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Comparison of Sample Preparation Methods for the Analysis of Volatile Organic Compounds in Soil Samples: Solvent Extraction vs Vapor Partitioning

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Presently, both direct vapor partitioning and solvent extraction methods of sample preparation are commonly used for the characterization of volatile organic compounds (VOCs) in soil. These two approaches of recovering VOCs from this matrix, and other forms of solid waste, are often used interchangeably without any recognition of how different parameters (enviromental and procedural) influence their performance. Three vapor partitioning headspace and three solvent extraction methods of preparing soil samples for the determination of VOCs were compared, without being confounded by volatilization or biodegradation losses. Soil samples were spiked with five aromatic and four chlorinated compounds using two different laboratory procedures. Recovery efficiencies for the preparation methods tested depended on soil organic carbon content, the octanol−water partition coefficients of specific analytes, and the duration of solvent extraction. Overall, methanol extraction was the most efficient and robust method for recovering spiked VOCs. Recovery of VOCs with tetraethylene glycol dimethyl ether and poly(propylene)glycol, as well as three vapor partitioning headspace methods, were frequently less than that obtained with methanol.

Introduction

Methods for the collection and analysis of soil samples from sites where volatile organic compound (VOC) contamination is present continue to be actively researched and debated. Over the last several years, an accumulating body of scientific evidence has shown that volatilization (*1*−*8*) and preservation (*9*−*11*) issues were not adequately addressed by Method 5030 (purge-and-trap) and Section 4.1 (sampling) of the U.S. Environmental Protection Agency's *Test Methods for Evaluating Solid Waste SW-846* (12). To address these concerns, the Office of Solid Waste, U.S. EPA, has adopted two new sample collection and analysis procedures, Methods 5035 and 5021. For sample analysis, Method 5035 uses dynamic purging, while static headspace is used for Method 5021. These methods both recommend in-vial methods to solve the volatilization issues that plague VOC determinations in solid waste matrices. When using an in-vial method, samples collected in the field or prepared in the laboratory are transferred directly to vessels that can be hermetically sealed. Furthermore, these vessels either contain an organic solvent or allow a vapor partitioning analysis (dynamic or static, i.e., purge-and-trap or headspace) to be performed without opening (*12*). In the case of solvent extraction, an aliquot of extractant is transferred to organic free water for either dynamic or static vapor partitioning analysis.

Distinguishing if these two (vapor partitioning or solvent extraction) general approaches to sample preparation are equivalent for the recovery of VOCs from a given matrix is not a simple task. The majority of past studies have only provided an assessment of total measurement of error, that is, they fail to separate and identify the various types and sources of determinant (systematic) and indeterminate (random) error. Therefore, providing no clear understanding of how environmental variables quantitatively influence the performance of various sample preparation metohds. Those studies that have minimized determinant error (e.g., volatilization and biological losses), while assessing indeterminate error associated with various methods of preparing samples for analysis, have used in-vial procedures (*5, 7, 13*−*15*).

Results from an in-vial approach have clearly shown that different sample preparation methods do not necessarily produce the same quantitative values. Samples prepared by aqueous dispersion-vapor partitioning often yield lower VOC concentration estimates than MeOH extraction (*13*−*17*). In general, this finding is consistent with numerous studies of VOCs in aquifer materials that have shown that sorption (reduction of analyte activity in the aqueous phase) is dependent on both the analyte's hydrophobicity or solubility and the organic carbon content of the matrix (*18, 19*).

This study assesses differences among three solvents and three headspace (HS) vapor partitioning methods used to recover VOCs from discrete soil (grab) samples for quantitative determination. The extraction solvents studied were MeOH, tetraethylene glycol dimethyl ether (tetraglyme), and poly(propylene)glycol (PPG). The three equilibrium HS sample preparation and analysis methods studied were direct moderate temperature (60 °C) heating (H-HS) (*20*), dispersion in water acidified with sodium bisulfate (Aq-$NaHSO_4$-HS) (*11*), and dispersion in water saturated with sodium chloride and acidified with phosphoric acid (Aq-NaCl saturated-HS) (*12, 21, 22*). With the exception of H-HS method of analysis, which is intended for rapid on-site screening, all of these sample preparation methods include a preservative (solvent immersion or acidification) to inhibit biological degradation of aromatic compounds (*9*−*11, 12*). Tetraglyme and PPG were studied in the interest of providing information about alternative solvents that do not have the same regulatory (e.g., flammability or toxicity) concerns as MeOH. The two aqueous dispersion methods were included to highlight the influence of using a high salt content (matrix modifier) to enhance analyte partitioning. All of these methods of sample preparation and analysis are of interest to state and federal agencies concerned with VOCs in the vadose zone, particularly, those agencies wishing to simplify their standard operating procedures, by specifying a single method of sample preparation.

For each comparison, all of the samples were handled in a fashion that prevented volatilization losses prior to and during HS gas chromatography (GC) analysis. The prepared laboratory samples included five soils of various organic carbon and clay contents, spiked with benzene (Ben), toluene (Tol), ethylbenzene (E-Ben), *p*-xylene (*p*-Xyl), *o*-xylene (*o*-Xyl), *trans*-1,2-dichloroethene (TDCE), *cis*-1,2-dichloroethene

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TABLE 1. Soil Characteristics

description	abbreviation	soil type	% organic carbon[a]
Ottawa sand	Ott	>99% sand	0.035
Ft. Edwards	Ft. E	>90% clay	0.5
CRREL	CR-A	silty/sand	1.5
Pt. Barrow Alaska	Pt. B	silty/clay	7.1
CRREL	CR-B	silty/sand	0.90

[a] Leco CR-12 furnace analysis (*32*).

