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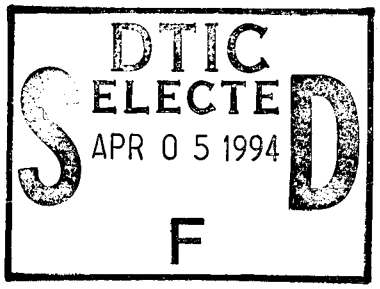
CRREL

Chemical Preservation of Volatile Organic Compounds in Soil Subsamples

Alan D. Hewitt

February 1995



Abstract

This study evaluated chemical preservation as a means of inhibiting the biological degradation of volatile organic compounds (VOCs) in soil subsamples held for 14 days or longer. Experiments were performed using a soil in which benzene and toluene were found to rapidly biodegrade under aerobic conditions while following protocols consistent with high-level (VOCs at >1 µg/g) and low-level (VOCs at <1 µg/g) purge-and-trap gas chromatography mass spectrometry and static headspace gas chromatography analysis. Chemical preservation consisted of immersing soil subsamples fortified with trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene and toluene in methanol or water acidified to a pH of less than 2 with $NaHSO_4$. These two methods of chemical preservation resulted in stable concentrations of these two aromatic hydrocarbons even when held at room temperature. The two chlorinated hydrocarbons showed stable concentrations with and without chemical preservation. This result, in conjunction with earlier findings, suggests that chemical preservation is more effective at suppressing biodegradation than the current practice of refrigeration (4°C).

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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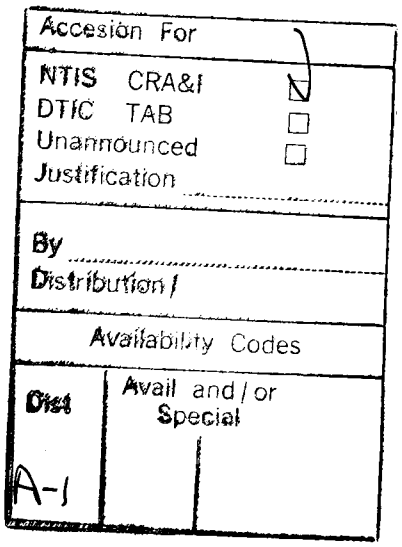

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PREFACE

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, Hanover, New Hampshire.

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Chemical Preservation of Volatile Organic Compounds in Soil Subsamples

ALAN D. HEWITT

INTRODUCTION

Soil samples collected during hazardous waste site investigations for determining the presence and concentration of volatile organic compounds (VOCs) can be stored, according to current protocols, for up to 14 days at 4°C prior to analysis (U.S. Environmental Protection Agency 1986). Laboratory studies addressing this holding period have shown large losses of VOCs when soil subsamples were held under these conditions (Jackson et al. 1991, Maskarinec et al. 1992, King 1993). In addition, studies associated with site investigations using bulk sample collection and handling protocols have shown that the length of storage is an important variable affecting the VOC concentrations (Hewitt 1994a,b). In general, the losses observed during these studies were correlated with analyte vapor pressure and were independent of analyte chemistry, i.e. halogenated recalcitrant compounds were lost as fast as readily degradable hydrocarbons (Suflita 1989, Russell et al. 1992). For these reasons the observed reductions in VOC concentrations can be attributed to volatilization.

To my knowledge there has only been one study that has clearly demonstrated that VOC concentrations in soil are subject to loss mechanisms independent of volatilization when refrigerated at 4°C and stored for 14 days (Hewitt 1994c). This study demonstrated that under aerobic conditions, concentrations of trans-1,2-dichloroethylene (TDCE) and trichloroethylene (TCE) tend to remain stable, while benzene (Ben) and toluene (Tol) levels rapidly decrease, sometimes to below detection. The rate of loss of these two hydrocarbons was even greater when subsamples were held at room temperature (22°C). The observed losses were consistent with the published degradation half-lives extrapolated from aqueous aerobic systems: 4 to 22 days for Ben and Tol and 4 weeks to 1 year for TDCE and TCE (Printup 1991). Thus, even though the breakdown products were not identified, the results for aqueous media strongly suggest that the losses of Ben and Tol were due to biodegradation (Hewitt 1994c).

