SPECIAL REPORT 94-6

Concentration Stability of Four Volatile Organic Compounds in Soil Subsamples

Alan D. Hewitt

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Abstract

This study assesses the short-term (14- to 20-day) concentration stability of benzene, toluene, trans-1,2-dichloroethylene and trichloroethylene in soil matrices, in the absence of volatilization losses. Previously, holding time studies failed to eliminate volatilization as a variable, making them difficult to interpret. Here, vapor-fortified soil subsamples, sealed in glass ampoules for 16 days, experienced appreciable reductions in benzene, presumably attributable only to biodegradation. Treated soil subsamples, on the other hand, prepared without vapor losses for either aqueous extraction headspace or purge-and-trap analyses, showed appreciable reductions in toluene and lost all the benzene over a 14-day holding period at 4°C. These findings suggest that chemical preservatives are necessary to maintain volatile organic compound concentrations in soil when more than a couple of days pass between collection and analysis.

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380-89a, *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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US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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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 (formerly the U.S. Army Toxic and Hazardous Materials Agency), Martin H. Stutz, Project Monitor.

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INTRODUCTION

Soil samples collected for analyzing volatile organic compounds (VOCs) during hazardous waste site investigations are routinely shipped off-site for laboratory analysis. This makes holding time, in addition to collection and handling practices, an important variable affecting the analyte concentrations found. Currently, most site investigations use a soil sample collection and handling procedure that has been recommended by the U.S. Environmental Protection Agency (U.S. EPA 1986). This procedure specifies that soils be first transferred to a shipping and storage container, from which a subsample is removed in the laboratory for analysis. The utensils commonly used for these soil sample transfers all have flat surfaces that allow the soil structure to crumble. Sometimes these utensils are also wider than the opening (2- to 3.5-cm diameter) of the vessel into which the material is being placed. As a result, a considerable amount of soil surface area is exposed at each transfer and VOCs are lost. In addition, when a container is filled to capacity with soil, the vessel closure surfaces often become covered with grains of soil that prevent a vapor-tight seal.

Recently, these practices that require multiple transfers and fail to maintain the native soil structure have come under criticism when used for the analysis of VOCs because of the likelihood for volatilization losses* (Urban et al. 1989, Siegrist and Jenssen 1990, Lewis et al. 1991, Hewitt 1992, Hewitt, in press[1]). One approach to minimizing these losses has been to use a single-transfer method that isolates an appropriately sized soil subsample during field collection. Additionally, the single-transfer procedure needs to be done rapidly (in less than 10 seconds), with limited disaggregation of the native substrate and no soiling of the vessel's closure surfaces. One transfer utensil that has been used successfully with a variety of soil types is a small coring device prepared by removing the tapered end from a 10-cm^3 disposable syringe* (Hewitt 1992). This device removes intact plugs of soils from freshly exposed surfaces and fits inside the mouth of a 40-mL VOA analysis bottle, which can either contain a preservative–solvent such as methanol (MeOH) or be equipped with a suitable cap to prevent the loss of vapors prior to and during analysis.

This single-step, less disruptive transfer method has resulted in VOC concentrations that were often two orders of magnitude greater than those taken following the current EPA guidelines (Urban et al. 1989, Hewitt 1992). Using this method, Urban et al. (1989) isolated subsamples by transferring them to bottles containing MeOH, while Hewitt (1992) used it along with another method suitable for low-level (less than 1 µg of VOC/g) purge-and-trap gas chromatography mass spectrometry (PT–GC–MS) and for headspace gas chromatography (HS–GC) analyses.

Although these studies addressed several of the problems with sample collection and handling, the stability of VOC concentrations, when subsamples were not immersed in MeOH, was not evaluated. Studies addressing a 14-day holding time or attempting to establish new holding time limits all included a transfer step or exposed the soil subsample prior to analysis (Jackson et al. 1991, Maskarinec et al. 1992, King 1993). For these reasons and others,

*Personal communication with T.M. Spittler, U.S. Environmental Protection Agency, Environmental Services Division-Region 1, Lexington, Massachusetts, 1989.

the observed losses were confounded by volatilization and may not necessarily be representative of the VOC concentration stability in isolated subsamples. Those losses that were observed either were directly related to analyte vapor pressure or were independent of analyte chemistry (i.e., highly halogenated, recalcitrant compounds that are resistant to biological degradation were lost as quickly as were biodegradable hydrocarbons). Both of these trends suggest that volatilization was the dominant loss mechanism during the experiments.

