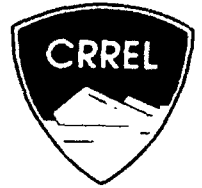


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Feasibility Study of Preparing Performance Evaluation Soils for Analyzing Volatile Organic Compounds

Alan D. Hewitt

May 1993

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Abstract

Vapor fortification, an alternative method for spiking soils with volatile organic compounds for quality assurance/quality control, was improved by minimizing the effects of numerous variables. The procedure developed resulted in average analyte concentrations for triplicate test samples that were not significantly different among three separate fortification treatments, and had relative standard deviations within each treatment of less than 9%, for three of the four analytes tested. The advantages of using vapor fortification instead of the conventional liquid injection methods are discussed.

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.

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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, Martin Stutz, Project Monitor.

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Feasibility Study of Preparing Performance Evaluation Soils for Analyzing Volatile Organic Compounds

ALAN D. HEWITT

INTRODUCTION

The improper disposal and handling of Volatile Organic Compounds (VOC) have made these analytes our most common hazardous waste problem (Plumb and Pitchford 1985, Zarrabi et al. 1991). Even so, there is no source for quality assurance/quality control (QA/QC) samples for evaluating the performance of contract laboratories and the various methods used to determine VOCs in soil (Zarrabi et al. 1991). This is particularly alarming because our present greatest concern is the effect that hazardous waste has on potable water, and soils in the vadose zone often serve as the pathway between surface spills and groundwater.

Currently, the accuracy and precision of both methods and laboratories used to determine VOC concentrations in soils are established by solution spike and recovery tests. Attempts to spike, homogenize and transfer VOC-contaminated solid matrices have proven unsatisfactory, however, because we can't control volatilization losses (Maskarinec et al. 1989). As a result, the common practice for quality control for site investigations has been to add the VOCs of interest, diluted in methanol (MeOH), to the purge vessel of a purge-and-trap system or to add the spikes to a suspension of the test sample. In either case this liquid spiking method is of dubious validity for several reasons: It evaluates only the determinative step, it allows no time for natural sorption, and it fails to simulate an environmentally logical pathway for soil contamination.

Vapor fortification, a precise means of spiking soils with VOCs for method comparison studies (Jenkins and Schumacher 1987, Hewitt et al. 1991, 1992), offers an alternative way to make quality control soil samples. This method of spiking is analogous to how vadose zone soils are contaminated by vapors from liquid pools of organic solutions, and avoids introducing either large quantities of water or MeOH to the test matrix. More-

over, a soil or sediment treated by vapor fortification requires both extraction and determination steps for analysis, thus evaluating laboratory or method performance more comprehensively.

STUDY OBJECTIVES

The objective of this study is to develop a robust and environmentally realistic approach by which independent laboratories can prepare quality control soil samples for VOCs. The vapor fortification method, used previously for studies comparing methods (Jenkins and Schumacher 1987, Hewitt et al. 1992), was evaluated by examining the following variables and procedures:

1. Sorption rate.
2. Exposure solution composition.
3. Exposure vessel.
4. Desiccation-soil moisture.
5. Temperature.
6. Concentration treatment range.
7. Holding time.

MATERIALS AND METHODS

Vapor fortification

Vapor fortification is done in the laboratory by exposing, in a closed desiccator, individually prepared soil subsamples to solutions of pure organic liquids. During exposure, open vessels hold both the test matrix and fortification solution (Fig. 1).

Equipment and chemicals

All of the chemicals were reagent grade quality or better. Building on previous studies, I chose trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben) and toluene (Tol) as the test analytes (Hewitt et al. 1991, 1992). Standard stock solutions, used both for fortification treatments and as analytical standards

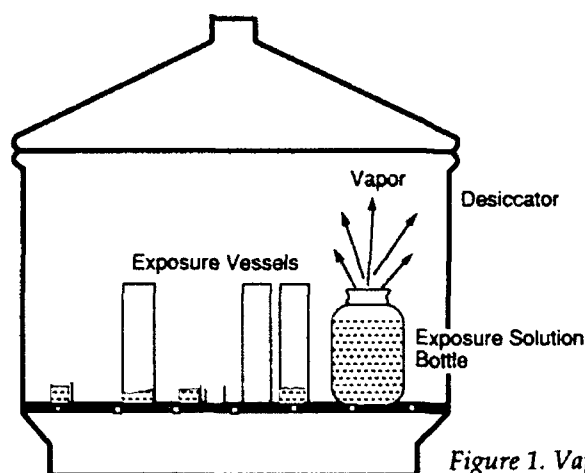


Figure 1. Vapor fortification chamber.