For this reason, when soils subsamples are held up to 14 days prior to analysis, preservation measures other than, or in addition to, refrigeration are necessary to inhibit the biological degradation of some VOCs. Two logical methods of chemical preservation are the use of acids and solvents. Acidification to a pH of 2 is already a recommended practice for water samples collected for the analysis of VOCs, while solvents are often used to extract these compounds from soils, particularly when concentrations are expected to exceed 1 μg/g (U.S. Environmental Protection Agency 1986).

For this study methanol (MeOH) and sodium bisulfate ($NaHSO_4$) were the solvent and acid tested. Methanol is often the solvent of choice for the extraction and dilution of VOCs, while the sodium salt of sulfuric acid has been successfully used to inhibit biodegradation of VOCs in laboratory water, surface water and groundwater samples (Maskarinec et al. 1990). In addition to using MeOH and $NaHSO_4$ as chemical preservatives, an experiment was performed to determine if elevated concentrations of the VOCs could suppress biological activity.

This study, then, consisted of four experiments. The first experiment varied the analyte concentration while following the protocols that successfully demonstrated the biological degradation of aromatic compounds (Hewitt 1994c). After the fortifi-

cation concentration range where biodegradation is uninhibited for this soil was established, tests of chemical preservation with MeOH and $NaHSO_4$ were performed within the region where rapid losses occurred. The experiment with $NaHSO_4$ was divided into two parts, one using high levels of the analyte and headspace gas chromatography (HS/GC) analysis, and the other using low levels of the analyte and purge-and-trap gas chromatography mass spectrometry (PT/GC/MS) analysis.

EXPERIMENTAL METHODS

The experimental approach used in this study combined a laboratory fortification method that is analogous to an environmental pollution pathway with a handling protocol that does not expose the subsample to the atmosphere. Volatilization was minimized by keeping the subsamples in gas-tight volatile organic compound analysis (VOA) vials during storage and analysis. This study also used the same bulk soil and experimental protocols that resulted in the rapid loss of the two aromatic hydrocarbons Ben and Tol, presumably due to biodegradation (Hewitt 1994c). All soil subsamples were spiked with Ben, Tol, TDCE and TCE using a vapor fortification treatment (Hewitt 1994d,e). These four analytes were chosen because they are frequently identified at hazardous waste sites (Plumb and Pitchford 1985, Zarrabi et al. 1991) and biodegrade either under anaerobic or aerobic conditions.

Except when MeOH was used as a chemical preservative, all fortified soil subsamples remained in closed VOA vials throughout storage and analysis. Vessels containing MeOH, which retards volatilization and inhibits biodegradation, can be briefly opened to withdraw an aliquot without large losses of the VOCs present as solutes. In contrast, soils and soil-water slurries with volatiles present in the headspace must be kept sealed because even rapid transfers or brief exposures to the atmosphere can result in large losses (Jenkins and Schumacher 1987, Urban et al. 1989, Siegrist and Jenssen 1990, Lewis et al. 1991, Hewitt et al. 1992, Voice and Kolb 1993).

Soil

The soil used here and previously is a silty sand with a 0.053% total organic carbon content. A bulk sample of this soil was obtained approximately 12 months prior to this study at the Cold Regions Research and Engineering Laboratory (CRREL). The soil was collected from the top horizon in an area where TCE contamination has been present for about 20 years. A bulk sample was prepared by air-drying, sieving through a 30-mesh screen and thoroughly mixing. This process reduced the background TCE concentration in the soil to below detection (<3 ng/g).