This study was designed to specifically assess the question of the stability of VOC concentrations, in the absence of volatilization losses over short periods (14–20 days), in soil subsamples or in subsamples prepared for either aqueous extraction PT–GC–MS or HS–GC analyses. To avoid volatilization losses during the holding time experiments, spiked (vapor fortified) soil subsamples were sealed in glass ampoules or held in vessels with closures that either had to be pierced by a syringe needle or quickly attached to a purge-and-trap system for the removal of VOCs.

The soil subsamples used in this study were spiked using a vapor fortification method (Hewitt 1993a, Hewitt, in press[2]). This method of spiking soils with VOCs is precise, does not require the injection of a carrier solvent, and is analogous to how vadose zone soils become contaminated by VOC vapors. The experiments assess the concentration stability of benzene (Ben), toluene (Tol), trans-1,2-dichloroethylene (TDCE), and trichloroethylene (TCE) in two soil matrices. These analytes are among the most frequently identified VOCs found at hazardous waste sites (Plumb and Pitchford 1985, Zarrabi et al. 1991), and are representative of compounds that biodegrade under anaerobic and aerobic conditions.

EXPERIMENTAL

Soils

Two soils were used to assess analyte concentration stability over periods that ranged from 14 to 20 days: a reference matrix from the U.S. Army Environmental Center that is a composite of several soils from the Rocky Mountain Arsenal (RMA) in Denver, Colorado, and a site-specific material collected at CRREL. The CRREL soil was obtained between 5 and 15 cm below the surface in a location where the vadose zone has been exposed to TCE vapors for the past 20 years. The RMA soil has a sandy texture and organic carbon content of 0.053%, while the CRREL soil has a silty texture and a 0.34% organic carbon content.

Soil preparation, treatment and handling

The soils were processed by air-drying, sieving through a 30-mesh screen and thoroughly mixing. Doing this before treatment reduces the background TCE in the CRREL soil to undetectable levels. Soil subsamples were transferred into 1-mL glass ampoules using a stainless-steel spatula and small plastic funnel; 2-g of the RMA soil was used, while either 1.25 or 1.75 g of the CRREL soil was used, depending on the wall thickness of the glass ampoule. These quantities of soil filled the ampoule to just below a score mark on the neck, and they were weighed to the nearest tenth of a milligram.

The soil subsamples were then placed inside of a large (5.6-L) desiccator with a dish of $CaSO_4$ for at least 24 hours. After desiccation the $CaSO_4$ was removed and in a 60-mL glass bottle containing a spiking solution was introduced. Stock solutions for spiking the soil matrices were prepared by taking approximately 0.60 g Tol, 0.59 g TCE, 0.50 g TDCE and 0.35 g Ben and diluting into 100 mL of MeOH, or 0.52 g Tol, 0.73 g TCE, 0.62 g TDCE and 0.44 g Ben and diluting into 25 mL of tetraethylene glycol dimethyl ether (tetraglyme). These two different stock solutions were further diluted with tetraglyme as shown in Table 1 to prepare the spiking solutions necessary to create the desired soil VOC treatment levels. All of the chemicals were reagent-grade quality.

This method of treatment relies on the vapor pressures of the analytes in the spiking solution to create a gaseous mixture in equilibrium with the liquid phase. During the equilibrium, the VOC vapors impregnate the soil grain surfaces. After 7 or more days of this vapor fortification treatment, the desiccator was opened and 5-mm-diameter glass beads were placed on top each of the ampoules as temporary caps. Then, the ampoules were quickly positioned in a clamp and the necks were heat-sealed using a propane plumber's torch (Hewitt 1993a; Hewitt, in press[2]).

Holding time experiments

The first holding time experiment assessed the analyte concentration stability for these two soils while they remained confined in the 1-mL sealed glass ampoules. In all, 12 subsamples of each soil were prepared, so that two sets of duplicate subsamples could be sacrificed and analyzed after 0, 10 and 20 days of storage. For this initial experiment, the soil subsamples were vapor fortified with the

Table 1. Fortification conditions and treatment sets.

Stock solution solvent	Volume of stock diluted in tetraglyme (mL)	Volume of fortification solution (mL)	Soil weight (g) RMA	Soil weight (g) CRREL	Soil subsample replicates
Experiment 1					
MeOH	25	50	2.0	1.75	6 duplicates
Experiment 2					
Tetraglyme	0.1	10	2.0	1.25	4 triplicates
Experiment 3					
Tetraglyme	0.2	10	2.0	1.75	4 triplicates
Experiment 4					
Tetraglyme	0.01	10	2.0	1.75	4 triplicates

MeOH-based stock solution (Table 1). In addition, just before the ampoules were heat-sealed, 200 µL of Type 1 water (Milli Q, Millipore Corp.) was added to five of the six duplicate sets, creating a moisture content of 10% or greater. This water was introduced to stimulate biological activity. To evaluate any influence that the introduction of 200 µL of water had on the VOC treatment levels, one of the two sets of subsamples analyzed on day 0 was the one that had not been moistened. The remaining subsample sets were split and stored at either 22 or 4°C (Table 2).

