled seven days after collection. Subsamples were removed in an alternating sequence, five using a tipless 10-cm³ syringe and five using a stainless steel spatula. Those transferred with the syringe were immediately placed into a VOA vial containing 30 mL of water and sealed; subsamples transferred with a spatula were placed into an empty VOA vial and weighed, and then 30 mL of water was added. The subsamples transferred with a spatula were exposed for three minutes to simulate the time it would take to transfer soil subsamples to a tared vessel, weigh it and then take it to an instrument for purge-and-trap analysis.

ANALYSIS

All of the soil subsamples weighed between 2 and 4 grams, and TCE concentrations were obtained by aqueous extraction HS/GC analysis (Kaing and Grob 1986, Hewitt et al. 1991). Prior to removing headspace samples with a gas-tight syringe (Hamilton), the VOA vials were vigorously hand shaken for two minutes, allowing them to reach equilibrium. Refrigerated samples were allowed to warm to room temperature prior to agitation and analysis. This method of analysis provides results that are often in good agreement with purge-and-trap gas chromatography mass spectrometry (PT/GC/MS) for the analysis of VOCs in low-organic-carbon soils (Hewitt et al. 1992).

RESULTS

Table 1 contains the results for samples collected with the LDE method during Phase II having TCE concentration estimates above 0.003 µg/g and for the respective co-located samples collected by the site investigators. The corresponding log-log plot of these co-located sample values (Fig. 1) includes the axis of theoretical agreement (solid line) and order-of-magnitude intervals about this axis (dashed lines).

Figure 1 clearly shows that the samples collected with the LDE method were consistently higher in TCE. In comparison, nearly half (25 out of 60, or 42%) of the subsamples removed from the storage bottles were below detection (0.003 µg TCE/g),

Table 1. Trichloroethylene concentrations for co-located subsamples collected by the site investigators and stored between 1 and 6 days compared to concentrations established with the LDE method.

Borehole	Depth (ft)	LDE* (µg TCE/g)	DT&SB† (µg TCE/g)	Holding time (days)	Soil type	DT&SB × 100% LDE
A	29-31	0.17	0.14	1	wet	82
A	44-46	0.015	0.0092	1	wet	61
B	10-12	5.3	0.075	1	fractured	14
B	45-47	3.0	0.019	1	fractured	0.63
C	15-17	2.5	0.24	2	clumped	9.6
C	30-32	3.8	0.20	2	clumped	5.3
C	40-42	2.4	0.87	2	clumped	36
C	50-52	2.1	0.064	2	clumped	3.0
C	55-57	1.4	0.58	2	clumped	41
D	15-17	0.95	0.75	2	clumped	79
D	30-32	8.7	0.092	2	clumped	1.1
D	37-39	10	4.9	2	clumped	49
D	45-47	2.7	0.25	2	clumped	9.3
D	50-52	1.0	0.13	2	clumped	13
E	9-11	0.41	0.017	3	clumped	4.1
E	19-21	2.0	0.057	3	fractured	2.8
E	24-26	1.7	0.633	3	wet	37
E	39-41	11	0.015	3	fractured	0.14
E	49-51	1.2	<0.003	3	fractured	—
E	59-61	0.15	<0.003	3	fractured	—
E	64-66	3.4	<0.003	3	fractured	—
E	69-71	0.37	<0.003	3	fractured	—
E	74-76	0.22	<0.003	3	fractured	—
E	79-81	0.63	<0.003	3	fractured	—
E	104-106	1.0	0.014	3	fractured	1.4
E	114-116	0.62	<0.003	3	fractured	—
F	15-17	1.2	0.015	3	clumped	1.2
F	25-27	8.9	0.093	3	clumped	1.0
F	35-37	4.3	0.14	3	clumped	3.3
F	40-42	2.1	0.088	3	clumped	4.2
F	45-47	1.7	0.051	3	clumped	3.0
G	15-17	2.1	0.011	4	fractured	0.52
G	20-22	38	0.21	4	fractured	0.55
G	25-27	26	0.77	4	clumped	3.0
G	30-32	75	0.85	4	clumped	1.1
G	35-37	130	4.1	4	clumped	3.2
G	45-47	31	5.9	4	clumped	19
G	50-52	17	0.031	4	fractured	0.18
G	55-57	7.3	1.8	4	fractured	25
G	65-67	0.89	0.024	4	fractured	2.7
G	70-72	4.8	0.027	4	fractured	0.56
H	5-7	1.6	<0.003	5	clumped	—
H	40-42	2.0	<0.003	5	fractured	—
H	50-52	2.5	<0.003	5	fractured	—
H	55-57	5.0	0.019	5	fractured	0.38
H	60-62	0.25	<0.003	5	fractured	—
H	65-67	0.41	<0.003	5	fractured	—
I	10-12	0.041	<0.003	6	fractured	—
I	15-17	0.097	<0.003	6	fractured	—
I	30-32	0.33	<0.003	6	fractured	—
I	35-37	0.32	<0.003	6	fractured	—
I	40-42	0.40	<0.003	6	fractured	—
I	50-52	0.41	<0.003	6	fractured	—
I	55-57	0.069	<0.003	6	fractured	—
I	60-62	0.10	<0.003	6	fractured	—
I	70-72	0.31	<0.003	6	fractured	—
I	80-82	0.29	<0.003	6	fractured	—
I	90-92	0.35	<0.003	6	fractured	—
I	100-102	0.22	<0.003	6	fractured	—
I	110-112	0.30	<0.003	6	fractured	—