Soil subsample preparation

Soil subsamples were prepared by transferring 1.50 ± 0.01 g of the bulk CRREL soil into 1-mL glass ampoules using a stainless steel spatula and a small plastic funnel. As many as 21 soil subsamples were then placed inside a glass desiccator with $CaSO_4$ for periods ranging between 24 and 48 hours. After desiccation the $CaSO_4$ was removed, and a vapor fortification solution contained in a 60-mL glass bottle was introduced. Stock solutions for spiking the soil matrices were prepared by combining approximately 0.27 g of Tol, 0.30 g of TCE, 0.25 g of TDCE and 0.18 g of Ben and taking the mixture to volume in 25 mL of tetraethylene glycol dimethyl ether (tetraglyme). This stock was further diluted with tetraglyme as show in Table 1 to create specific soil VOC treatment levels for the different experiments. All of the chemicals were reagent-grade quality.

This method of soil subsample treatment relies on the partial pressures of the analytes in the spiking solution to create a gaseous phase concentration to impregnate the soil grain surfaces. After three or more days of equilibration the desiccator was opened, and 5-mm-diameter glass beads were placed on top of each of the ampoules, providing temporary caps. Then, without hesitation, the ampoules were positioned in a clamp and the necks were heat-sealed using a propane plumber's torch.

Table 1. Fortification solutions.

Experiment	*Volume of stock (mL)*	*Volume of tetraglyme (mL)*	*No. of subsamples fortified*
Analyte concentration			
A	0.1	10	6
B	0.5	9.5	6
C	2.0	8.0	6
$NaHSO_4$ - HS/GC	0.1	10	21
$NaHSO_4$ - PT/GC/MS	0.01	10	14
Immersion in MeOH	0.5	9.5	12

Table 2. Subsample sets, holding times and storage conditions.

Experiment	*Holding time and conditions*				
Analyte concentration	*Day 0*	*Day 8*	*Day 14*		
	22°C†	22°C	22°C		
	(*n*=2) × 3*	(*n*=2) × 3	(*n*=2) × 3		
$NaHSO_4$ - HS/GC	*Day 0*	*Day 4*	*Day 8*	*Day 14*	
	22°C	22/4°C	22/4°C	22/4°C	
	(*n*=3)	(*n*=3) × 2	(*n*=3) × 2	(*n*=3) × 2	
$NaHSO_4$ - PT/GC/MS	*Day 0*	*Day 5*	*Day 7*	*Day 14*	*Day 21*
	22°C	22°C	22°C	22°C	22°C
	(*n*=3)	(*n*=3)	(*n*=3)	(*n*=3)	(*n*=2)
MeOH immersion	*Day 0*	*Day 14*	*Day 28*	*Day 42*	
	22°C	22°C	22°C	22°C	
	(*n*=3)	(*n*=3)	(*n*=3)	(*n*=3)	

† Storage temperature
* Number of subsamples sacrificed for analysis

The ampoules were transferred (with their sealed tips pointing down) to VOA vials and positioned.

Effect of analyte concentration

The first experiment assessed if the analyte concentration could inhibit the biodegradation of Ben and Tol. Three sets (A, B, C) of six soil subsamples were vapor-fortified to different analyte levels (Table 1). The storage period was initiated once an ampoule had been broken and the soil completely dispersed into 30 mL of water contained in the VOA vial. Breaking the ampoule and dispersing the soil was accomplished by hand agitation. Duplicates of these soil-water subsamples were sacrificed and analyzed by HS/GC after 0, 8 and 14 days at room temperature (22°C) storage (Table 2).