For the second experiment, 12 subsamples of each soil were fortified and stored in sealed glass ampoules from which triplicates sets were analyzed after holding periods of 0, 7 and 16 days. This experiment, as well as those that follow, used fortification solutions with no MeOH (Table 1). The soil subsamples for this experiment were also moistened just prior to the sealing of the ampoule; however, this time, 200 µL of groundwater contaminated with 1.76 mg TCE/L was added. Triplicate subsamples of each soil type were held for 0 days, refrigerated (4°C) and held for 7 and 16 days, or held for 16 days at room temperature (22°C), prior to being sacrificed and analyzed (Table 2).

The third holding time experiment was designed to look at the stability of the VOC concentrations in subsamples that had been prepared for HS–GC analysis. On day 0, sealed ampoules containing fortified soils were placed inverted into VOA vials, equipped with open-faced caps, having a Teflon-lined silicone septum, and containing 30 mL of Type 1 water. After the VOA vials were closed, the ampoules were broken and the soil dispersed by hand shaking. Six replicates of each soil were prepared for this experiment, all of which were analyzed after 0, 2, 5, 9 and 14 days by removing headspace vapors with a gas-tight syringe. Following the analysis on day 0, the subsample sets were split as shown in Table 2, so that triplicates of each soil type could be stored refrigerated (4°C) or at room temperature (22°C).

The fourth experiment was designed to assess analyte stability for samples obtained for Method 8240, low-level PT–GC–MS analysis. On day 0, sealed ampoules of fortified soils were placed in VOA vials containing 200 µL of groundwater contaminated with 18.4 µg TCE/L and equipped with a purge-and-trap adapter (Associated Design and Manufacturing Company, Alexandria, Virginia, Model PT-6005-0002). After the VOA vials were closed, the inverted ampoules were broken and the contents dispersed by hand shaking. Of each soil type, 12 replicates were prepared for this experiment, so that triplicate subsamples could be sacrificed and analyzed after 0, 4, 7 and 14 days of storage at 4°C (Table 2).

Analysis

The subsamples from the first three experiments were analyzed by HS–GC. Soil subsamples in sealed glass ampoules (experiments 1 and 2) were prepared for analysis by opening them inside closed 40-mL VOA vials equipped with Teflon-lined silicone septum caps and containing 30 mL of Type 1 water. Inverted ampoules were opened by shaking the VOA vial and causing the sealed tip of the enclosed ampoule to break. All headspace samples were shaken for 2 minutes prior to analysis to attain equilibrium. Samples that were refrigerated between analyses were allowed to warm to room temperature before they were agitated and analyzed. Headspace vapors were transferred from the VOA vials with gas-tight syringes (Hamilton) and concentrations were established by comparison to aqueous headspace standards (Hewitt et al. 1992).

Table 2. Holding times and storage conditions.

Experiment 1				
Sealed ampoules				
Day 0	Day 10	Day 20		
Moist/Dry	22/4°C	22/4°C		
Experiment 2				
Sealed ampoules				
Day 0	Day 7	Day 16		
—	4°C	22/4°C		
Experiment 3				
Dispersed in 30 mL of water				
Day 0	Day 2	Day 5	Day 9	Day 14
—	22/4°C	22/4°C	22/4°C	22/4°C
Experiment 4				
Dispersed in VOA vial with PT adapter				
Day 0	Day 4	Day 7	Day 14	
—	4°C	4°C	4°C	

The subsamples from the fourth experiment were analyzed by PT–GC–MS, following the general SW-846 Method 8240 guidelines for soils containing less than 1 µg of VOCs/g (U.S. EPA 1986). These subsamples were held in VOA vials equipped with a special adapter that allowed them to be quickly attached to a purge-and-trap system without exposing the subsample. By design, this special adapter attaches to the purge-and-trap manifold after a Teflon ball is pushed out of an air-tight seat, which momentarily (less than 1 second) creates an opening of less than 1 mm^2 in the lid of the 44-cm^3 vial.

RESULTS

Sealed ampoules

In both experiments 1 and 2, the VOC-fortified soils were held in sealed ampoules for various periods and stored both refrigerated (4°C) and at room temperature (22°C). This way of subsample storage is ideally what has been intended for contaminated soils (containment in an air-tight vessel filled to near capacity). The results of the first experiment (Table 3) show that neither the addition of 200 µL of water just prior to sealing nor the two holding periods and temperatures tested caused analyte concentration changes that were more than ±13% of the values for the day 0 moist subsamples. This suggests that contaminated soils that do not have vapor losses retain their VOC concentrations over a 20-day period.