* LDE—Limited disruption and exposure method.

† DT&SB—Double transfer and storage bottle method

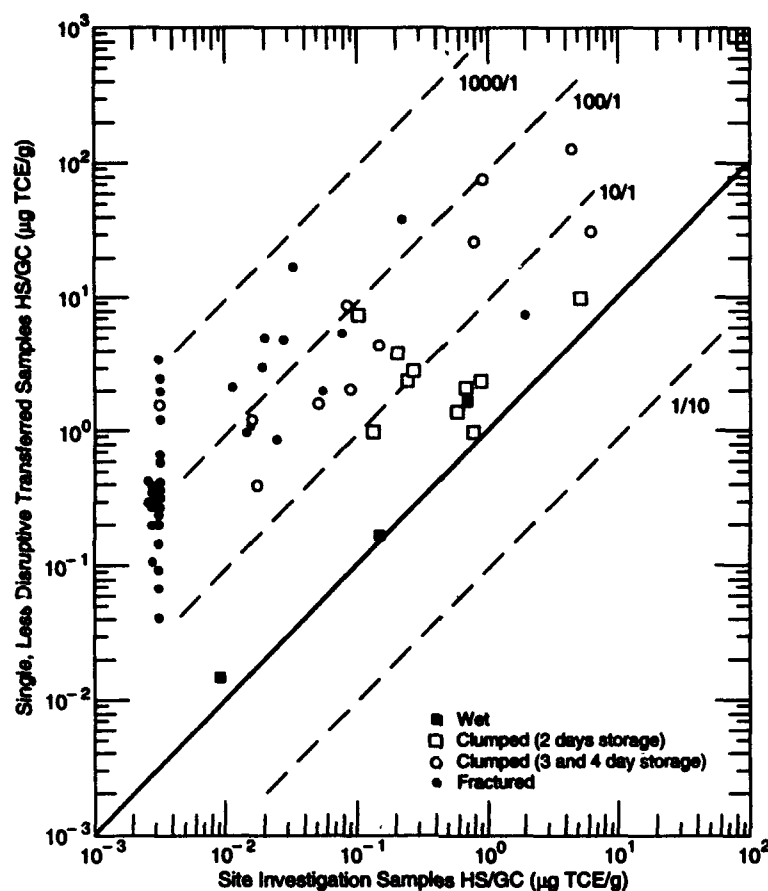


Figure 1. TCE concentrations in co-located samples collected during Phase II using two methods: the LDE method and the procedure used by the site investigators.

while the remainder ranged from 82% to 0.18% of the amount found for the co-located LDE samples. This random pattern and range of discrepancy is consistent with the sample collection and handling comparison performed during Phase I of this site investigation (Fig. 2) (Hewitt 1992, in press). The only difference between these two comparisons is that the results in Figure 2 are from two separate laboratories. The similarity between these plots supports the premise that the disparities are attributable to differences in the sample collection and handling and not in the laboratory analysis.

The visual classification (wet, clumped or fractured) given to the physical state of the soils in the storage bottle appears to explain some of the randomness present when comparing these two collection and handling methods (Fig. 1). Co-located subsamples described as wet were between the 1/1 to 10/1 concentration bands, showing a mean recovery percentage of 60%. Likewise, clumped soils were between 1/1 to 100/1, with a mean recovery of 14%, and the majority (10 of 11) of fractured soils

were between 10/1 to 1000/1, with a mean recovery of 4.3%. A nonparametric analysis using the Wilcoxon-Mann-Whitney test found that these three groupings were different at the 95% confidence level. This finding suggests that the TCE concentrations in the site investigator samples were inversely related to the extent that the soil structure broke apart. In soils with a texture that easily disaggregated and conformed to fill the vessel void, an average of 96% of the TCE was liberated from the matrix. Those soil samples that were more cohesive and remained as clumps (>1 cm diameter) in the storage bottle, or were water saturated, exposed less surface area and showed average TCE losses of 86% and 40%, respectively. The ease with which a soil breaks into small aggregates is a function of texture, grain size, moisture and organic content. Thus, it was not surprising that those storage bottles characterized as fractured typically contained sandy soils, while those classified as clumped contained silts.