Chemical preservation with $NaHSO_4$

HS/GC

Twenty-one soil-filled ampoules were fortified for the holding time study of acidified subsamples prepared for HS/GC analysis (Table 1). These 1.50-g subsamples of the CRREL soil were acidified by adding 0.25 g of granular $NaHSO_4$ (pKa = 1.92) to VOA vials containing 30 mL of Type 1 water. Both the holding period and the acidification started once the ampoules containing the VOC-treated soil had been broken inside closed VOA vials with Teflon-faced silicon septa. One set of triplicates was analyzed on day 0, while the remaining sets were split; half were stored at room temperature (22°C) and half were refrigerated (4°C). A set of triplicates from each storage condition were sacrificed and analyzed by HS/GC after holding periods of 4, 8 and 14 days (Table 2).

PT/GC/MS

Fourteen subsamples were fortified for the low-level PT/GC/MS holding time study (Table 1). These 1.50-g CRREL soil subsamples were acidified by adding 0.25 g of granular $NaHSO_4$ to VOA vials containing 3 mL of Type 1 water. As before, both the holding period and the acidification started once the ampoules' contents had been dispersed inside closed VOA vials. For this experiment the VOA vials were equipped with purge-and-trap adapter caps (Associated Design and Manufacturing Company, Alexandria, Virginia, Model PT-6005-0002). Four sets of triplicates and a set of duplicates were sacrificed and analyzed by PT/GC/MS after 0, 5, 7, 14 and 21 days of storage at 22°C (Table 2).

MeOH immersion

The MeOH immersion experiment was performed with 12 vapor-fortified soil subsamples (Table 1). Each subsample was enclosed in a VOA vial with a Teflon-faced silicon septum cap, then shaken to break the ampoule and disperse the contents into 10 mL of MeOH. Sets of triplicate subsamples were sacrificed after storage at room temperature for periods of 0, 14, 28 and 42 days. Unlike the other experiments, the VOA vial containing the methanolic-soil slurry was opened and a 100-µL volume was transferred into a VOA vial containing 30 mL of Type 1 water by piercing the

septum. This aqueous solution was then analyzed by HS/GC.

Analysis

Both the HS/GC and PT/GC/MS analyses of subsamples were performed following procedures that have been described in more detail elsewhere (Hewitt et al. 1992). Briefly, HS/GC analysis was performed at room temperature after shaking the VOA vials for two minutes to obtain a headspace equilibrium. Headspace vapors were removed from the sealed VOA vial using a gas-tight syringe to penetrate the Teflon-faced silicon septum. These headspace vapors were then injected into a Photo-Vac gas chromatograph (model 10S10, PhotoVac, Inc.) equipped with a packed column containing 10% Se-30 on Chromsorb 80/100 mesh. Sample analyte concentrations were established relative to aqueous headspace standards. For those samples treated by adding 0.25 g of $NaHSO_4$, this same amount of acid was added to the standards to compensate for the small (approximately 5%) salting-out effect.

Subsamples analyzed by PT/GC/MS followed the general SW-846 Method 8240 guidelines for soils containing VOCs at less than 1 µg/g (U.S. Environmental Protection Agency 1986). These subsamples were held in VOA vials equipped with a special adapter so that they could be quickly attached to a purge-and-trap system. 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 (<1 s) creates a circular opening (<1 mm in diameter) in the lid of the 44-cm^3 vial. Since the low-level PT/GC/MS subsample already contained 3 mL of water, only an additional 3 mL was used to introduce the internal standard.

RESULTS

Effect of analyte concentration

The initial (day 0) cumulative VOC concentrations for the treatment batches A, B and C were approximately 5.2, 160 and 240 µg/g, respectively (Table 3). After storage for 14 days at room temperature, the cumulative concentrations had decreased for these three treatment batches by 71, 61 and 8%. With the exception of one TCE value, which is perhaps aberrant, the variations in concentrations between holding times were no greater than 13% for the two chlorinated compounds, independent of treatment level. Similarly, treatment C, which had the highest cumulative VOC concentration, showed no reductions in concentration greater than 13% for any of the four analytes. In contrast, the concentrations Ben and Tol decreased by more than 90% over the 14-day holding period in the A and B treatment batches.