TABLE 2. Octanol−Water Partition Coefficients and Boiling Points of Analytes

compound (abbreviation)	log octanol−water partition coefficient[a]	boiling pt (°C)
trans-1,2-dichloroethene (TDCE)	2.09	47.2
cis-1,2-dichloroethene (CDCE)		55.0
benzene (Ben)	2.13	80.1
trichloroethene (TCE)	2.53	87.2
tetrachloroethene (PCE)	2.60	121.0
toluene (Tol)	2.65	110.6
o-xylene (o-Xyl)	2.95	144.0
ethylbenzene (E-Ben)	3.13	136.2
p-xylene (p-Xyl)	3.18	138.4

[a] Log of octanol−water partition coefficient.

(CDCE), trichloroethene (TCE), and tetrachloroethene (PCE). Two laboratory spiking methods were used: an aqueous treatment with a 2-day sample equilibration and vapor fortification with a 6-week sample equilibration period.

Experimental Methods

Two laboratory sample spiking procedures, six sample preparation methods, and one analysis method are described below. Characteristics of the various soil matrices studied and the octanol−water partition coefficients and boiling points of the analytes are presented in Tables 1 and 2, respectively.

Soil Subsample Preparation: *Aqueous Treatment*. An aqueous spiking solution was prepared by adding microliter volumes (3.1−5.8 μL) of reagent grade Ben, Tol, E-Ben, *p*-Xyl, *o*-Xyl, TDCE, CDCE, TCE, and PCE to a 100-mL volumetric flask containing about 103 mL of groundwater. Once all the analytes had been transferred via a microliter syringe (Hamilton), the solution was mixed for 48 h with a stirring bar. The target concentration of each analyte was 50 mg/L; however, some volatilization losses occurred.

Four different air-dried soils were spiked with this aqueous solution (Table 3). Fifteen 2.00 ± 0.01-g subsamples of each soil type were transferred to 1-mL glass ampoules using a funnel and spatula. This weight of soil completely filled the main body of the ampoules. To spike, each soil-filled ampoule was placed in a metal tension clamp, a 0.200-mL aqueous spike was introduced using a 0.500-mL glass syringe (Hamilton), the aqueous solution was allowed to soak in for a few seconds, and then the ampoule was heat-sealed with a propane torch. All spike aliquots were taken from well below the water−air interface, and the stainless steel needle was wiped prior to being inserted into the ampoule neck.

In addition to being used for preparing the soil subsamples, the spiking solution, in 0.200-mL aliquots was also placed into three separate auto sampler volatile organic compound analysis (VOA) vials (22 mL, Tekmar) containing 10 mL of organic free water and immediately capped with crimp-top caps and Teflon-faced butyl rubber septa (Wheaton). These aliquots were taken at the beginning, middle and end of the soil sample preparation process (~1 h) to assess the spiking solution concentration and to determine whether there were any significant changes in VOC concentration during sample treatment.

The 60 sealed ampoules containing treated soil were placed in a refrigerator at 4 °C for 2 days to allow the analytes to interact with the matrix. Longer or warmer equilibration conditions were not used because of possible losses due to biodegradation of the aromatic compounds (*11*). Then they were removed, and triplicates of each soil type (3 × 4) were randomly assigned to each of five different sample preparation and analysis protocols (Table 3). Each ampoule was then placed inside a VOA vial, and after capping, the soil was dispersed by hand shakingthe vial, causing only the ampoule to break. Once the soil had been completely removed from the broken ampoule, the VOA vials were returned to the refrigerator for storage until analysis (Table 3). The three auto sampler vials used to monitor spike concentration and solution homogeneity were analyzed by HS/GC within 24 h of preparation.

Vapor Fortification Treatment. For this experiment, 18 replicate subsamples of the CR-B soil were vapor fortified. A more complete description of this vapor fortification protocol, which was originally development to create performance evaluation samples, can be found elsewhere (*23*). Briefly, ampoules containing 2.00 ± 0.01 g of soil were first placed in a desiccator with anhydrous $CaSO_4$ for 48 h. After desiccation, the $CaSO_4$ was replaced with a small glass bottles containing 5 mL of tetraglyme and 0.5 mL of a MeOH-based stock standard. The stock standard had been prepared by adding (and weighing) 0.100 mL each of TDCE, CDCE, Ben, TCE, and PCE and 0.150 mL of Tol, E-Ben, *p*-Xyl, and *o*-Xyl to MeOH; this was taken to volume in a 25-mL volumetric flask. The fortification solution and open ampoules of soil were left in the desiccator at room temperature (21 ± 2 °C) for about 6 weeks. At the end the vapor fortification treatment period, the desiccator was opened and a 5-mm glass bead was placed on top of each ampoule, to serve as a temporary cap. Then, as quickly as possible, each was heat sealed with a propane torch.

The sealed ampoules were stored for 4 or 6 days in a refrigerator (4 °C) before triplicates were removed for different sample preparation and analysis protocols. Sample preparation was staggered over 2 days so that analyte determinations could be made within 2 h of the ampoule being broken for the vapor partitioning methods or a 0.100-mL aliquot of the solvent could be removed after 2 h of extraction.