for instrumental analysis, were prepared monthly by taking the following approximate analyte quantities to volume in 100 mL of MeOH: either 1.20 or 0.600 g of Tol, 0.586 g of TCE, 0.503 g of TDCE and 0.351 g of Ben. Two solvents were used to further dilute the analytes of interest for vapor fortification treatments—MeOH and tetraethylene glycol dimethyl ether (tetraglyme). The soils used as test matrices were two different standard reference soils, bottle numbers AO46 and 130, from the U.S. Army Environmental Center (formerly the U.S. Army Toxic and Hazardous Materials Agency—USATHAMA), along with a high organic carbon (6.69%) soil from Point Barrow, Alaska. All of the soils tested had been sieved to less than the 500- μ m grain size, thoroughly mixed and air dried. Volatile Organic compound Analysis (VOA) vials were used to hold either the soil during exposure or the treated soils after fortification. Since these vessels also served as the analysis vials, once they were capped and the treated matrix contained, soil subsamples became test samples. During fortification a 60-mL glass bottle held the exposure solution, and glass desiccators of 2.6- and 5.6-L capacity served as the exposure chambers.

Sample analysis

Samples were analyzed by either HeadSpace Gas Chromatography (HS/GC) or by Purge-and-Trap Gas Chromatography Mass Spectrometry (PT/GC/MS).

The aqueous extraction and HS/GC analysis method followed the guidelines of Spittler* and others (Dietz and Singley 1979). This method uses 30 mL of type 1 water to extract VOCs from a soil subsample held in a 40-mL VOA vial fitted with an open-faced cap and Teflon-lined silicone septum. After 2 minutes of vigorous shaking by hand, soils that were easily dispersed by

water were completely extracted. Gas-tight syringes transferred the headspace vapors for GC analysis (Hewitt et al. 1991).

Other subsamples were analyzed by PT/GC/MS, following the procedures outlined EPA SW 846, Method 8240 (EPA 1986) for low level (<1 μ g/g) VOC determinations in soil matrices. The VOA vials holding the test samples were equipped with modified purge-and-trap adapters (Associated Design & Manufacturing Company, Alexandria, Virginia) for analysis by direct purge PT/GC/MS. These adapters allow the VOA vials to be attached to a purge-and-trap system without exposing the samples.

ASSESSMENT OF VARIABLES AND PROCEDURES

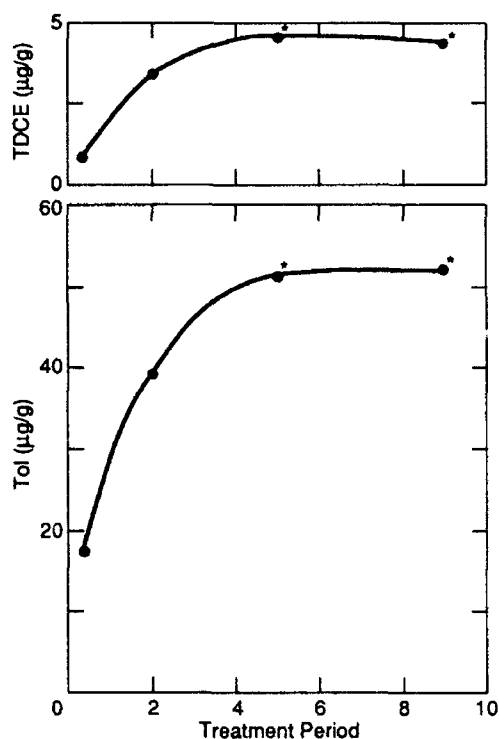
Sorption rate

The rate at which a soil matrix sorbed VOCs was studied using 2-g subsamples of one of the standard soils (AO46), fortified by exposure in VOA vials to a 50-mL, 50:50 mixture of the MeOH stock solution and tetraglyme. Triplicate subsamples were removed from the exposure chamber after 0.3, 2, 5 and 9 days. Figure 2 shows the analyte uptake established by HS/GC analysis for these various treatment periods. A student's *t*-test, comparing mean analyte concentrations of test samples taken after 5 and 9 days of treatment, showed no statistical difference at the 95% confidence level. This indicates that VOC fortification had reached a maximum concentration level after 5 days of treatment, and that no more VOCs were sorbed over the additional 4 days.