Table 3. Holding time concentration (µg/g) results for soil subsamples treated at three different analyte levels and prepared for HS/GC analysis.

Analyte	*Day 0*	*Day 8*	*Day 14*
		Treatment A	
TDCE	0.71±0.01	0.66±0	0.64±0.03
Ben	1.0±0	0.59±0	ND*
TCE	0.88±0	0.78±0.02	0.84±0.03
Tol	2.6±0	1.4±0	ND
Total	5.19	3.43	1.48
		Treatment B	
TDCE	32±0	32±1	30±1
Ben	50±1	8.8±4.2	ND
TCE	41±1	36±0	28±2
Tol	40±1	24±2	3.6±1.6
Total	163	100.8	61.6
		Treatment C	
TDCE	33±1	35±0	34±1
Ben	65±0	65±4	58±1
TCE	53±1	55±2	48±1
Tol	92±3	88±4	82±5
Total	243	243	222

*ND—not detected

Effect of acidification

Tables 4 and 5 show the results obtained for the two holding time experiments involving subsamples chemically preserved by acidification. The subsamples prepared for HS/GC analysis showed no losses that exceeded 10% for any of the com-

Table 4. Analyte concentrations (µg/g) for soil subsamples prepared for HS/GC with 0.25 g of $NaHSO_4$ and stored refrigerated and at room temperatures.

Analyte	*Day 0*	*Day 4*	*Day 8*	*Day 14*
		$NaHSO_4$/22 °C		
TDCE	4.5±0.1	4.4±0.1	4.3±0.1	4.3±0.2
Ben	8.6±0.2	8.4±0.1	8.7±0.3	8.7±0.1
TCE	9.1±0.3	8.5±0.3	8.7±0.2	8.6±0.3
Tol	13±0	12±0	13±0	13±0
		$NaHSO_4$/4 °C		
TDCE		4.1±0.2	4.6±0.2	4.3±0.2
Ben		7.9±0.3	9.1±0.4	8.5±0.5
TCE		8.1±0.3	9.0±0.4	8.4±0.4
Tol		12±0.6	13±0.6	13±0.6

Table 5. Analyte concentrations (ng/g) for soil subsamples held at room temperature and prepared for low-level PT/GC/MS analysis.

Analyte	*Day 0*	*Day 5*	*Day 7*	*Day 14*	*Day 21*
			$NaHSO_4$/22 °C		
TDCE	194±7	228±11	210±9	239±14	212±16
Ben	286±18	325±12	323±14	347±18	318±6
TCE	254±15	297±12	293±18	347±18	272±7
Tol	282±21	311±14	289±27	328±17	286±2

pounds over the 14-day holding period, regardless of storage temperature. Those prepared for low-level PT/GC/MS and stored at room temperature showed variations in analyte concentrations up to 25%; however, no consistent trends were observed.

MeOH immersion

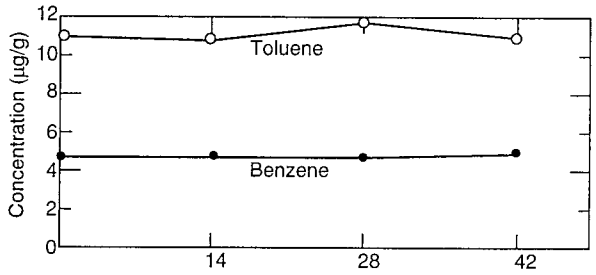
The results for the soil subsamples immersed in MeOH and held at room temperature are shown in Table 6. In this experiment there were only small changes in the analyte concentrations for subsamples stored over a 42-day period.

Table 6. Analyte concentrations (µg/g) for soil subsamples stored immersed in 10 mL of MeOH and held at room temperature.