This data set also can be used to look for a poten-

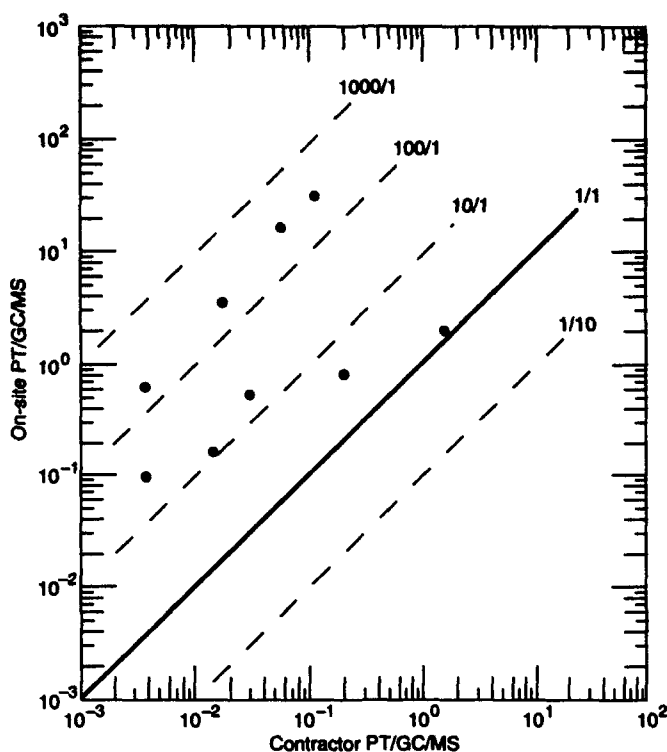


Figure 2. TCE concentrations in co-located samples collected during Phase I using two methods: the LDE method with on-site analysis and the procedure used by the site investigators with analysis in a contract laboratory.

tial storage effect on the TCE concentrations determined for the site investigator samples. This comparison was only made for storage bottles with clumped soils since the losses from most (24 of 36, or 67%) of the fractured soils extended below the level of detection, and there were only three samples classified as wet. The sample bottles subsampled two days after collection and the sample bottles subsampled three or four days after collection also appear to create two distinct populations (Fig. 1). The majority (7 of 10) of clumped soil subsamples analyzed after being held for two days were between the 1/1 and 10/1 bands, while those subsampled after three or four days of storage showed the majority (9 of 11) to exist between the 10/1 and 100/1 bands. The means of the TCE values relative to co-located samples collected by LDE method for these two storage periods were, respectively, 27% and 4.3%. The Wilcoxon-Mann-Whitney test of these two groups also showed that they were different at the 95% confidence level. This finding shows that the amount of TCE lost from the site investigator samples was also a function of holding time.

Two additional tests were performed to confirm that VOC vapors can escape from the site investigators' sample storage bottles. Table 2 shows that TCE concentrations decreased when subsamples were removed periodically over the course of several days from storage bottles containing wet

Table 2. Periodic subsampling and analysis of wet samples collected by the site investigators.

Borehole	Depth (ft)	TCE concentration ($\mu\text{g/g}$) after various periods of storage				
		1	3	7	9	11 days
A	29-31	0.14	—	0.063	—	0.056
A	44-46	0.0092	—	0.0046	—	<0.003
E	24-26	—	0.63	0.35	—	0.28

Table 3. Clean vs. dirty closures on bottles used to store aqueous solutions containing trans-1,2-dichloroethylene, trichloroethylene, benzene and toluene.

	Concentration ($\mu\text{g/L}$)	
	Clean	Dirty
Trans-1,2-dichloroethylene (TDCE)	480 $\pm$ 50*	260 $\pm$ 22
Trichloroethylene (TCE)	560 $\pm$ 7	320 $\pm$ 20
Benzene	350 $\pm$ 32	200 $\pm$ 14
Toluene	630 $\pm$ 48	370 $\pm$ 17

* Average $\pm$ standard deviation.

soils. Table 3 shows that randomly selected storage bottles with unwashed closures failed to retain VOCs in solution as well as bottles with clean closures (95% confidence level, Student's *t*-test). Although the results in Table 2 were confounded by headspace VOC losses each time the storage bottle was opened, the combination of these tests along with the holding time trend seen for clumped soils

Table 4. Laboratory subsampling method comparison of site investigator samples.

