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Preparing Soil Samples for
Volatile Organic Compound Analysis

Alan D. Hewitt

April 1997

Abstract: Three equilibrium headspace and three solvent extraction methods of preparing soil samples for determining volatile organic compounds (VOCs) were compared. Soil samples were spiked with five gasoline range aromatic compounds and four chlorinated compounds using two different laboratory procedures that limit volatilization and biodegradation losses. All comparisons were made with sample triplicates of one or more soil types. Recovery efficiencies for the preparation methods depended on soil organic carbon content, octanol–water partition coefficients of specific analytes, length of solvent extraction, and the spiking procedure used. In general, methanol extraction was the most robust method for recovering spiked VOCs. Recovery efficiencies for VOCs with tetraethylene glycol dimethyl ether and poly(propylene)glycol, as well as three equilibrium headspace methods, varied with the parameters tested.

Special Report 97-11

**US Army Corps
of Engineers**®
Cold Regions Research &
Engineering Laboratory

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PREFACE

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Preparing Soil Samples for
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INTRODUCTION

Methods for the collection and analysis of soil samples thought to be contaminated with Volatile Organic Compounds (VOCs) continues to be an actively researched and debated topic. Over the last several years, an accumulating body of scientific evidence has shown that volatilization (Urban et al. 1989, Siegrist and Jenssen 1990, Illias and Jaeger 1993, Voice and Kolb 1993, Hewitt 1994, Lewis et al. 1994, Hewitt et al. 1995, Hewitt and Lukash 1996) and preservation (Hewitt 1995a,b; Turriff et al. 1995; Hewitt 1997) 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 (U.S. EPA 1986). To address these concerns, the U.S. EPA has drafted two new sample collection and analysis procedures, Methods 5035 and 5021, for the third update of this document, while, independently, several States have either considered or adopted the use of an in-field methanol (MeOH) sample preservation–extraction method.

Distinguishing which method of sample preparation for VOC analysis is best is not a simple task. This is because most of the evidence showing that quantitative VOC soil determinations depend on sample collection, handling, and analysis fails to identify and separate the determinant (systematic) and indeterminate (random) errors associated with each of the steps involved. On the basis of this total measurement error approach, several methods of sample preparation (extraction–equilibrium) for analysis are in use without a clear understanding of how each variable quantitatively influences the results. Only a few studies, to our knowledge, have minimized determi-

nant error (i.e., volatilization and biological losses) while assessing indeterminate error associated with various methods of preparing samples for analysis (Hewitt et al. 1992, Hewitt 1994, Hewitt et al. 1995, Askari et al. 1996, Minnich et al. 1996). Studies addressing only sample preparation have used in-vial procedures, similar to what is now being recommended in draft Methods 5035 and 5021. With this approach, soil samples collected in the field or prepared in the laboratory are transferred directly to hermetically sealed vessels that contain an organic solvent or from which the analysis could be done.

Results from using an in-vial approach have clearly shown that different sample preparation methods do not produce the same quantitative values. For example, samples prepared by aqueous dispersion–extraction often yield lower VOC concentration estimates than MeOH extraction (Hewitt et al. 1992, Hewitt 1996, Askari et al. 1996, Minnich et al. 1996). Explanations for these differences have often focused on the organic carbon content in the soil matrix and the octanol–water partition coefficient of the specific VOC being measured.

This study examines potential differences among various methods used to prepare discrete soil (grab) samples for VOC analysis. The extraction solvents studied were MeOH, tetraethylene glycol dimethyl ether (tetraglyme), and poly (propylene)glycol (PPG). In addition, three equilibrium headspace analysis methods were also studied—direct heating (H-HS), dispersion–extraction in water acidified with sodium bisulfate (Aq-NaHSO$_4$-HS), and dispersion–extraction in water saturated with sodium chloride and acidified with phosphoric acid (Aq-NaCl sat'd-HS). The H-HS (thermal desorption) procedure was consis-

tent with that described in the *Draft Statement of Work for Quick Turnaround Analysis* (U.S. EPA 1993), while the Aq-NaCl sat'd-HS (salting-out) method was recommended in the initial draft of Method 5021 (U.S. EPA 1986).