The results in Table 4, for the second experiment—which also used similar holding periods and storage conditions—however, showed large losses of benzene and toluene for one of the fortified soils. After 16 days of storage at room temperature, the CRREL soil lost benzene in excess of two orders of magnitude (Fig. 1), while toluene decreased by about 35% relative to the day 0 subsamples. Benzene also dropped by 30% in the refrigerated CRREL soil

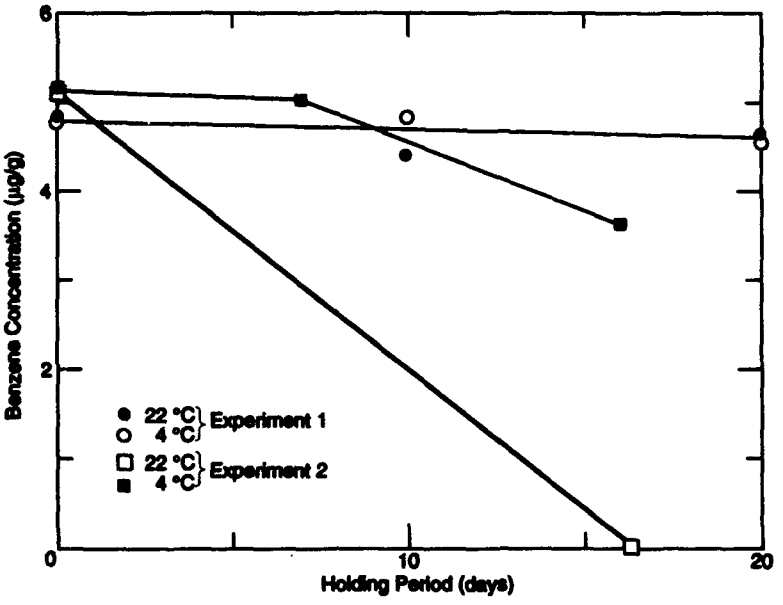

Figure 1. Stability of benzene concentrations (µg/g) in the CRREL soil subsamples that were isolated in sealed ampoules.

Table 3. Analyte concentrations (µg/g) from the first experiment for soil subsamples stored in sealed glass ampoules.

	Day 0		Day 10		Day 20	
	Dry	Moist	22°C	4°C	22°C	4°C
RMA Soil						
TDCE	21±1.1	22±1.8	24±0.4	25±0.1	24±0.4	25±0.1
Ben	27±0.9	28±0.9	29±0.4	30±0.2	27±0.8	27±1.1
TCE	33±1.1	33±1.3	35±0.8	37±0.0	34±1.3	33±1.5
Tol	34±0.8	35±0.8	37±0.8	39±0.0	35±1.3	35±1.7
CRREL Soil						
TDCE	4.0±0.4	4.0±0.2	3.6±0.2	4.0±0.4	3.5±0.2	3.7±0.0
Ben	4.8±0.2	4.8±0.0	4.4±0.2	4.8±0.3	4.6±0.1	4.5±0.0
TCE	8.8±0.1	8.5±0.1	8.1±0.2	8.8±0.5	8.0±0.2	8.1±0.1
Tol	10±0.2	9.8±0.2	9.3±0.2	10±0.6	9.3±0.2	9.1±0.2

Table 4. Analyte concentrations (µg/g) from the second experiment for soil subsamples stored in sealed glass ampoules.

	Day 0	Day 7	Day 16	
		4°C	22°C	4°C
RMA Soil				
TDCE	4.3±0.2	4.0±0.3	4.2±0.1	4.2±0.1
Ben	16±0.4	15±0.9	15±0.2	15±1.0
TCE	8.1±0.2	7.2±0.5	7.4±0.1	7.5±0.4
Tol	14±0.1	12±0.5	13±0.3	13±0.9
CRREL Soil				
TDCE	3.3±0.2	2.8±0.1	3.5±0.4	3.3±0.4
Ben	5.1±0.2	5.0±0.2	< 0.01	3.6±0.9
TCE	5.1±0.2	4.3±0.2	4.8±0.1	4.8±0.4
Tol	12±0.1	11±0.4	7.7±0.2	11±1.1