Subsample Preparation for Analysis. *Heated Equilibrium HS/GC Analysis (H-HS)*. Ampoules containing laboratory-spiked soil were transferred to empty auto sampler VOA vials that were then capped. Once the vials were hermetically sealed, the ampoules were broken and the soil completely dispersed by careful hand shaking the vial. In all cases HS vapors were removed the same day the ampoules were broken after the samples were heated to 60 °C for 50 min (20).

Aqueous Dispersion/Extraction in a NaCl-Saturated Solution Acidified with H_3PO_4, Equilibrium HS/GC Analysis (Aq-NaCL saturatedd-HS). An aqueous dispersion solution was prepared by acidifying 500 mL of organic free water with H_3PO_4 to pH 2, then adding 180 g of NaCl; 10 mL of this solution was transferred to an auto sampler VOA vial, and an ampoule of spiked soil was added. Once the vials were sealed, the ampoules were broken and their contents completely dispersed. Prior to HS vapors being removed, the soil water slurry was heated to 85 °C for 60 min (*12*, *21*, *22*).

Aqueous Dispersion/Extraction in a Solution Acidified with $NaHSO_4$, Equilibrium HS/GC Analysis (Aq-$NaHSO_4$-HS). Organic free water (10 mL) and 0.25 g of $NaHSO_4$ were placed into auto sampler VOA vials, then ampoules were introduced. Once the vials were sealed, the ampoules were broken and

TABLE 3. Experimental Designs: Soil Types, Sample Replicates, and Methods of Sample Preparation for Analysis

experiment	no. of rep	soil types	methods of sample preparation[a]	extraction/partitioning period and conditions
aqueous spike	15	Ott	a. heated HS	<1 day
	15	Ft. E	b. aqueous solution acidified with $NaHSO_4$	2 days, 4°C
	15	CR-A		
	15	Pt. B	c. aqueous solution NaCl saturated and acidified with H_3PO_4	1 day, 4 °C
			d. MeOH extraction	5 days, 4°C
			e. tetraglyme extraction	6 days, 4°C
vapor fortification treatment	18	CR-B	a. heated HS	<2 h
			b. aqueous solution acidified with $NaHSO_4$	<2 h
			c. aqueous solution NaCl saturated and acidified with H_3PO_4	<2 h
			d. MeOH extraction	<2 h, 2,4, and 29 days, 22 °C
			e. tetraglyme extraction	same as MeOH
			f. PPG extraction	same as MeOH

[a] Triplicates of a soil type were used for each method of sample preparation.

their contents completely dispersed. Prior to HS vapors being removed, the VOA vial was held for 20 min at 25 °C.

MeOH, Tetraglyme and PPG Solvent Extraction. Five milliliters of HPLC grade MeOH, reagent grade tetraglyme or PPG was transferred to separate VOA vials and an ampoule containing spiked soil was placed in each. After the vials were capped, the ampoules were broken, and the soil was completely dispersed by hand shaking the vial. A 0.100-mL aliquot was removed from each and transferred to an auto sampler vial containing 10 mL of organic free water for analysis. Prior to removal of HS vapors from the VOA vials containing the aqueous-solvent solutions, they were held for 20 min at 25 °C.

Analysis

All samples were analyzed with a HS auto sampler (Tekmar 7000) coupled to a GC (SRI model 8610-0050) equipped with a 15-m DB1 0.53 capillary column and sequential photo ionization-flame ionization detectors. Prior to the VOA vials (22 mL) being transferred to the auto sampler system, they were allowed to reach room temperature and each was shaken for approximately 2 min. Vial pressurization settings of 7 and 10 lb/in^2 (48 and 69 kPa) were used, respectively, for the 25 and 85 °C equilibration temperature settings. When using the vapor partitioning HS methods, each sample was sacrificed upon analysis, due to the approximately 5 mL of headspace vapor that is removed during the analysis step. In contrast, several aliquots could be removed when samples were placed in an extraction solvent, thus allowing for an assessment of extraction kinetics (Table 3). Between solvent extraction periods, samples were held at room temperature (21 ± 2 °C), and only briefly shaken some 30 min prior to the removal of an aliquot of the extractant.

For each sample preparation procedure, analyte concentrations were established relative to HS standards prepared by adding small (≤ 2 μL) quantities of a MeOH stock solution to auto sampler vials containing the same solution composition and volume as the samples (e.g., 10 mL of organic free water and 0.100 mL of organic solvent, to match the volume of sample extract, or the appropriate acid-salt to match the preservative/matrix modifier). Therefore, the composition of the aqueous solutions analyzed was identical for samples and standards, except for the presence of the treated soil and glass ampoule in those samples prepared by vapor partitioning methods. Because 2 g of soil and the broken glass ampoules were present for the three vapor partitioning HS methods, these samples contained an additional phase that reduced the vapor phase volume (i.e., the glass ampoule and soil occupied approximately 2 cm^3, the total VOA vial volume was 22 mL) as compared to the standards. No correction was made for this HS volume discrepancy between the samples and standards. On the basis of both empirical and theoretical evaluations, the reduced headspace volume of approximately 2 cm^3 for these samples may cause as much as a 10% enhancement in analyte concentration (*17, 24*).