	TCE concentration ($\mu\text{g/L}$)			
	<i>B</i> at 15–17 ft		<i>G</i> at 45–47 ft	
	Syringe	Spatula	Syringe	Spatula
1	0.042	0.015	0.27	0.15
2	0.020	0.021	0.24	0.15
3	0.034	0.026	0.34	0.14
4	0.025	0.023	0.51	0.17
5	0.038	0.024	0.56	0.27
	0.032*	0.022	0.38	0.18
	0.009†	0.004	0.14	0.054

* Average ($\mu\text{g/g}$).

† Standard deviation.

(Fig. 1) indicates that vapors were continuously escaping from the storage bottles filled by the site investigators.

The final test assessed the loss of TCE that occurs when the subsample is transferred with a spatula or similar device, and the sample handling and weighing does not occur in the same room as the analysis. Under these circumstances a three-minute exposure period is reasonable. The results in Table 4 show significant (95% confidence level, Students *t*-test) differences that approach a factor of 2 when this transfer procedure was compared to the LDE method.

DISCUSSION

Previously, laboratory studies established that sample disturbance can cause VOC losses up to 80%, relative to undisturbed controls (Siegrist and Jenssen 1990, Lewis et al. 1991) and that significant (95% confidence level) differences exist when comparing subsamples that were transferred from one vessel to others that were either empty or contained a solvent (Jenkins and Schumacher 1987). While in agreement with the findings of these earlier efforts, this study shows that much greater losses are likely to occur with environmental samples than seen for laboratory-prepared samples. One explanation for the greater losses is that environmental samples not only experience disruption and exposure but are also subjected to storage in vessels that are not vapor tight. Understandably, laboratory studies would tend to overlook this potential loss mechanism since collection protocols usually specify that the storage bottle threads be cleaned before capping. The problem, as was observed during both phases of this site investigation, is two-fold. First, "clean" is subjective, and

second, a much greater emphasis is placed on speed than on cleanliness. Moreover, under field conditions, once a glass surface becomes soiled, it is for all practical purposes impossible to return it to a grit-free condition by quickly wiping it with either a soiled (gloved) hand or towel.

A visual inspection of all of the site investigators' chemistry sample bottles made available for this comparison study found grains of soil on the bottles' threads and lip (brim) and ground into the Teflon lining of the cap. Although the storage bottles filled during Phase I were not visually inspected in this fashion, the sound of glass scoring could often be heard as the caps were tightened, giving a clear impression that a similar condition existed (Hewitt 1992).

Since all of the bottles had soiled closures, it is impossible to separate the losses solely attributable to the initial transfer of soil from losses caused when vapors escaped during storage. Based on the findings of this study it appears that the extent of VOC losses during field collection and sample storage are likely to depend on time and the state of the soil. Figure 1 shows that losses of VOCs during the initial transfer is related to the cohesiveness of the material and that the storage time is significant. Most likely, the losses that occurred during these two steps are comparable, each capable of reducing VOC concentrations by an order of magnitude or more, compared to a co-located sample collected by the LDE method. When subsamples are transferred for a second time after several days of storage, the VOC losses that are anticipated for common laboratory protocols appear to be relatively small (Table 4). Clearly the potential for losses at this point has been greatly diminished since little of the easily liberated VOCs remains. If, on the other hand, this was the first disruption and exposure the soil experiences, differences between this procedure and the LDE method would likely be greater. Thus, samples that have been shipped intact, inside of a core liner (ASTM 1991), should also be subsampled with an LDE method.

The initial disaggregation of soil structure and subsequent sample storage in bottles that fail to prevent vapor losses are the two greatest sources of indeterminate error that confound the determination of representative VOC concentrations in soils. Both of these sources of error are easily avoided when care is taken to maintain the soil structure and transfer the subsample to a vessel that isolates the VOCs from vapor losses during storage and analysis. Besides using VOA vials

prepared for HS/GC analysis, the LDE soil sample collection method described here can also be used in conjunction with bottles (VOA vials) equipped with special adapters (Associated Design & Manufacturing Co., Alexandria, Virginia) or containing methanol (Urban et al. 1989, ASTM 1991, Hewitt 1992). Both of these alternative methods of isolating subsamples are well suited for the Method 8240 PT/GC/MS outlined in SW-846 (U.S. Environmental Protection Agency 1986).