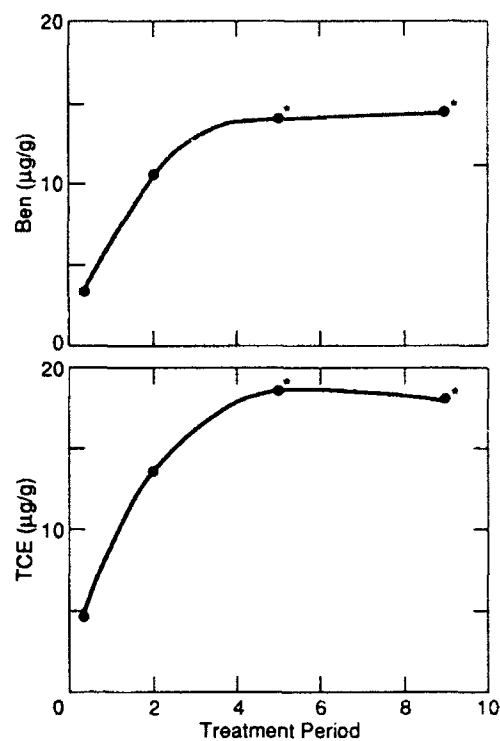
Exposure solution composition

During a method comparison study (Hewitt et al. 1992), four different mixtures of exposure solvents were studied. Analyte sorption decreased on the soil exposed in VOA vials as the MeOH stock solution was diluted with tetraglyme. Figure 3 shows the various average

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

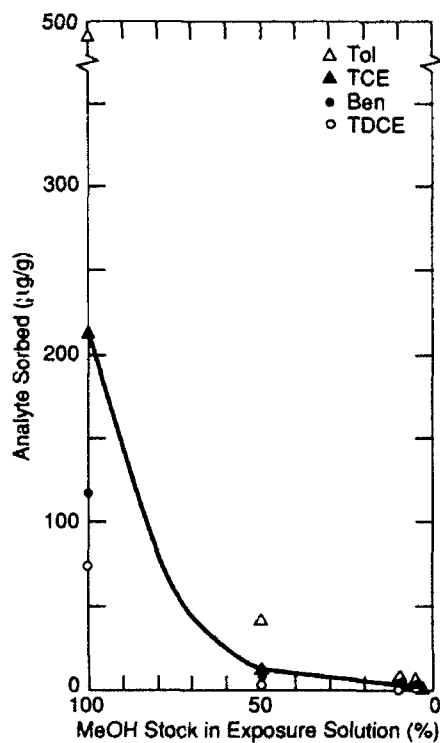


a. TDCE and Tol

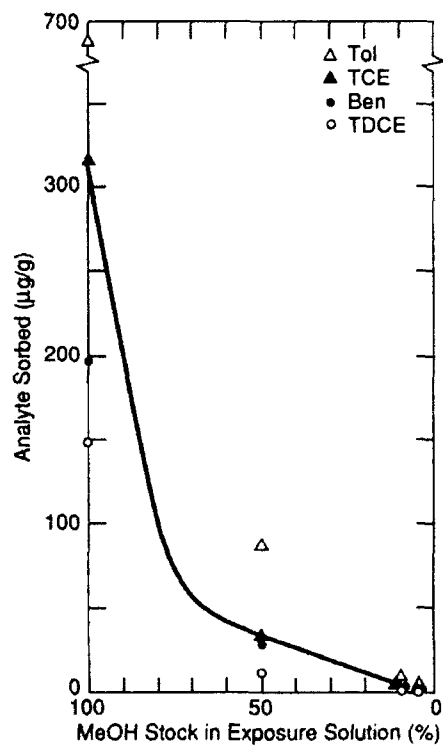


b. Ben and TCE.