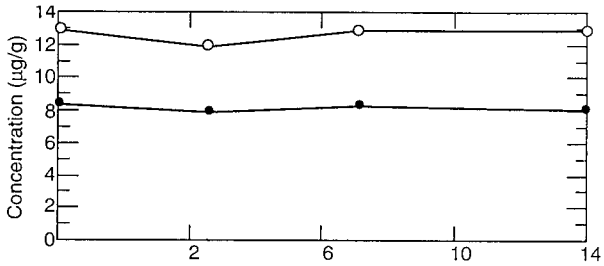
Analyte	*Day 0*	*Day 14*	*Day 28*	*Day 42*
		MeOH/22 °C		
TDCE	2.6±0.1	2.7±0	2.8±0.2	2.6±0.1
Ben	4.8±0.1	4.8±0.2	4.9±0.2	5.1±0.1
TCE	4.3±0.1	4.3±0.2	4.4±0.2	4.3±0.1
Tol	11±1	11±1	12±1	11±0

DISCUSSION

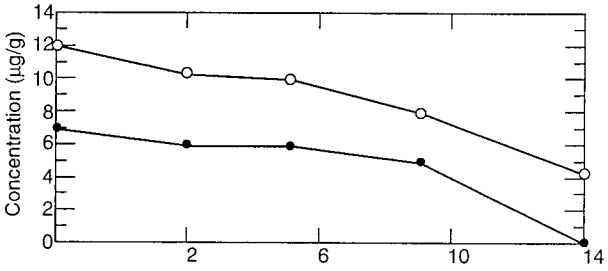
Since in all of these studies, the soils were fortified in an air-filled chamber and the ampoules were opened in VOA vials with at least 14 cm^3 of headspace, the experimental conditions were aerobic. Even so, the experimental protocol successfully isolated the VOCs, allowing holding time studies to address biodegradation in the absence of volatilization. For example, TDCE, the analyte with the highest vapor pressure, was remarkably stable in concentration over periods exceeding 14 days. A similar stability in concentration was also observed for TCE. In contrast, Ben and Tol often underwent rapid reductions in concentration unless the subsamples were chemically preserved, a process that has long been suspected, since these two aromatic compounds aerobically biodegrade



a. Subsamples immersed in methanol and held at 22 °C.



b. Subsamples dispersed into 30 mL of water acidified with $NaHSO_4$ and held at 22 °C.

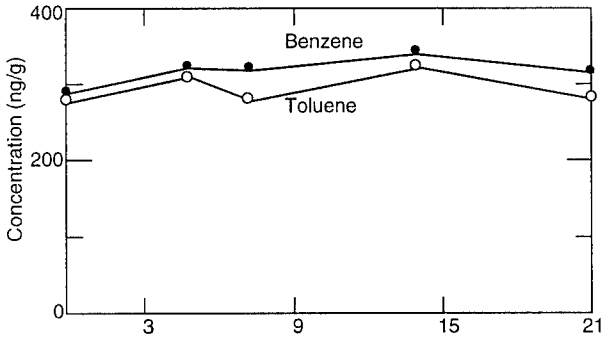


c. Subsample dispersed into 30 mL of water and held at 4 °C. (Hewitt 1994c).

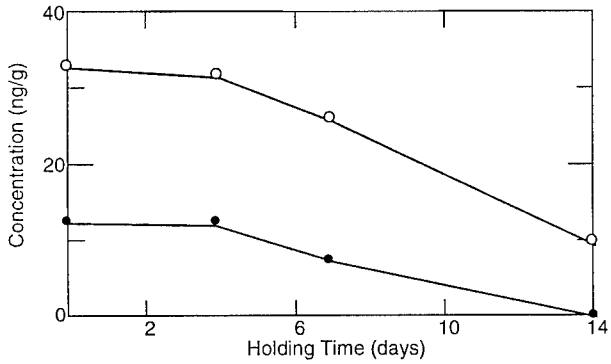
Figure 1. Holding time results for subsamples prepared for HS/GC analysis.