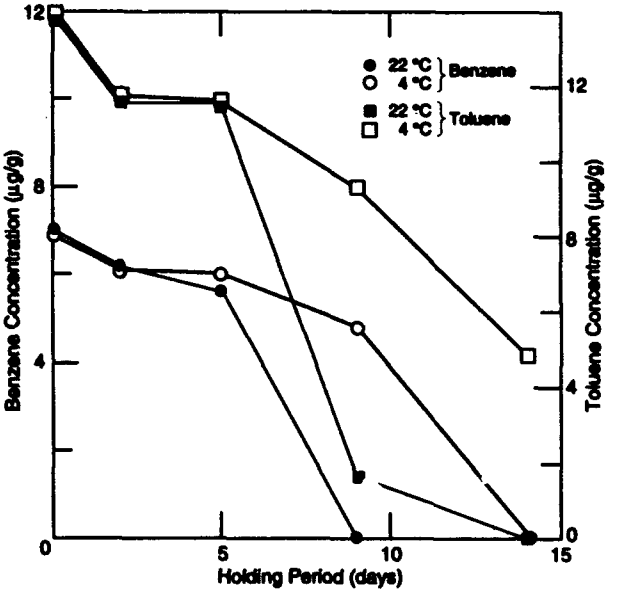

Figure 2. Stability of benzene and toluene concentrations (µg/g) in the CRREL soil subsamples prepared for HS–GC analysis.

subsamples after 16 days. As in the first experiment, there were no large (more than 13%) losses of the two chlorinated analytes from either soil, while the RMA soil didn't lose any of the analytes tested. Overall, the results in Table 4 suggest that VOC losses, presumably caused by biological degradation, are likely to depend on holding time, analyte, soil type and storage temperature.

The first two experiments differed in the use of MeOH as a solvent in the fortification stock solution and by the type of water used to moisten the treated soils before the ampoules were sealed. A previous study determined that soils fortified with a 50-mL solution containing equal volumes of MeOH and tetraglyme would sorb on the order of 10 mg MeOH/g, a level some three orders of magnitude above the analytes of interest (Hewitt 1993b). The differences in the benzene stability between these two experiments may be explained by either the presence of MeOH, on a percent weight basis, inhibiting biological degradation, or the groundwater introducing or stimulating biological activity. More important than the reasons for the different results is that these two experiments demonstrate the dependency of analyte concentration stability on the experimental design. The second experiment, which did not introduce MeOH to the substrate, more realistically portrays contaminated soils from a hazardous waste site. Thus, depending on the type of soil, aromatic VOCs such as benzene and toluene are susceptible to rapid biodegradation, even when confined in air-tight vessels.

Table 5. Analyte concentrations (μg/g) for soil subsamples stored in VOA vials with 30 mL of water.

	Day 0	Day 2	Day 5	Day 9	Day 14
			a. Room temperature (22°C)		
RMA					
TDCE	4.6±0.2	4.6±0.1	4.4±0.2	4.3±0.1	4.2±0.1
Ben	22±1.1	21±0.7	20±0.7	14±11	14±12
TCE	8.7±0.5	8.4±0.2	8.1±0.4	7.6±0.1	7.6±0.1
Tol	24±1.4	23±0.9	23±1.5	20±4.4	18±4.6
CRREL					
TDCE	3.7±0.2	3.7±0.1	3.6±0.1	3.5±0.1	3.3±0.1
Ben	7.1±0.2	6.3±0.1	5.7±0.1	< 0.1	< 0.1
TCE	6.0±0.2	5.6±0.1	5.4±0.1	4.8±0.2	4.4±0.3
Tol	14±0.4	12±0.2	12±0.5	1.8±0.9	< 0.3
			b. Refrigerated (4°C)		
RMA					
TDCE	4.6±0.2	4.4±0.2	4.2±0.1	4.2±0.1	4.1±0.1
Ben	22±1.1	20±1.0	20±0.3	20±0.3	20±0.6
TCE	8.7±0.5	8.1±0.4	7.5±0.2	7.5±0.1	7.3±0.2
Tol	24±1.4	23±1.3	21±0.4	22±0.6	20±0.6
CRREL					
TDCE	3.7±0.2	3.6±0.1	3.5±0.1	3.3±0.1	3.2±0.1
Ben	7.1±0.2	6.2±0.2	6.1±0.2	4.8±0.4	< 0.1
TCE	6.0±0.2	5.6±0.2	5.4±0.2	4.9±0.1	4.8±0.3
Tol	14±0.4	12±0.4	12±0.5	10±0.7	5.2±1.1

Headspace subsamples

Table 5 shows the results for those subsamples stored as headspace samples (sealed VOA vials with 30 mL of Type 1 water). Regardless of storage temperature (22 and 4°C), the concentration of benzene decreased in excess of two orders of magnitude over the 14-day holding period in the CRREL soil. However, as shown in Figure 2, the rate of benzene loss was faster for the samples held at room temperature than those that were refrigerated. Toluene also decreased in concentration in the CRREL soil subsamples. From day 0, about 97 and 60% of the toluene concentrations were lost after 14 days, under both storage conditions (Fig. 2). These two aromatic VOCs also appeared to decrease in the RMA subsamples held at 22°C. However, here the 36 and 25% decreases in benzene and toluene, respectively, over the 14-day holding period were caused by reductions in only one of the subsample triplicates.