Figure 2. Vapor fortification sorption curves for soils exposed in VOA vials. Points marked with the asterisk indicate that the student's *t*-test showed no difference in mean concentration at the 95% confidence level.



a. AO46 soil.



b. Point Barrow, Alaska, soil.

Figure 3. Analyte concentrations for soils exposed to different solution mixtures of MeOH and tetraglyme.

Table 1. Physical constants of test analytes and solvents.

Compound	Boiling point* (°C)	Vapor pressure* (mm @ 20°C)
TDCE	48	260
MeOH	65	83
Ben	80.1	53
TCE	86.7	67
Tol	111	22
tetraglyme	275	< 1 [†]

* Values obtained from Lide (1990).

† Based on a value given for an ether with the same number of carbon and hydrogen atoms.

analyte concentrations in triplicate samples after 4 days of treatment versus the ratio of MeOH to tetraglyme in the exposure solution, determinations being made by HS/GC. The diagrams show that the sorption of VOCs was not proportional to the analyte concentration in the fortification solution. As shown in Table 1, tetraglyme has a much higher boiling point and lower vapor pressure than all of the other constituents and exhibits surfactant characteristics. Thus, the introduction of tetraglyme not only dilutes the volatile constituents, but imposes molecular interactions that inhibit their vaporization from the solution (Anderson 1992).

The method comparison study (Hewitt et al. 1992) also included short and long treatment periods of 4 and 39–46 days. Table 2 compares triplicate HS/GC analyte determinations for the two treatment periods by showing the percentage of relative change between the 39–46-day and the 4-day concentrations. Both soils exposed to the straight MeOH stock solution showed a consistently large (average of 155%) increase in concentrations, indicating that maximum analyte concen-

Table 2. Percentage of relative change for concentrations after 39–46 days compared to concentrations after 4 days for different solution compositions.

Compound	MeOH/tetraglyme ratio (%)			
	100/0	50/50	10/90	5/95
AO46 soil				
TDCE	185	105 *	79.0*	62.2
Ben	157	100*	91.9*	89.3*
TCE	174	99.1*	95.4*	81.7*
Tol	180	101*	118	112*
Point Barrow soil				
TDCE	152	95.1 *	58.6	78.7
Ben	129	89.7*	95.8*	102*
TCE	130	100*	90.7*	106*
Tol	135	105*	93.2 *	110*

* Concentrations for the two treatment periods are not significantly different at the 95% confidence level using the student's *t*-test.

trations were not obtained after 4 days of treatment. The exposure solutions that contained tetraglyme showed no consistent pattern in analyte concentration with treatment period and often had relative changes within 10% for the three least volatile analytes. Furthermore, a *t*-test analysis at the 95% confidence level often failed to establish a significant concentration difference. These findings suggest that the maximum analyte concentrations remained constant for up to 35 days when the exposure solution was composed of at least a 50:50 mixture of MeOH and tetraglyme.

Exposure vessel

Vapor fortification passively contaminates sorptive materials. Although this hasn't been rigorously demonstrated, once the treatment chamber is sealed, an equilibrium is created between liquid and vapor phases of the constituents present. When soils are exposed in VOA vials, vapor concentrations within the dead volume (volume of vessel not occupied by soil) of the sample vial (< 38 cm³) rival or exceed the levels retained within a 2-g soil test sample on a mass per mass basis. For example, the chamber vapor concentration of Ben, when using a 50:50 fortification solution of the MeOH stock and tetraglyme, was about 2.7 ppm (weight/volume), making the VOA mass about 100 µg. Depending on the soil type, we established between 5 and 30 ppm (µg/g, soil AO46 and the Point Barrow, Alaska, soil respectively) for the test samples. This made it necessary to displace the majority of the vapors not associated with the test matrix before adding an extraction solvent and sealing.