For each comparison, all of the samples were handled in a manner that prevented volatization losses prior to and during headspace–gas chromatography (HS/GC) analysis. In addition, many of the samples extracted with a solvent were analyzed over time to assess extraction kinetics and long term analyte concentration stability. 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 (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 4- to 6-week sample equilibration. Longer analyte–matrix equilibration periods were not used with the aqueous spiking method, since under these conditions biodegradation of aromatic compounds is likely (Hewitt 1995a,b; Hewitt 1997).

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—experiment I

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 using a microliter syringe (Hamilton), the solution was mixed for 48 hours with a stirring bar. The target concentration of each analyte was 50 mg/L; however, there were some volatilization losses.

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.

Table 1. Soil characteristics.

Description	Abbreviation	Soil type	% organic carbon*
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

* Leco CR-12 furnace analysis (Merry and Spouncer 1988).

Table 2. Octanol–water partition coefficients and boiling points of analytes.

Compound (abbreviation)	Log of octanol–water partition coefficient	Boiling point (°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

Table 3. Experimental designs: soil types, sample replicates, and methods of sample preparation for analysis.

No. of rep.	Soil types	Methods of sample preparation*
I. Aqueous spike		
15	Ott	a. Heated HS
15	Ft. E	b. Aqueous solution acidified with
15	CR-A	NaHSO$_4$
15	Pt. B	c. Aqueous solution NaCl-saturated
		and acidified with H$_3$PO$_4$
		d. MeOH extraction
		e. Tetraglyme extraction
II. Vapor fortification treatment		
6	Ott	a. MeOH extraction
6	Ft. E	b. Tetraglyme extraction
6	CR-A	
6	Pt. B	
III. Vapor fortification treatment		
18	CR-B	a. Heated HS
		b. Aqueous solution acidified with
		NaHSO$_4$
		c. Aqueous solution NaCl saturated
		and acidified with H$_3$PO$_4$
		d. MeOH extraction
		e. Tetraglyme extraction
		f. PPG extraction

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

Just before spiking, each soil-filled ampoule was placed in a metal tension clamp. Immediately after a 0.200-mL aqueous spike was introduced using a 0.500-mL glass syringe (Hamilton), 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 before being inserted into the ampoule neck. Depending on the soil, the aqueous spike wetted the surface of between $^1/_2$ and $^1/_4$ of the grains.

In addition to the soil subsamples, 0.200-mL aliquots of the spiking solution were also placed into three separate auto sampler Volatile Organic-compound Analysis (VOA) vials (22 mL, Tekmar) containing 10 mL of Type 1 water, which were immediately given crimp-top caps and Teflon-faced butyl rubber septa (Wheaton). These vials were spiked at the beginning, middle, and end of the soil sample preparation process (about 1 hour) to assess whether there were changes in VOC concentration of the spiking solution.

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. 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 shaking, 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. The three auto sampler vials used to monitor spike concentration and solution homogeneity were analyzed by HS/GC within 24 hours of preparation.

Vapor fortification treatment—experiments II and III

Two separate experiments were performed with vapor-fortified soils. The first used six replicates of four soil types (Table 3). The second experiment used 18 replicates of the CR-B soil (Table 3). For both experiments, ampoules containing 2.00 ±0.01 g of soil were placed in a desiccator with anhydrous $CaSO_4$ for 48 hours (Hewitt and Grant 1995). After desiccation, the $CaSO_4$ was replaced with a small glass bottle 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 of TDCE, CDCE, Ben, TCE, and PCE, and 0.150 mL of Tol, E-Ben, p-Xyl, and o-Xyl to MeOH, then taking it to volume in a 25-mL volumetric flask. The fortification solution and open ampoules of soil were left in the desiccator at room temperature (22 ±2°C) for periods of 33 and 44 days for experiments I and II respectively. At the end of this period, the desiccator was opened and a 5-mm glass bead was placed on top of each ampoule. Then, as quickly as possible, each was heat sealed with a propane torch.

The sealed ampoules were then stored for 4 or 7 days in a refrigerator (4°C) before triplicates were removed for different sample preparation and analysis protocols. In experiment II, triplicates of each of the four soil types were transferred to VOA vials (44 mL) containing either 10 mL of MeOH or tetraglyme. In experiment III, preparation of samples for analysis was staggered over a 2-day period so that analyte determinations could be made within 2 hours of the ampoule being broken or when a 0.100-mL aliquot of the extraction solvent was removed after 2 hours of contact with the specimen.