Results

Aqueous Treatment. The spike concentrations and the analyte recoveries from the different soil matrices, as achieved by five different subsample preparation methods, appear in Table 4. The standard deviations of these analyte determinations demonstrate that each sample preparation and analysis procedure was precise (RSDs were generally less than 5%). A one-way of variance (ANOVA) and least significant difference (Fishers Protected LSD) test, both conducted at the 95% confidence level, were performed for each sample preparation method and for each analyte, to see if there were any significant differences between the spike and measured concentrations for the various soil matrices.

MeOH extraction was the only sample preparation method that yielded quantitative recoveries for all the analytes in all soils tested (Table 4). In general, tetraglyme showed good recoveries of TDCE, CDCE, Ben, and TCE; however, recoveries of the other analytes from the soils, other than Ott sand, often were significantly lower than expected. The recoveries declined as the percent organic carbon in the soil matrix and the octanol−water partition coefficients of the analytes increased. For example, less than 80% of the *o*-Xyl, E-Ben, and *p*-Xyl were recovered from the Pt. B soil as compared to the Ott sand.

In general, the pattern established for tetraglyme was also repeated by each of the vapor partitioning HS sample preparation and analysis methods, i.e., total recovery from the Ott soil and less than total for the other three matrices, except that the number and magnitude of differences between the spiked and recovered amounts increased (Table 3). In particular, percent recoveries were much lower for high K_{ow} analytes in soils with high organic carbon. In the worst case, only about 8% of the *o*-Xyl spiked onto the Pt. B soil was recovered using the Aq-NaCl saturated-HS method, as compared to the Ott sand.

Vapor Fortification Treatment. Table 5 shows the mean and the standard deviation for the analyte concentrations of the vapor fortified samples as established by six different sample preparation methods. Two one-way ANOVA tests were performed at the 95% confidence level with this data set. In each case, the Fisher's Protected LSD was performed to determine which values were significantly different. First, a six-method comparison was made for samples prepared

TABLE 4. Means and Standard Deviations of Triplicate Analyte Spike and Recovery Concentrations[a]