We attempted to displace the dead volume analyte vapor molecules by aspiration and diffusion so that detector responses for empty vials (blanks) would be less than 10% of the test samples. For the method comparison study mentioned above, as well as for the majority of the experiments described here, we did this by aspirating uncapped VOA vials for 10 minutes immediately after removing them from the exposure chamber by placing them along the front edge of a partially closed exhaust hood, where the velocity of air passing over a vial's top was approximately 1.3 m/s (Hewitt et al. 1992). We also tried vapor removal by diffusion under quiescent conditions. Table 3 shows the comparison of average analyte concentrations for vials holding test sample triplicates, identically fortified, but either aspirated for 10 minutes, or allowed sit uncapped for 10, 20 or 30 minutes on a counter top. A student's *t*-test analysis at the 95% confidence level shows that there was no statistical difference between the 10-minute aspiration and 20-minute quiescent treatments for the analyte levels established for the test matrix.

Regardless of which method was used to displace the dead volume vapors, TDCE showed the largest and most

Table 3. Comparison of methods to eliminate VOCs in the VOA dead volume before sample vials are closed. All values ($\mu\text{g/g}$) obtained by HS/GC and reported as mean concentrations $\pm$ standard deviation.

Compound	Aspiration	Diffusion		
	10 min	10 min	20 min	30 min
TDCE	1.79 $\pm$ 0.34*	2.30 $\pm$ 0.25	1.68 $\pm$ 0.08 *	0.51 $\pm$ 0.02
Ben	4.39 $\pm$ 0.17*	5.12 $\pm$ 0.24	4.22 $\pm$ 0.09 *	2.62 $\pm$ 0.13
TCE	4.55 $\pm$ 0.24*	5.16 $\pm$ 0.17	4.60 $\pm$ 0.01 *	2.25 $\pm$ 0.08
Tol	15.2 $\pm$ 0.26*	18.9 $\pm$ 0.87	15.2 $\pm$ 0.07 *	13.8 $\pm$ 0.44

* Values marked are not significantly different at the 95% confidence level.

variable responses for blank vial concentrations, often exceeding 10% of the test samples' response. Blank vial results for the other analytes (Ben, TCE and Tol) were usually less than 5% of the responses obtained for test samples. Values for the blank vial only showed our ability to remove analytes in the dead volume, and no corrections were made on the test samples. In any case, it was apparent that attempts to remove analyte vapors in the dead volume also reduced the concentrations of analytes associated with the test matrix (Table 3); thus, dead space vapors remained an undesirable and potentially troublesome variable.

Another approach that we used was to physically limit the dead volume as a factor by using small, 2.5-mL aluminum foil cups, made to just contain 2 g of soil. Once filled, the dead volume above the soil surface was about 0.5 mL. After vapor fortification, we immediately transferred these cups to a VOA vial using metal tweezers; we paid special attention to not disturbing the soil before we sealed the analysis vessel. Analyses of empty cups serving as blanks typically showed quantities that were less than 1% of the analyte concentrations established for test samples.

Desiccation-soil moisture

To assess the effect of moisture during vapor fortification of soil subsamples, we did separate experiments with a desiccant (anhydrous CaSO_4) and a salt solution. The KCl salt solution created a water vapor pressure (P_A) of approximately 2300 Pa, which corresponds to a relative humidity of around 87%. Fortification, which included either the desiccant or salt solution, consisted of 4-day exposures of the AO46 soil in uncapped VOA vials to a 50:50 solution of the MeOH stock and tetraglyme. Table 4 shows the mean results of HS/GC analysis for these two fortification experiments, as well as a typical set of results obtained when only air drying was used to control the soil moisture content. Clearly, the moisture content of the soil dramatically influenced the concentrations of VOCs retained in the test soil matrix.

These findings are consistent with several studies

(Chiou and Shoup 1985, Smith et al. 1990, Ong and Lion 1991, Goss 1992) that have shown that soil moisture plays an important role in controlling the number of sites available to sorb VOCs. Under typical field conditions (soil relative humidity of 68%), the sorbent (soil grains) is covered with water (Goss 1992), thus transfer of VOCs to the soil surface must cross the air/liquid interface, a process that is governed by Henry's law (Ong and Lion 1991). The VOC's phase, which is especially important for this study since there was little organic matter in the USATHAMA standard materials for aqueous phase partitioning, remains as a transient vapor or is so weakly bound by the hydrated grain surfaces that disaggregation causes immediate release (Hewitt 1992).