Subsample preparation for analysis

We evaluated six different sample preparation procedures to determine how efficiently they recovered VOCs from the laboratory-treated soils. With a HS equilibrium method, each sample could only be analyzed once. In contrast, several aliquots could be removed when samples were placed in an extraction solvent, thus allowing for an assessment of extraction kinetics and holding time analyte concentration stability (Table 4).

Table 4. Solvent extraction periods and conditions.

Solvent	Extraction period and conditions
I. Aqueous spike	
MeOH	5 days
Tetraglyme	6 days
II. Vapor fortification treatment	
MeOH	1) <2 hours
	2) 2 days
	3) 4 days
	4) 41 days
	5) 79 days
Tetragylme	Same as MeOH
III. Vapor fortification treatment	
MeOH	1) <2 hours
	2) 2 days
	3) 4 days
	4) 29 days
Tetraglyme	Same as MeOH
PPG	Same as MeOH

3

Heated equilibrium HS/GC analysis (H-HS)

Ampoules containing laboratory spiked soil were transferred to empty auto sampler VOA vials, which were then capped. Once the vials were hermetically sealed, the ampoules were broken and the soil was completely dispersed by careful hand shaking. In all cases the samples were analyzed on the same day that the ampoules were broken; after the sample was heated to 60°C for 50 minutes, HS vapors were removed. This procedure is consistent with that described in the *Draft Statement of Work for Quick Turnaround Analysis* (U.S. EPA 1993).

Aqueous dispersion–extraction in a NaCl-saturated solution acidified with H_3PO_4, using equilibrium HS/GC analysis (Aq-NaCL sat'd-HS)

An aqueous dispersion–extraction solution was prepared by acidifying 500 mL of Type 1 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. These samples were analyzed 1 day after the ampoules were broken when they were spiked with an aqueous solution (experiment I), and within 2 hours when they were vapor fortified (experiment III). Before HS vapors were removed, the soil water slurry was heated to 85°C for 60 minutes. This sample preparation and analysis procedure is consistent with that currently described in draft Method 5021 (U.S. EPA 1986).

Aqueous dispersion–extraction in a solution acidified with $NaHSO_4$, using equilibrium HS/GC analysis (Aq-$NaHSO_4$-HS)

We placed 10 mL of Type 1 water and 0.25 g of $NaHSO_4$ into auto sampler VOA vials, then introduced ampoules. Once the vials were sealed, the ampoules were broken and their contents completely dispersed. Samples were analyzed 2 days after dispersion–extraction when prepared by aqueous treatment, and within 2 hours when vapor-fortified. Before HS vapors were removed, the VOA vial was held for 20 minutes at 25°C.

MeOH extraction

HPLC grade MeOH was transferred to VOA vials and an ampoule was placed in each. A 10-mL volume was used for the aqueous treatment and 5 mL was used for vapor-fortified soils. After we capped the vials, the ampoules were broken, and the soil was completely dispersed by hand shak-

ing. For the aqueous spiked samples, a 0.100-mL aliquot was removed from each 5 days after we initiated extraction. Each aliquot was transferred to an auto sampler vial containing 10 mL of Type 1 water. Using this same procedure, we did analyses after various extraction times, ranging from less than 2 hours to 79 days (Table 4) for the vapor-fortified soils. Before HS vapors were removed from the VOA vials containing the aqueous-MeOH solutions, they were held for 20 minutes at 25°C.

Tetraglyme extraction

Samples extracted with tetraglyme used the same solvent volumes and were analyzed using the same procedure as described for MeOH. For the aqueous spiked samples, a 0.500-mL aliquot was transferred 6 days after we initiated the extraction. These aliquots were placed into VOA vials, and 9.5 mL of Type 1 NaCl-saturated water was added. For the vapor-fortified soils, 0.100-mL aliquots were transferred to VOA vials containing 10 mL of Type 1 water. As for MeOH, several extraction periods were used (Table 4).

Poly(propylene)glycol extraction

Only soil samples prepared for the second vapor fortification experiment (experiment III) were extracted with PPG. Extraction and analysis were identical to those described for MeOH and tetraglyme.

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-mm i.d. capillary column and sequential photo ionization–flame ionization detectors. Just before the VOA vials (22 mL) were transferred to the auto sampler system, each was shaken for approximately 2 minutes. 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.