(Suflita 1989). This feature is illustrated in Figures 1 and 2, which show the results for subsamples stored with and without chemical preservation.

Figure 3 is a plot of the percent cumulative VOC concentration relative to day 0 for the treatment level experiment (Table 3). Also included in this plot are the results from a previous study (Hewitt



a. Subsample wetted with 3 mL of water acidified with $NaHSO_4$ and stored at 22°C.



b. Subsample moistened with 0.2 mL of water and stored at 4°C. (From Hewitt 1994c.)

Figure 2. Holding time results for subsamples prepared for PT/GC/MS analysis.

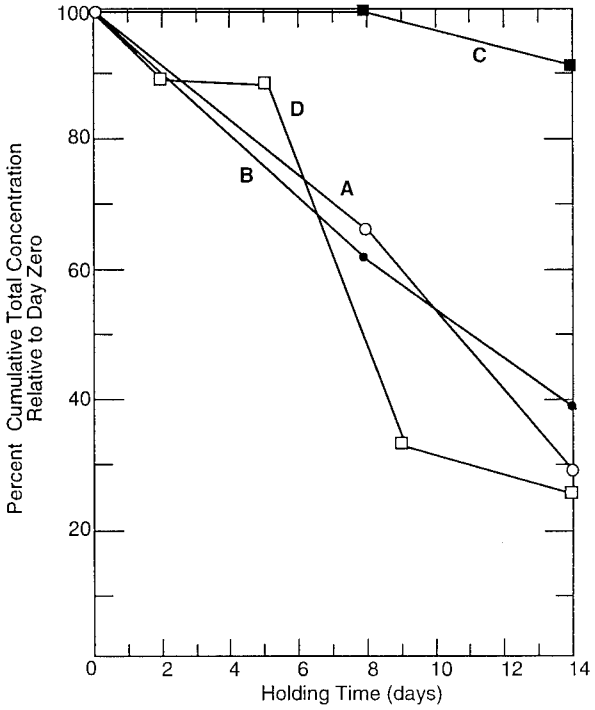


Figure 3. Percent cumulative concentration relative to day 0 for the treatment level soil subsample sets (A, B, C; Table 3) and for a set (D) handled under similar protocols (Hewitt 1994c). All subsamples were prepared for HS/GC analysis and held at room temperature without chemical preservation.

1994c) for a set of subsamples held under similar conditions. The only difference between these experiments was that subsamples were sacrificed upon analysis in the treatment level study, where as previously the subsamples had been repeatedly analyzed. In the absence of chemical preservation, the rate of loss due to biodegradation in the CRREL soil is fairly reproducible. This figure also indicates that biodegradation in a given soil can be suppressed when treated with high concentrations of these four VOCs. The cumulative VOC concentration where biodegradation appears to be inhibited in the CRREL soil is around 240 µg/g, well above the treatment level used in the chemical preservation studies. Therefore, we can be reasonably certain that the stability of the Ben and Tol concentrations in acidified samples and samples immersed in MeOH is attributable solely to chemical preservation.

Even though the success of these two methods of chemical preservation were relative to laboratory-fortified samples, field samples most likely will behave similarly. The reasoning for this assumption is that the chemical preservatives inhibited the activity of the microbes that were indigenous to the soil. Furthermore, since the soil subsamples were vapor-fortified just prior to initiating the experimental conditions, the VOCs were most likely readily available. For this reason, laboratory vapor-fortified soil samples may represent a worst-case scenario. There are, however, some precautions that need to be addressed. For instance, only four VOCs were tested in this study. Moreover, when acidification is used, it is most likely important that a pH of 2 or lower is obtained and that the soil subsample becomes completely dispersed once enclosed in the VOA vial.

Analyte transformations due to the MeOH or $NaHSO_4$ are unlikely. Methanol is commonly used as the solvent for preparing VOC standards, and a study performed with laboratory water, surface water and groundwater treated with 25 VOCs and acidified with $NaHSO_4$ showed no chemical interferences (Maskarinec et al. 1990).