	analyte concentration (μg)[b]				
analyte	**spike**	**Ott**	**Ft. E**	**CR-A**	**Pt. B**
			MeOH Extraction		
TDCE	8.26 ± 0.25	8.23 ± 0.21	8.57 ± 0.10	8.23 ± 0.46	8.33 ± 0.17
CDCE	8.45 ± 0.24	8.15 ± 0.41	8.70 ± 0.16	8.42 ± 0.44	8.53 ± 0.28
Ben	5.83 ± 0.18	5.60 ± 0.21	5.93 ± 0.11	5.75 ± 0.30	5.86 ± 0.20
TCE	9.98 ± 0.29	9.58 ± 0.46	9.75 ± 0.14	9.64 ± 0.40	9.82 ± 0.33
PCE	9.10 ± 0.28	8.66 ± 0.35	9.24 ± 0.16	8.95 ± 0.45	8.94 ± 0.46
Tol	6.54 ± 0.20	6.58 ± 0.28	6.69 ± 0.18	6.64 ± 0.43	6.56 ± 0.18
o-Xyl	6.71 ± 0.20	7.03 ± 0.57	7.20 ± 0.08	7.10 ± 0.29	6.92 ± 0.19
E-Ben	6.23 ± 0.26	6.08 ± 0.27	6.50 ± 0.16	6.38 ± 0.48	6.29 ± 0.40
p-Xyl	6.22 ± 0.14	6.27 ± 0.20	6.50 ± 0.16	6.55 ± 0.65	6.34 ± 0.31
			Tetraglyme Extraction		
TDCE	8.26 ± 0.25a	8.30 ± 0.12a	7.76 ± 0.03b	7.68 ± 0.32b	8.02 ± 0.28a,b
CDCE	8.45 ± 0.24a	8.28 ± 0.10a,b	7.93 ± 0.16b	7.87 ± 0.40b	8.17 ± 0.18a,b
Ben	5.83 ± 0.18	5.82 ± 0.12	5.57 ± 0.06	5.55 ± 0.17	5.62 ± 0.19
TCE	9.98 ± 0.29a	10.0 ± 0.26a	9.42 ± 0.10b	9.56 ± 0.40a,b	9.38 ± 0.35b
PCE	9.10 ± 0.28a	8.87 ± 0.16a,b	8.42 ± 0.36b	8.39 ± 0.10b	7.64 ± 0.51c
Tol	6.54 ± 0.20a	6.42 ± 0.14a,b	6.13 ± 0.15b,c	6.14 ± 0.15b,c	5.87 ± 0.27c
o-Xyl	6.71 ± 0.20a	6.58 ± 0.18a	6.32 ± 0.42a	6.32 ± 0.04a	5.03 ± 0.35b
E-Ben	6.23 ± 0.26a	5.87 ± 0.14a	5.48 ± 0.20b	5.47 ± 0.08b	4.56 ± 0.25c
p-Xyl	6.22 ± 0.14a	6.02 ± 0.13a,b	5.67 ± 0.25b,c	5.53 ± 0.12c	4.64 ± 0.28c
			H-HS Analysis		
TDCE	8.26 ± 0.25a,b	8.68 ± 0.22a	8.12 ± 0.41b	8.22 ± 0.20a,b	8.09 ± 0.20b
CDCE	8.45 ± 0.24b	9.24 ± 0.16a	8.56 ± 0.38b	8.30 ± 0.27b	6.94 ± 0.08c
Ben	5.83 ± 0.18a,b	6.10 ± 0.14a	5.75 ± 0.26b	5.73 ±'.09b	4.47 ± 0.06c
TCE	9.98 ± 0.29a,b	10.5 ± 0.15a	9.72 ± 0.44b,c	9.28 ± 0.42c	7.17 ± 0.07d
PCE	9.10 ± 0.28a,b	9.74 ± 0.32a	8.86 ± 0.46b,c	8.45 ± 0.39c	5.38 ± 0.29d
Tol	6.54 ± 0.20b	7.00 ± 0.23a	6.18 ± 0.39b	6.15 ± 0.05b	3.84 ± 0.10c
o-Xyl	6.71 ± 0.20b	7.38 ± 0.16a	5.98 ± 0.28c	5.48 ± 0.04d	2.24 ± 0.13e
E-Ben	6.23 ± 0.26b	6.93 ± 0.20a	5.68 ± 0.40c	5.58 ± 0.18c	2.72 ± 0.06d
p-Xyl	6.22 ± 0.14b	6.80 ± 0.16a	5.70 ± 0.16c	5.40 ± 0.13d	2.57 ± 0.14e
			HS-$NaHSO_4$		
TDCE	8.26 ± 0.25a	8.35 ± 0.09a	5.56 ± 0.37d	7.81 ± 0.21b	6.54 ± 0.21c
CDCE	8.45 ± 0.24a	8.37 ± 0.06a	5.58 ± 0.41d	7.83 ± 0.17b	6.40 ± 0.24c
Ben	5.83 ± 0.18a	5.83 ± 0.02a	3.95 ± 0.25c	5.41 ± 0.12b	4.03 ± 0.13c
TCE	9.98 ± 0.29a	10.2 ± 0.21a	6.60 ± 0.74c	8.71 ± 0.21b	5.21 ± 0.10d
PCE	9.10 ± 0.28a	9.10 ± 0.07a	5.71 ± 0.34b	5.85 ± 0.13b	2.32 ± 0.06c
Tol	6.54 ± 0.20a	6.51 ± 0.05a	4.34 ± 0.28c	5.46 ± 0.17b	2.95 ± 0.08d
o-Xyl	6.71 ± 0.20a	6.62 ± 0.16a	4.37 ± 0.20b	3.91 ± 0.15c	1.46 ± 0.08d
E-Ben	6.23 ± 0.26a	6.37 ± 0.08a	4.09 ± 0.23b	3.99 ± 0.18b	1.53 ± 0.05c
p-Xyl	6.22 ± 0.14a	6.00 ± 0.16a	3.87 ± 0.26b	3.51 ± 0.14c	1.31 ± 0.07d
			HS-NaCl/H_3PO_4		
TDCE	8.26 ± 0.25a	8.85 ± 0.46a	6.74 ± 0.69b	6.67 ± 0.10b	4.58 ± 0.09c
CDCE	8.45 ± 0.24a	8.66 ± 0.29a	6.45 ± 0.75b	6.10 ± 0.21b	3.42 ± 0.04c
Ben	5.83 ± 0.18a	6.33 ± 0.31a	4.71 ± 0.55b	4.24 ± 0.17b	2.09 ± 0.20c
TCE	9.98 ± 0.29a	10.8 ± 0.61a	7.37 ± 0.95b	5.91 ± 0.39c	2.51 ± 0.15d
PCE	9.10 ± 0.28b	9.99 ± 0.51a	5.39 ± 0.34c	3.45 ± 0.37d	1.24 ± 0.13e
Tol	6.54 ± 0.20b	7.16 ± 0.28a	4.69 ± 0.32c	3.20 ± 0.22d	1.18 ± 0.08e
o-Xyl	6.71 ± 0.20a	6.93 ± 0.32a	3.33 ± 0.27b	1.60 ± 0.10c	0.53 ± 0.02d
E-Ben	6.23 ± 0.26b	6.94 ± 0.30a	3.40 ± 0.18c	1.84 ± 0.16d	0.62 ± 0.02e
p-Xyl	6.22 ± 0.14a	6.54 ± 0.37a	3.07 ± 0.29b	1.61 ± 0.14c	0.54 ± 0.03d

[a] For each analyte with the same method of sample preparation and analysis, values with the same letter (or no letter at all) are not significantly different from each other at the 95% confidence level. [b] Benzene (Ben), toluene (Tol), ethylbenzene (E-Ben), *p*-xylene (*p*-Xyl), *o*-xylene (*o*-Xyl), *trans*-1,2-dichloroethylene (TDCE), *cis*-1,2-dichloroethylene (CDCE), trichloroethylene (TCE), and tetrachloroethylene (PCE).

for vapor partitioning and analyzed within 2 h or extracted with a solvent for 2 h. Secondly, an analysis was performed comparing the analyte concentrations relative to the length of the solvent extraction period.

The results of the statistical analysis of the six sample preparation analyses procedures performed within a 2-h period showed that MeOH extraction and Aq-$NaHSO_4$-HS usually produced the highest analyte concentrations (eight of the nine VOCs tested; Table 4). H-HS gave the highest recovery for TDCE, the most volatile analyte; however, recoveries tended to decline relative to MeOH extraction for the lower boiling point compounds, to the extent that H-HS obtained the lowest recovery among the six methods for E-Ben, *p*-Xyl, and *o*-Xyl. Tetraglyme and Aq-NaCl saturated-HS gave similar recoveries that were significantly below MeOH and Aq-$NaHSO_4$-HS, but above PPG solvent extraction.