It was evident during these attempts to control moisture that extraneous variables were potentially being introduced. Crystals formed in the KCl salt solution, and the color of the CaSO_4 desiccant changed. These observations suggest that the chamber conditions were not stable; that is, the moisture or the analyte vapor concentrations in the desiccator, or both, were most likely dynamic. Results of an experiment indicated that about 80% of the weight loss from a fortification solution could be accounted for by the weight gain of the CaSO_4 desiccant rather than sorption on the soil.

Table 4. Mean concentrations ($\mu\text{g/g}$) for air-dried soils, both treated and untreated, during vapor fortification.

Compound	Treatment		
	CaSO_4	None*	KCl
TDCE	4.6	1.6	0.72
Ben	24	8.8	1.5
TCE	24	11.7	2.0
Tol	108	43	8.1

* Soil sample only air dried.

To avoid the potential problems introduced when attempting to control moisture during vapor fortification, we conditioned soil subsamples ahead of time to eliminate unavoidable variation in air-drying conditions. Desiccation was chosen instead of oven drying, since the latter is more disruptive to a soil's chemical and physical properties. This final preparation step was taken after the soil subsamples had been placed into exposure vessels then placed into the fortification chamber. A 24-hour desiccation period was arbitrarily chosen.

Influence of temperature on vapor treatment

In anticipation of laboratories not being able to precisely control the temperature during vapor fortification, we conducted tests to assess this variable's potential effect. For this experiment, triplicate subsamples of the 130 soil were exposed for 4 days in uncapped VOA vials to 10-mL volumes of a 50:50 MeOH stock and tetraglyme solution. The treatment temperatures—17–18, 20–21 (room temperature) and 23–24°C—were controlled with an environmental chamber. The soil concentrations determined for the three different temperatures are shown in Table 5. An analysis of variance (ANOVA) at the 95% confidence level showed no significant differences for the four test analytes among the different treatment temperatures.

Table 5. Concentrations obtained by HS/GC for vapor fortification at various temperatures. All values reported as mean concentrations ($\mu\text{g/g}$) $\pm$ standard deviation.

Compound	Temperature ($^{\circ}\text{C}$)		
	17–18	20–21	23–24
FDCE	1.1 $\pm$ 0.22	0.92 $\pm$ 0.22	0.70 $\pm$ 0.34
Ben	3.4 $\pm$ 0.34	3.0 $\pm$ 0.22	3.0 $\pm$ 0.46
TCE	4.1 $\pm$ 0.36	3.7 $\pm$ 0.27	3.6 $\pm$ 0.52
Tol	14.6 $\pm$ 0.63	13.6 $\pm$ 0.64	13.7 $\pm$ 0.81

Concentration range

In practice, vapor fortified QA/QC soil samples could be used in-house or for monitoring the performance of contract laboratories. For these applications and others, it would be useful to be able to create test samples at different concentrations. To assess the range of analyte concentrations that could be readily achieved with the present stock solution, triplicate test samples of the 130 soil were exposed in VOA vials to a mixture composed of 25 mL of both MeOH and tetraglyme. Analyte concentrations were varied in the exposure solution by using the straight MeOH stock and 10- and 100-fold dilutions of this stock solution with MeOH before combining with tetraglyme.

Table 6. Concentrations obtained by HS/GC for three vapor fortification experiments performed with different levels of analytes. All values reported as mean concentrations ($\mu\text{g/g}$) $\pm$ standard deviation.

Compound	Volume of stock standard (mL)		
	25	2.5	0.25
TDCE	1.60 $\pm$ 0.45	0.312 $\pm$ 0.074	0.0495 $\pm$ 0.0063
Ben	4.19 $\pm$ 0.31	0.464 $\pm$ 0.039	0.0604 $\pm$ 0.0019
TCE	4.84 $\pm$ 0.38	0.504 $\pm$ 0.039	0.0664 $\pm$ 0.0022
Tol	7.32 $\pm$ 0.43	0.784 $\pm$ 0.039	0.1020 $\pm$ 0.0000

The results (Table 6) show that the HS/GC concentrations established approach values that would have been predicted based on dilution of the stock standard. This range in concentration, approximately 5 $\mu\text{g/g}$ to 50 ng/g , encompasses the action levels typically used to guide site investigators for the treatment of contaminated soils. In comparison to the correlation between analyte concentration in the fortification solution and analyte sorption by the test matrix shown in Figure 3, this approach results in a more linear correlation. Thus, by using a constant ratio of MeOH to tetraglyme, another troublesome variable could be avoided. This stands to reason since MeOH has a boiling point and vapor pressure similar to those of the test analytes (Table 1); thus, changing its solution concentration would affect its vapor pressure (i.e., vapor concentration).