This analysis was done before the off-site laboratory distributed their results for VOC concentrations for the Phase II soil samples. A future comparison of these TCE values to those found for co-located subsamples collected with the LDE method should result in discrepancies similar to those shown in Figure 1 or worse. The discrepancies will likely be greater if the off-site laboratory stores the samples for more than six days, the maximum time shown in Table 1.

CONCLUSION

Investigations following the standard procedure of filling bottles for shipment and storage of soils from hazardous waste sites often underestimate the in-situ VOC concentrations by one or more orders of magnitude. The greatest losses of VOCs occur when soils become disaggregated for the first time and during storage in a bottle with soiled closures. Only sample-handling protocols that limit soil structure disruption, require a single transfer step and isolate the subsample from vapor losses during storage and analysis should be used when characterizing sites for VOC concentrations in the vadose zone.

LITERATURE CITED

- ASTM (1991) Standard practice for sampling waste and soils for volatile organics. ASTM Committee D-34, D4547-91.
- Hewitt, A.D. (1992) Review of current and potential future sampling practices for volatile organic compounds in soil. In *Proceedings, 16th Annual Army Environmental R&D Symposium, June, Williamsburg, Virginia*, p. 75-82.
- Hewitt, A.D. (1993) Comparison of site characterization for trichloroethylene by headspace gas chromatography and purge-and-trap gas chromatography mass spectrometry. In *Proceedings of the 1993 US EPA/A&WMA International Symposium, Field Screening Methods for Hazardous Waste and Toxic Chemicals, Las Vegas, Nevada*, p. 195-202.
- Hewitt, A.D. (in press) Comparison of sampling methods for trichloroethylene in vadose zone soils. *Journal of the Association of Analytical Chemists*.
- Hewitt, A.D. and S. Shoop (in prep.) Rapid assessment of trichloroethylene in ground water. *Ground Water Monitoring and Remediation*.
- Hewitt, A.D., P.H. Miyares, D.C. Leggett and T.F. Jenkins (1991) Comparison of headspace gas chromatography with EPA SW-846 method 8240 for determination of volatile organic compounds in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 91-4.
- Hewitt, A.D., P.H. Miyares, D.C. Leggett and T.F. Jenkins (1992) Comparison of analytical methods for determination of volatile organic compounds in soils. *Environmental Science and Technology*, 26: 1932-1938.
- Hewitt, A.D., P.H. Miyares and R.S. Sletten (1993) Determination of two chlorinated volatile organic compounds in soils by headspace gas chromatography and purge-and-trap gas chromatography mass spectrometry. In *Hydrocarbon Contaminated Soils*. Boca Raton, Florida: CRC Press, vol. III, p. 135-145.
- 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.
- Kaing, P.H. and R.L. Grob (1986) A headspace technique for the determination of volatile compounds in soil. *Journal of Environmental Science and Health*, 21: 71-100.
- Lewis, T.E., A.B. Crockett, R.L. Siegrist and K. Zarra-bi (1991) Soil sampling and analysis for volatile organic compounds. USA EPA, Washington, D.C., EPA/590/4-91/001, Technology Innovation Office, Office of Solid Waste and Emergency Response.
- Siegrist, R.L. and P.D. Jenssen (1990) Evaluation of sampling method effects on volatile organic compound measurements in contaminated soils. *Environmental Science and Technology*, 24: 1387-1392.
- 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 *Proceedings, 5th Annual Waste Testing & Quality Assurance Symposium*. U.S. Environmental Protection Agency, Washington, D.C., p. II-87 to II-101.
- U.S. Environmental Protection Agency (1986) Test Methods for Evaluating Solid Waste, vol. 1B.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestion for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 1994		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE Losses of Trichloroethylene from Soil During Sample Collection, Storage and Laboratory Handling				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 94-8	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Environmental Center Aberdeen, Maryland				10. SPONSORING/MONITORING AGENCY REPORT NUMBER SFIM-AEC-TS-CR-94033	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. Available from NTIS, Springfield, Virginia 22161.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The losses of trichloroethylene (TCE) from soil samples transferred to and from a storage bottle were evaluated by comparing them to values obtained using a method that limits sample disruption and exposure and prevents vapor losses from a subsample after a single transfer step. The results strongly suggest that volatile organic compounds (VOCs) are readily lost from contaminated soils when care is not taken to limit surface area exposure and prevent vapor loss. For this site investigation and others using similar sample handling protocols, VOC losses are most abundant during field collection operations and storage. The magnitude of the VOC losses during these two steps far exceeds those anticipated when a subsample is transferred from these storage bottles prior to off-site laboratory analysis.					
14. SUBJECT TERMS Sample collection Trichloroethylene Soil samples Volatile organic compounds				15. NUMBER OF PAGES 11	
				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		