Figure 1 is an example of trends established by plotting the mean concentrations of Tol as determined by the analysis of three solvent extracts for the various extraction periods. In this figure, points designated with different letters are significantly different at the 95% confidence level. With the exception of the 2- and 4-day extraction periods, which often showed no significant change, MeOH extraction gave increasingly higher analyte concentrations with time. In contrast, after the initial extraction period, tetraglyme failed to show a significant increase in analyte concentration for TDCE, CDCE, Ben, TCE, and PCE, but did for the other four analytes. PPG only showed an initial increase in concentra-

TABLE 5. Means and Standard Deviations of Triplicate Analyte Determinations for the Vapor Fortified CR-B Soil

		analyte concentration (μg/g)[a]								
method	time	TDCE	CDCE	Ben	TCE	Tol	PCE	E-Ben	*p*-Xyl	*o*-Xyl
HS-$NaHSO_4$	1−2 h	0.68c[b] ± 0.05	1.53a ± 0.12	1.40a ± 0.08	1.64a ± 0.07	2.54a ± 0.05	2.49a ± 0.07	2.56a ± 0.12	2.41b ± 0.06	2.36b ± 0.05
HS-NaCl/H_3PO_4	1−2 h	0.45d ± 0.02	1.15b ± 0.01	0.99c ± 0.01	1.05c ± 0.02	1.61c ± 0.01	1.62c ± 0.03	1.58c ± 0.02	1.40d ± 0.03	1.37b ± 0.05
heated-HS	1−2 h	1.28a ± 0.02	1.12b ± 0.08	1.04bc ± 0.02	1.34b ± 0.03	1.57c ± 0.01	1.95b ± 0.03	1.20d ± 0.01	1.09e ± 0.02	0.93e ± 0.01
MeOH	<2 h	0.89b ± 0.02	1.47a ± 0.00	1.14b ± 0.01	1.52a ± 0.05	2.26b ± 0.08	2.29a ± 0.10	2.59a ± 0.10	2.76a ± 0.14	2.79a ± 0.07
tetraglyme	<2 h	0.50d ± 0.07	1.10b ± 0.11	0.76d ± 0.08	1.04c ± 0.11	1.45c ± 0.12	1.64c ± 0.16	1.81c ± 0.13	1.71c ± 0.18	1.63c ± 0.10
PPG	<2 h	0.51d ± 0.09	0.99b ± 0.19	0.68d ± 0.14	0.91c ± 0.18	1.10d ± 0.25	1.34d ± 0.30	1.26d ± 0.22	1.20de ± 0.33	1.18d ± 0.24
MeOH	2 days	2.47 ± 0.04	2.37 ± 0.03	1.54 ± 0.04	2.44 ± 0.07	3.44 ± 0.17	3.46 ± 0.11	4.04 ± 0.18	4.99 ± 0.16	4.40 ± 0.23
tetraglyme	2 days	0.68 ± 0.02	1.26 ± 0.15	0.93 ± 0.10	1.22 ± 0.11	1.89 ± 0.12	2.14 ± 0.14	2.40 ± 0.17	2.48 ± 0.11	2.42 ± 0.16
PPG	2 days	0.59 ± 0.06	1.11 ± 0.17	0.76 ± 0.12	1.04 ± 0.16	1.32 ± 0.27	1.57 ± 0.29	1.49 ± 0.32	1.39 ± 0.25	1.31 ± 0.25
MeOH	4 days	2.83 ± 0.04	2.68 ± 0.03	1.58 ± 0.07	2.52 ± 0.09	3.52 ± 0.11	3.04 ± 0.17	3.85 ± 0.35	4.97 ± 0.40	4.30 ± 0.37
tetragylme	4 days	0.69 ± 0.21	1.27 ± 0.14	0.96 ± 0.09	1.18 ± 0.11	2.04 ± 0.17	2.05 ± 0.16	2.50 ± 0.18	2.76 ± 0.22	2.58 ± 0.28
PPG	4 days	0.64 ± 0.06	1.21 ± 0.14	0.82 ± 0.09	1.11 ± 0.14	1.46 ± 0.20	1.63 ± 0.24	1.65 ± 0.24	1.58 ± 0.21	1.48 ± 0.26
MeOH	29 days	4.09 ± 0.08	3.77 ± 0.06	2.16 ± 0.05	4.03 ± 0.17	4.80 ± 0.07	4.44 ± 0.02	5.04 ± 0.07	6.66 ± 0.19	5.54 ± 0.17
tetragylme	29 days	0.77 ± 0.25	1.34 ± 0.17	1.04 ± 0.06	0.99 ± 0.20	2.46 ± 0.13	2.23 ± 0.15	3.17 ± 0.015	3.49 ± 0.20	3.36 ± 0.25
PPG	29 days	0.77 ± 0.07	1.26 ± 0.14	0.85 ± 0.13	1.25 ± 0.18	1.55 ± 0.29	1.79 ± 0.30	1.78 ± 0.36	1.80 ± 0.41	1.59 ± 0.21

[a] Benzene (Ben), toluene (Tol), ethylbenzene (E-Ben), *p*-xylene (*p*-Xyl), *o*-xylene (*o*-Xyl), *trans*-1,2-dichloroethylene (TDCE), *cis*-1,2-dichloroethylene (CDCE), trichloroethylene (TCE), and tetrachloroethylene (PCE).
[b] For samples analyzed after 2 h of extraction, each analyte concentration with the same letter (or no letter at all) is not significantly different from each other.