To assess the amount of MeOH sorbed, 2-g test samples of the 130 soil were exposed in VOA vials to a 50:50 mixture of the MeOH stock solution and tetraglyme, aspirated for 10 minutes, then prepared for HS/GC analysis by extracting with 30 mL of water. Analysis of the aqueous extracts by differential refractometry established 4.6 $\pm$ 0.3 mg MeOH/g , while empty VOA vials were below detection (1.5 mg/VOA). Gravimetric analysis for identically treated samples taken directly from a desiccator without aspiration established weight gains of 5.1 $\pm$ 0.2 mg MeOH/g for test samples. These two sets of results show that MeOH was the dominant analyte sorbed by the soil.

Holding time

For hazardous waste site investigations, fortified soil used for performance evaluation must remain stable, in the absence of biological activity, for at least the 14-day holding period specified by EPA SW 846 (EPA 1986). To assess this parameter, we studied holding time with duplicate test samples of the 130 soil in VOA vials fortified by exposure to a 1:20 dilution of an MeOH stock solution with tetraglyme. After treatment, test samples were aspirated for 10 minutes. Before the vials were capped, either 30 mL of type I water was added for HS/GC analysis or the special purge-and-trap adapter for PT/GC/MS analysis was used.

Table 7. Concentrations ($\mu\text{g/g}$) obtained for holding time study. All values reported as mean concentrations $\pm$ standard deviation.

Compound	HS/GC		PT/GC/MS	
	0-day	14-day	0-day	14-day
TDCE	0.13 ± 0.029	0.13 ± 0.034	0.30 ± 0.18	0.29 ± 0.032
Ben	0.60 ± 0.083	0.56 ± 0.086	0.59 ± 0.15	0.54 ± 0.053
TCE	0.37 ± 0.054	0.33 ± 0.064	0.42 ± 0.12	0.38 ± 0.039
Tol	2.10 ± 0.22	1.90 ± 0.28	1.70 ± 0.35	1.60 ± 0.078

One set of test samples was analyzed on the day they were removed from the exposure chamber by both HS/GC and PT/GC/MS. A second set was stored refrigerated at 4°C for 14 days prior to analysis. According to *t*-tests of the concentrations obtained for the two holding periods (Table 7), no significant changes were detected for each method of analysis at the 95% confidence level. Moreover, only the TDCE concentrations were significantly different between the methods of analysis when the values for each of the two holding times were compared. These results suggest that fortified samples can be stored for at least 14 days without significant VOC losses. It is uncertain, however, whether the effects of air drying, desiccation and the amount of MeOH sorbed will completely inhibit biological degradation in unknown soil matrices.

SUMMARY AND RECOMMENDATIONS

This preliminary study evaluates some of the parameters and handling protocols required to create VOC-contaminated QA/QC soil samples. If this procedure is to be robust, as few variables as possible should be involved, and those that remain should have diminished influences. With this in mind, the overall results showed that when vapor fortification solutions contained tetraglyme, along with MeOH, analyte sorption reached maximum concentration levels after relatively short treatment periods (Fig. 2, Table 2). Results also indicated that VOC concentrations were not significantly influenced by small temperature fluctuations (Table 5). For site investigations, the results from using a constant MeOH-to-tetraglyme ratio suggest that both predictable and stable (at least for 14 days) concentrations, covering the range now used for action guidelines, could be easily achieved. Moreover, maintaining a constant ratio of major constituents in the exposure solution eliminates the amount of MeOH sorbed by the test material from becoming a variable. Conditioning an air-dried, sieved and thoroughly mixed soil by 24 hours of desiccation appears to be a reasonable approach to removing the potential influence of relative humidity. Additionally, using an exposure vessel with limited dead volume eliminates another potentially problematic variable.

I recommend the following procedure to prepare vapor fortified soils for use as performance evaluation samples.