The concentrations of both benzene and toluene in the refrigerated RMA soil subsamples and the two chlorinated VOCs in all of the subsamples showed a slight decreasing trend (Table 5). This same trend was observed for a standard that was also stored inverted in the refrigerator and analyzed along with the subsamples (data not given here). Since both the aqueous standard and soil slurry headspace subsamples behaved similarly, all having this 10 to 20% decrease in analyte concentration over the 14-day holding period, this effect was attributed to losses caused by multiple punctures in the septa. The removal of headspace vapors creates needle punctures through the Teflon faced VOA septum, providing a pathway for the loss of VOCs from solution by sorption into the silicone septum. As in the second experiment, VOC losses depended on the analyte, soil type, storage temperature and holding time. To avoid losses of these two aromatic hydrocarbons, HS–GC analysis should be done within a couple days of preparation.

Low level PT–GC–MS subsamples

The results in Table 6 again show that benzene and toluene in the CRREL soil had the greatest losses. Relative to day 0, more than 99 and 70%, respectively, of these two aromatic VOCs were lost after 14 days of storage at 4°C (Fig. 3). Concentration reductions were less than 22% for the two chlorinated VOCs in either soil and for the two aromatic

Table 6. Analyte concentrations (ng/g) for soil subsamples stored in VOA vials with purge-and-trap adaptor cap (refrigerated at 4°C).

	Day 0	Day 4	Day 7	Day 14
RMA				
TDCE	19.9±1.4	17.2±1.6	19.2±0.5	19.0±0.3
Ben	67.0±3.9	58.8±6.0	61.9±0.8	57.1±2.6
TCE	31.1±2.9	24.4±3.4	27.1±1.3	25.5±1.4
Tol	60.9±5.1	50.3±7.9	56.5±2.3	48.3±4.3
CRREL				
TDCE	9.52±0.46	8.96±0.23	9.59±0.32	9.2±1.2
Ben	12.7±0.35	12.7±0.20	7.41±1.8	ND*
TCE	13.8±0.70	12.6±0.15	12.4±0.67	11.9±1.5
Tol	33.1±0.47	31.9±0.97	26.5±3.8	10.0±2.5

* ND = not detected.

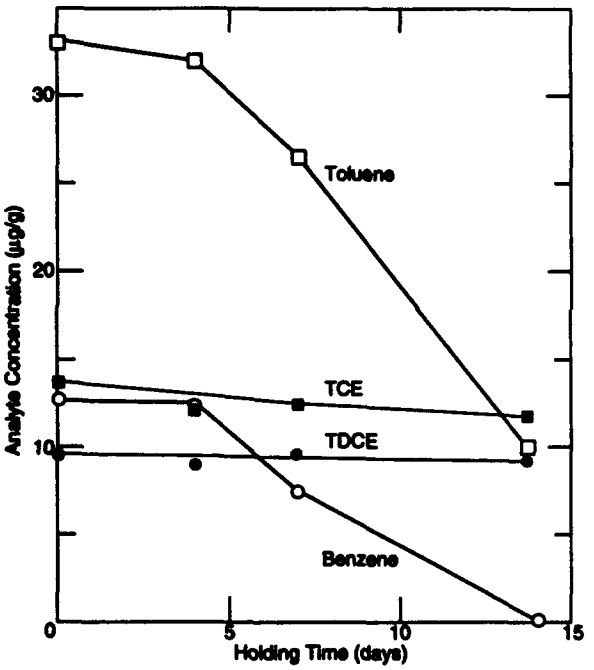

Figure 3. Stability of benzene, toluene, trans-1,2-dichloroethylene and trichloroethylene in CRREL soil subsamples prepared for PT–GC–MS analysis.

VOCs in the RMA soil. Consistent with the other experiments in which these two soils were fortified in the absence of MeOH, VOC stability depended on analyte, holding period and soil type. Although not tested, the concentration stability of both benzene and toluene under these conditions would also likely depend on storage temperature. Thus, in a way similar to the soil subsamples prepared for HS–GC analysis, subsamples prepared for low level PT–GC–MS analysis and held for more than a couple of days would be questionable for the assessment of benzene and toluene.