Not included in this report are the results from an experiment using $NaHSO_4$ to acidify subsam-

ples prepared for HS/GC analysis, which failed to prevent the loss of Ben and Tol. The reason for not including this experiment is that an artifact was detected. Close inspection of the treated soil subsamples established that some had not been completely dispersed at the start of the storage period. These subsamples, which contained clumps of wetted soil trapped in partially broken ampoules, showed losses of Ben and Tol, while there were no detectable losses of these two analytes in subsamples where dispersion was complete. Because of this artifact the experiment was repeated, taking special care to completely disperse the soil in the acidified water. The results of this second experiment found that there were no changes in any of the analyte concentrations greater than 10% (Table 4). Thus, depending on the soil texture and composition, field subsamples may require vortex or sonication mixing. In addition, more than 3 mL of water may be necessary when preparing for low-level PT/GC/MS. Also, since the buffering capacity of soils varies widely, the amount of $NaHSO_4$ necessary to achieve a pH of 2 should be evaluated on a case-by-case basis. Lastly, when high levels of calcium carbonate are present in the soil, acidification may not be feasible.

The selection of subsample preservation by either acidification or immersion in MeOH depends on the VOC concentrations expected and the method of analysis. The two methods of analysis used here were HS/GC and PT/GC/MS. The former is very compatible with on-site operations, while the latter is often required for fixed (off-site) laboratories involved with government-regulated site investigations. Acidification with $NaHSO_4$ is compatible with low levels of VOC (<1 μg/g), while immersion in MeOH is preferable with high levels (>1 μg/g).

By using chemical preservation with sample collection protocols that minimize volatilization losses during storage and analysis, environmentally representative analyte concentrations are more apt to remain stable for 14 days (Hewitt et al., in press). Some small VOC losses may occur independent of acidification since Teflon (the septum cap liner) is believed to sorb VOCs (Leggett and Parker 1994). Another advantage that could be gained by using chemical preservation is that refrigeration would not be as critical. Relaxing this requirement would lower the cost of both on-site operations and shipping. Furthermore, the results (Tables 5 and 6) show that the concentration stability obtained by either acidification or immersion in MeOH may permit holding times to be increased beyond 14 days. Increasing holding times would not only be beneficial to site investigations performed in remote locations where turn-around limits are hard to achieve, but may also allow some samples to be archived.

CONCLUSION

Chemical preservation can maintain stable concentrations of Ben and Tol in soil subsamples that exhibited biodegradation of these two compounds when held for 14 days at 4°C. Concentrations of TDCE and TCE were stable with and without preservation. The two methods of chemical preservation used—immersion in MeOH and acidification with $NaHSO_4$—are compatible with subsamples collected and handled for both PT/GC/MS and HS/GC analysis. Prior to performing chemical preservation studies, the range where biodegradation is uninhibited by analyte concentration must be established.

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This study evaluated chemical preservation as a means of inhibiting the biological degradation of volatile organic compounds (VOCs) in soil subsamples held for 14 days or longer. Experiments were performed using a soil in which benzene and toluene were found to rapidly biodegrade under aerobic conditions while following protocols consistent with high-level (VOCs at >1 μg/g) and low-level (VOCs at <1 μg/g) purge-and-trap gas chromatography mass spectrometry and static headspace gas chromatography analysis. Chemical preservation consisted of immersing soil subsamples fortified with trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene and toluene in methanol or water acidified to a pH of less than 2 with $NaHSO_4$. These two methods of chemical preservation resulted in stable concentrations of these two aromatic hydrocarbons even when held at room temperature. The two chlorinated hydrocarbons showed stable concentrations with and without chemical preservation. This result, in conjunction with earlier findings, suggests that chemical preservation is more effective at suppressing biodegradation than the current practice of refrigeration (4°C).

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