Soil preparation before exposure

The test soil should be sieved through a 30 mesh to remove large particles and debris, mixed thoroughly, air dried, desiccated with anhydrous CaSO_4 for 24 hours after being placed into sample vessels and transferred to the treatment desiccator.

Vapor fortification

An exposure solution, composed of 50 mL of a 50:50 mixture of MeOH and tetraglyme, should be prepared containing the analytes of interest and placed in an open glass bottle inside the desiccator. The soil samples should be exposed to vapors generated by the organic solution for at least 5 days in the closed chamber.

Sample collection

After fortification, the chamber should be opened and the vessel removed; care must be taken not to agitate the test matrix. Dead volume vapors will have been addressed before the analysis vessel is sealed, the method for doing this depending on whether VOA vials or aluminum cups were used.

To assess the precision of this protocol when 2.5-mL aluminum foil cups were used as the exposure vessels, three separate fortification tests were done with triplicate samples. The test matrix was 2-g subsamples of the 130 soil. Upon removal from the exposure chamber, the aluminum foil cups were placed with minimal disruption into VOA vials containing 30 mL of water, being capped before submersion. Only the exposure periods used—7 and 9 days—were not held constant. The 100-mL MeOH stock solution contained approximately 0.490 g of TDCE, 0.369 g of Ben, 0.597 g of TCE and 0.600 g of Tol. The HS/GC results for these three separate fortifications are shown in Table 8. An ANOVA failed to establish any significant differences among the three sets of average analyte concentrations. The relative standard deviation for the triplicate test samples ranged from 23 to 2%, and showed an inverse relationship with the boiling points (direct relationship with vapor pressure) of the VOCs tested.

Table 8. Concentrations ($\mu\text{g/g}$) obtained for three separate vapor fortifications.

Compound	A	B	C
TDCE	$5.87 \pm 1.34^*$ (22.9%) [†]	5.77 ± 1.29 (22.3%)	5.84 ± 0.83 (14.2%)
Ben	6.83 ± 0.61 (8.90%)	7.06 ± 0.48 (6.78%)	6.96 ± 0.44 (6.35%)
TCE	8.17 ± 0.66 (8.10%)	8.66 ± 0.40 (4.62%)	8.41 ± 0.61 (7.31%)
Tol	9.82 ± 0.44 (4.47%)	10.5 ± 0.21 (1.98%)	10.2 ± 0.34 (3.31%)

* Mean $\pm$ standard deviation.

[†] Relative standard deviation.

The results show vapor fortification to be a promising alternative way of producing VOC-treated soils for performance evaluation. The procedure selected attempts to limit the number of parameters requiring special attention. The experimental results suggest that the following variables and potential variables can be easily controlled: treatment period, typical laboratory treatment temperatures, laboratory relative humidity and the composition of major constituents used in the exposure solution (i.e., the amount of MeOH sorbed by the test matrix). The sample handling protocols that were established resulted in precise test sample triplicates, with relative standard deviations of less than 9% for the three least volatile analytes. Moreover, the average analyte concentrations from among three separate fortifications were not significantly different at the 95% confidence interval.

The advantages of using vapor fortification as a method of preparing quality control samples versus direct injection of either aqueous or methanolic solutions is that it allows for evaluation of both the extraction process and instrumental performance (Hewitt et al. 1992). The efficiency of an extraction method is often attributed to the influence that soil organic matter has on the partition coefficients, and is particularly important for the more hydrophobic VOCs (Karickhoff et al. 1979, Chiou et al. 1983, Kiang and Grob 1986, Boyd and Sun 1990). This phenomenon, however, has not been addressed by other methods for creating soils matrix standards. Vapor fortification could provide quality control samples that could simultaneously be certified for both portable GC methods using aqueous extraction suitable for on-site analysis and EPA accepted laboratory protocols.

I do not want to imply that this method, as it is now, is suitable for quality control and performance evaluation standards. Standards require that the concentration of the analytes be obtained accurately and quality control reference materials require large-scale replication

and long-term stability. Although there is no reason to believe that these criteria cannot be met using vapor fortification, additional studies will be required. A logical first step would be to see if precise performance evaluation samples could be prepared in glass ampoules, thus packaging the samples in a manner common to several current quality control and performance evaluation standard materials.

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