DISCUSSION

These four compounds degrade microbially at different rates under different environmental conditions. Labile hydrocarbons such as benzene and toluene degrade rapidly in the presence of aerobic heterotropic microorganisms (Suflita 1989). Under aerobic conditions, chlorinated aliphatic organic compounds resist degradation because of their oxidized state (Russell et al. 1992). Compounds that exist in an oxidized state are more likely to degrade under reducing environmental conditions.

The analyte stability characteristics observed during this study were consistent with both holding time studies for natural waters and studies of biological degradation under aerobic conditions. Maskarinec et al. (1990) observed that, in general, chlorinated compounds were more stable than aromatic hydrocarbons, while Roe et al. (1989) found benzene to be more rapidly degraded than toluene. Likewise, we found the two chlorinated compounds to be recalcitrant and benzene to degrade faster than toluene. Furthermore, the rate of degradation of these two hydrocarbons increased when subsamples were prepared for analysis by either HS–GC or PT–GC–MS, most likely because of the increased amount of oxygen that was available once the ampoules had been broken.

Both the activity of microorganisms and the amount of total organic carbon (TOC) in soils vary widely; however, often they are correlated. This, combined with microbial activity being sensitive to temperature, should result in VOC concentration stabilities that depend on soil and temperature. Thus, it is not surprising that the RMA soil with 0.053% TOC showed greater fortified analyte stability than the CRREL soil, which was taken from within the top horizon that contained 0.34% TOC. Moreover, analyte concentration stability improved at the lower storage temperature.

Even though the analytes of interest were introduced to the soil substrate in a fashion consistent with what takes place at hazardous waste sites, the desiccated state necessary for precise treatment during vapor fortification inhibits microbial activity (Hewitt 1993b). Furthermore, since water was not introduced until the start of the holding period, it is likely that the microbial activity continued to be below normal for some period, perhaps days. Sup-

pressed biological activity at the start of these experiments is another example how an experimental design may have influenced the results. For this reason, along with the limited number of soils tested, caution must be used when applying the results of this study. At best these findings are conservative, underestimating the rate in which labile VOCs can degrade in soil subsamples that await analysis.

These experiments successfully prevented losses from volatilization, as shown by the stability of the two chlorinated compounds in all cases and that of benzene and toluene in the RMA soil matrix. In particular TDCE, the compound with the highest vapor pressure, was remarkably stable during these different tests. The analyte stability that was found in many of the cases tested also infers that the vials and adapters used for the HS–GC and low-level PT–GC–MS analyses did not influence the VOC concentrations. Since both of these subsample preparation protocols use partially filled VOA vials to hold the sample between collection and analysis, it would be easy to introduce a preservative prior to collection to prevent biodegradation over periods of 14 days or longer. Another advantage that would be gained by using a preservative is that refrigeration would no longer be necessary. This would not only lower shipping charges but reduce the amount refrigeration needed on-site.

In terms of providing a single procedure for all soils and VOCs of concern, the findings of this study show that, even under ideal conditions (air-tight vessel filled to near capacity), the present 14-day holding period at 4°C is likely too long. Keeping in mind that soil samples should only be transferred once for the most representative VOC concentrations, workers must place subsamples into vessels that are suitable for analysis or that contains a solvent in which VOCs are soluble. If prepared for either HS–GC or low level PT–GC–MS (not immersed in MeOH), subsamples should be analyzed within a couple of days, or less. For practical reasons, a holding time of less than 14 days will seldom be achieved when samples are shipped off-site for laboratory analysis. Sample chemical preservation is the most reasonable way to maintain representative VOC concentrations in soils when holding times cannot be avoided.

CONCLUSION

Holding time studies for VOCs in a soil matrix not susceptible to volatilization losses found that concentration stability depended on analyte, soil type, temperature and experimental design. Benzene, in particular, appears to be susceptible to rapid reductions, presumably by biological degradation, even when soil samples were stored in a sealed glass ampoule. Soil subsamples prepared for either HS–GC or PT–GC–MS analysis showed complete or appreciable reductions in benzene and toluene, respectively, over 14 days at 4°C. Soil samples that are not immersed in MeOH and are held for several days without preservation measures beyond refrigeration at 4°C will be compromised for VOC analysis.

LITERATURE CITED

Hewitt, A.D. (1992) Review of current and potential future sampling practices for volatile organic compounds in soil. In *Proceedings of 16th Annual Army Environmental R&D Symposium, June, Williamsburg, Virginia*, p. 75–82.