FIGURE 1. Mean Tol concentration determined for each extractant and extraction period for the CR-B vapor fortified soil. Extraction periods designated with different letters are significantly different at the 95% confidence level.

tion for TDCE. Among these three solvents, MeOH extraction showed significantly higher yields throughout this experiment.

Discussion

When analytical methods for environmental samples are developed, one of the most important considerations is method robustness, i.e., consistent accuracy despite inevitable variations in the sample matrix and procedural details. The experiments performed here included four soil types, several of the most frequently identified constituents at hazardous waste sites (*25*), two of the more likely pathways (vapor and aqueous transfer) of vadose zone contamination, and short (days) and moderate (weeks) analyte-matrix residence times. Of the sample preparation methods tested, solvent extraction with MeOH best fulfills the above mentioned criterion. Recovery of VOCs from these laboratory-fortified soil samples with MeOH extraction was found to be quantitative for all soils tested with aqueous spikes (Table 4) and ultimately achieved the highest analyte concentrations for laboratory samples experiencing a moderate (weeks) analyte equilibration period (Table 5).

The recovery of VOCs from vapor fortified soil samples can continue over a very long period (29 days, Figure 1). Slow extraction kinetics is consistent with studies showing a benefit from using elevated temperatures to speed up the release of VOCs from field samples to MeOH (*14, 16*). Results for Tol in a similarly performed experiment (same nine analytes), however in this case the CR-A, Ft. E, and Pt. B soils were vapor fortified for 5 weeks and MeOH extracts were removed after <2 h, 2, 4, 41, and 79 days, are shown in Figure 2 (*17*). This additional information suggests that slow desorption kinetics with regard to MeOH extraction was unique to the CR-A/B soils among these three types of soils. However, in comparison to the CR-B soil, MeOH extraction for the CR-A appears to reach a maximum concentration much earlier (approx. 2 days). The slow desorption kinetics cannot be unambiguously attributed to either the organic carbon or the clay content, because both Pt. B and Ft. E soils failed to show this phenomenon. Furthermore, the CR-A soil has more organic carbon than the CR-B soil (Table 1).

Of the two other solvents studied, tetraglyme often failed to show extraction efficiencies and kinetics that were equivalent to MeOH; however, the results were generally better than those achieved with the vapor partitioning HS

TABLE 6. Correction Factors Based on Two Exposure Conditions and Periods between Analytes and the Pt. B Soil as Prepared for Aq-NaCl Saturated-HS Analysis

	analyte								
	TDCE	CDCE	Ben	TCE	Tol	PCE	E-Ben	*p*-Xyl	*o*-Xyl
correction factors[a]	1.47	1.92	2.00	2.36	3.19	3.00	4.67	5.20	7.10
corrected values[b]	6.73	6.57	4.18	5.92	3.76	3.72	2.90	2.81	3.76
spiked values[c]	8.26	8.45	5.83	9.98	6.54	9.10	6.23	6.22	6.71

[a] Correction factors based on analytes added to aqueous slurry 2−4 h prior to analysis. [b] Corrected analyte estimates (μg) from Table 4, for the aqueous treated Pt. B soil. [c] Analytes concentrations (μg) in aqueous spike.

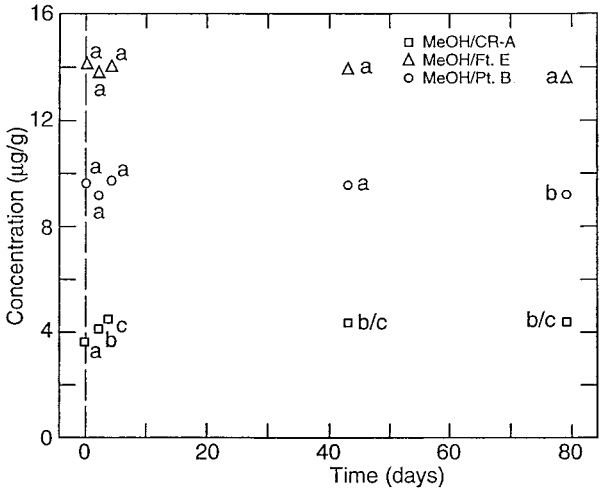

FIGURE 2. Mean Tol concentration determined for MeOH extraction of three vapor fortified soils. Extraction periods designated with different letters are significantly different at the 95% confidence level.

techniques. In general, the discrepancies between tetraglyme and MeOH, which had been previously observed (*26*), were found to increase with percent organic carbon in the test matrix and with analyte octanol−water partition coefficients and were independent of the laboratory spiking method and matrix-analyte residence time.

The other solvent tested, PPG, which was used in only one experiment, also failed to show extraction efficiencies and kinetics equivalent to MeOH (Table 5). Moreover, tetraglyme gave significantly higher concentrations than PPG for five of the nine analytes for the less than 2-h extraction period and beyond. The discrepancy between these two solvents and MeOH most likely can be attributed to their molecular size and solubility parameters (e.g., cohesiveness, etc.).