Hewitt, A.D. (1993a) Vapor fortification: A method to prepare quality assurance soil samples for the analysis of volatile organic compounds. In *National Symposium on Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs, January 12–14, Las Vegas, Nevada*, Tab 39.

Hewitt, A.D. (1993b) Feasibility study of preparing evaluation soils for analyzing volatile organic compounds. USA Cold Regions Research and Engineering Laboratory, Special Report 93-5.

Hewitt, A.D. (in press[1]) Comparison of sampling methods for trichloroethylene in vadose zone soils. *Journal of the Association of Official Analytical Chemists.*

Hewitt, A.D. (in press[2]) Preparation of spiked soils for volatile organic compound analysis by vapor fortification. *Journal of the Association of Official Analytical Chemists.*

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.

Jackson, J., N. Thomey and L.F. Dietlein (1991) Degradation of hydrocarbons in soil samples analyzed within accepted analytical holding times. In *Proceedings of the 5th Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring, and Geophysical Methods, May 13–16, Las Vegas, Nevada*, p. 567–576.

King, P. (1993) Evaluation of sample holding times and preservation methods for gasoline in fine-grained sand. In *National Symposium on Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs, January 12–14, Las Vegas, Nevada*, Tab 19.

Lewis, T.E., A.B. Crockett, R.L. Siegrist and K. Zarrabi (1991) Ground-water issue: soil sampling and analysis for volatile organic compounds. Washington, D.C.: Technology Innovation Office, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, EPA/590/4-91/001.

Maskarinec, M.P., L.H. Johnson, S.K. Holladay, R.L. Moody, C.K. Bayne and R.A. Jenkins (1990) Stability of volatile organic compounds in environmental water samples during transportation and storage. *Environmental Science and Technology,* **24**: 1665–1670.

Maskarinec, M.P., C.K. Bayne, R.A. Jenkins, L.H. Johnson and S.K. Holladay (1992) Stability of volatile organics in environmental soil samples. Oak Ridge, Tennessee: Office of Scientific and Technical Information, ORNL/TM-12128.

Plumb, R.H., Jr., and A.M. Pitchford (1985) Volatile organic scans: Implications for ground water monitoring. In *Proceedings of the National Water Well Association/American Petroleum Institute Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, November 13–15, Houston, Texas.*

Roe V.D., M.J. Lacy, J.D. Stuart and G.A. Robbins (1989) Manual headspace method to analyze for the volatile aromatics of gasoline in groundwater and soil samples. *Analytical Chemistry,* **61**: 2584–2585

Russell, H.H., J.E. Matthews and G.W. Sewell (1992) TCE removal from contaminated soil and groundwater. Washington, D.C.: Technology Innovation Office, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, EPA/540/S-92/002.

Siegrist, R.L. and P.D. Jenssen (1990) Evaluation of sampling methods effects on volatile organic compound measurements in contaminated soils. *Environmental Science and Technology,* **24**: 1387–1392.

Suflita, J.M. (1989) Transport and fate of contaminants in the subsurface. Cincinnati, Ohio, and Ada, Oklahoma: U.S. Environmental Protection Agency, Technical Report no. EPA/625/4-89/019, p. 67.

Urban, M.J., J.S. Smith, E.K. Schultz and R.K. Dickinson (1989) Volatile organic analysis for a soil sediment or waste sample. In *5th Annual Waste Testing and Quality Assurance Symposium.* Washington, D.C.: U.S. Environmental Protection Agency, p. II-87–II-101.

U.S. Environmental Protection Agency (1986) Test methods for evaluating solid waste, vol. 1B. Washington, D.C.

Zarrabi, K., A.J. Cross-Smiecinski and T. Starks (1991) A review of existing soil quality assurance materials. In *Second International Symposium, Field Screening Methods for Hazardous Waste and Toxic Chemical, February 12–14, Las Vegas, Nevada,* p. 235–252.

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This study assesses the short-term (14- to 20-day) concentration stability of benzene, toluene, trans-1,2-dichloroethylene and trichloroethylene in soil matrices, in the absence of volatilization losses. Previously, holding time studies failed to eliminate volatilization as a variable, making them difficult to interpret. Here, vapor-fortified soil subsamples, sealed in glass ampoules for 16 days, experienced appreciable reductions in benzene, presumably attributable only to biodegradation. Treated soil subsamples, on the other hand, prepared without vapor losses for either aqueous extraction headspace or purge-and-trap analyses, showed appreciable reductions in toluene and lost all the benzene over a 14-day holding period at 4°C. These findings suggest that chemical preservatives are necessary to maintain volatile organic compound concentrations in soil when more than a couple of days pass between collection and analysis.

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