In this study, all three vapor partitioning HS methods often provided lower estimates than obtained by MeOH extraction for the two sets of prepared samples. In general, the differences between estimates using vapor partitioning methods and those obtained by MeOH extraction increase with organic carbon content in the soil matrix and analyte octanol−water partition coefficient. Two notable exceptions were for the Ott soil (Table 4) and for the concentrations established after less than 2 h of sample preparation, i.e., Aq-$NaHSO_4$-HS vapor partitioning or MeOH extraction (Table 5). However, beyond 2 h, the MeOH extraction showed much greater analyte recoveries than what had been achieved by Aq-$NaHSO_4$-HS. These findings reinforce the point that sample preparation method comparisons must include different matrices, analytes, and extraction periods for us to begin to understand their performance capabilities. Potentially, other vapor partition methods would have performed better than those tested here, for example, the full evaporative techniques which use an equilibrium temperature of at least 95 °C for H-HS analysis (*27*, *28*).

A feature common to the vapor partitioning methods, is that analytes are removed from a sample vessel that still contains the sample matrix. The magnitude of differences caused by analyte loss due to partitioning with the soil matrices used in this study ranged from nonconsequential to >90%, Table 4. Clearly, losses due to analyte partitioning can result in very poor recoveries of VOCs for certain soils when a vapor partitioning sample preparation and analysis method is used.

Low recoveries due to analyte−matrix partitioning were not only found to increase with the organic carbon content in the soil and with the analyte octanol−water partition coefficient, but also with the salt content of the sample preparation solution. The aqueous solution acidified with $NaHSO_4$ was 0.21 M, and the NaCl saturated solution acidified with phosphoric acid was at least 6.2 M. Lower analyte recoveries, due to using a salting-out approach, are apparent in Tables 4 and 5 for the CR-A/B and Pt. B soils by comparing results obtained by Aq-NaCl saturated-HS and Aq-$NaHSO_4$-HS analysis.

When HS analysis is used on an aqueous sample, the partitioning of VOCs into the vapor phase from solution is more strongly influenced by salt addition than by temperature (*29*). Usually, in the analysis of aqueous samples, both parameters are managed in concert for optimal analyte vapor phase partitioning. However, this salting-out approach can cause enhanced matrix-analyte interactions when applied to soils (Tables 4 and 5). A possible explanation for this phenomenon is that organic carbon, which serves as a hydrophobic phase, has increasingly greater partitioning coefficients under salting-out conditions. Indeed, organic compounds can be efficiently salted-out of a large volume of an aqueous solution and into a small volume of an organic solvent as a method of aqueous sample preconcentration (*30*).

To correct for the matrix effects encountered with vapor partitioning methods, correction factors based on surrogate recoveries have been suggested (*21*, *22*). However, for all practical purposes, it is impossible to achieve meaningful correction factors because analytes that are introduced as surrogates do not necessary partition to the same extent as the contaminants (*19*, *31*). To illustrate this point, the following comparison was made.

Recovery estimates from surrogates (same compounds) added to 2-g slurries of the Pt. B soil in 10 mL of Aq-NaCl saturated-HS solution were used to correct the analyte estimates shown in Table 4, for the same soil and sample preparation solution. The discrepancies shown in Table 6 between the corrected and spiked values, while improved, still are far from accurate (19−59% low). In this example, the difference in the length of analyte−matrix equilibration for the two sets of samples was a 2- to 4-h analyte−slurry sample preparation period vs a 2-day sample treatment and a 1-day sample preparation period.

Summary

This comparison of different sample preparation methods for the analysis of VOCs in soils was performed on samples

that exclude the systematic error associated with sample collection and handling. Investigators who have taken precautions to eliminate confounding effects have all concluded that MeOH extraction can be a far more robust method of recovering VOCs from soil, especially for analytes with high octanol−water partitioning coefficients and matrices with organic carbon, than methods relying solely on vapor partitioning. To my knowledge, all reported studies with contrary findings have failed to limit or at least normalize the error associated with sample handling. Furthermore, soil matrix effects do not only increase with increasing analyte octanol−water partition coefficients and organic carbon content of soils, but also with increasing solution electrolyte concentrations. For this reason using a salting-out approach with soils may increase these matrix effects, therefore serving as a matrix enhancer, not a matrix modifier.

These matrix effects, however, can be small, perhaps even insignificant, when vadose-zone soils have very low (<0.1%) organic carbon and low clay contents. Under these circumstances, any of the vapor partitioning HS methods described here may be adequate (*13*). In addition, alternative solvents such as tetraglyme or PPG would also be adequate under these conditions and may help to reduce regulatory concerns. The intent of this study was to make users of vapor partitioning methods and alternative solvents aware of potential matrix-analyte interactions. On a site-per-site basis, these interactions can easily be identified as a potential concern by tracking recoveries of known spikes from the matrix of concern, provided reasonable periods of equilibration are used. When matrix interferences are expected or identified, MeOH extraction should be the method of choice. If MeOH extraction is not used, then it should be recognized that in comparison, most alternative procedures will result in lower quantitative recoveries.

In the development of a performance based measurement system for the analysis of VOCs in soil matrices, determinant and indeterminate error associated with sample collection and analysis must be clearly identified. Furthermore, aggressive or long term MeOH extraction, matrices other than quartz sand (a single low organic carbon soil), analytes of various octanol−water partition coefficients, and sample treatment procedures that are consistent with pollution pathways should be included in the performance evaluation study.

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