For each sample preparation procedure, analyte concentrations were established relative to HS standards prepared by adding small (microliter) 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 Type 1 water and 0.100 mL of solvent or appropriate salt–acid). However, since the 2 g of soil and the broken glass ampoules were present for the three equilibrium methods, these samples contained an additional phase and had a reduced HS volume (i.e., the glass ampoule and soil occupied approx-

imately 2 cm³) compared to the standards. No corrections were made for this discrepancy between the samples and standards.

To determine if there were any significant matrix effects, and if analyte concentrations varied between sample preparation methods or with length of extraction, a one-way analysis of variance (ANOVA) and least-significant-differences (Fisher's Protected LSD) analysis were applied at the 95% confidence level.

RESULTS

Aqueous treatment—experiment I

The spike amounts and the analyte recoveries from the different soil matrices, as achieved by five different subsample preparation methods, appear in Table 5. The standard deviations of these analyte determinations (μg VOC) demonstrate that each sample preparation and analysis procedure was precise (Relative Standard Deviations [RSDs] were generally less than 5%). A one-way ANOVA was conducted at the 95% confidence level for each sample preparation method and each analyte to see if there were any significant differences between the spiked and measured concentrations for the various soil matrices. In addition, Fisher's Protected LSD was used to determine which values were significantly different from each other.

Results for the aqueous spiked samples are presented in Table 5. This table is arranged with analytes of increasing octanol–water partition coefficient going down the column, and soil matricies with increasing organic carbon content across the row. These results are also presented as percent recoveries in Figure 1.

MeOH extraction was the only sample preparation method that was able to achieve quantitative recoveries for all the analytes in all soils tested (Fig. 1). Tetraglyme showed good recoveries of TDCE, CDCE, and Ben; however, recoveries of the other analytes from the soils, other than Ott sand, often were significantly lower than expected. Percent recoveries declined as the percent organic carbon in the soil matrix and the octanol–water partition coefficients of the analytes increased (Table 5). In the worst case, recovery of E-Ben from the Pt. B soil was about 73%.

In general, the pattern established for tetraglyme was also repeated by each of the equilibrium HS sample preparation and analysis methods, except that the number and magnitude of differences between the spiked and recovered amounts increased (Fig. 1). For the HS methods, percent re-coveries 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 sat'd-HS method.

Vapor fortification treatment—experiment II

Table 6 shows means and standard deviations of the analyte concentration estimates for five separate extraction periods, using MeOH and tetraglyme, with the Ft. E, CR-A, and Pt. B soils. In addition, concentrations for a single extraction period with tetraglyme are reported for the Ott soil. As with the aqueous treatment method, the procedure for preparing vapor fortification samples was precise (RSDs were generally less than 5%, except for the Ott soil). Two ANOVAs were calculated at the 95% confidence level with this data set. One analyzed changes in analyte concentration for each soil type and solvent relative to extraction period; the other compared the analyte concentrations established by the two solvents for the 4-day extraction period only. In each case the Fisher's Protected LSD was used to determine when values were significantly different.

Examination of Table 6 shows that each soil matrix sorbed different amounts of the analytes during the vapor fortification process, as expected. The Ott soil, which mainly consists of quartz (SiO_2), showed very little affinity for VOC sorption. Indeed, the concentration estimates for the Ott soil were only a few percent of those estimates for other matrices. To determine the VOC concentrations on the Ott soil, a 1.00-mL aliquot of the tetraglyme extract had to be transferred to a VOA vial, then 9 mL of NaCl saturated solution added. Among the other matrices, sorption capacity for VOCs was greatest for the Ft. E soil, followed closely by the Pt. B soil, while the CR-A soil sorbed only about half as much.

Figure 2 gives plots of the mean concentrations determined for each extraction period by solvent extraction of the Ft. E, CR-A, and Pt. B soils. Points on these figures labeled with the same letter are not significantly different among extraction periods. Several patterns were established relative to a given solvent and soil. The rate of extraction was fast (often attaining the maximum concentration in 2 hours) for MeOH with the Pt. B soil and the Ft. E soil. For the CR-A soil, both solvents, and for the Pt. B soil extracted with tetraglyme, VOCs were slowly extracted over the first 4 to 41 days, followed sometimes by a small concentration decrease. Lastly, a very distinct re-adsorption,

Table 5. Means and standard deviations of triplicate analyte amounts for aqueous spiked samples. 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.

| Analyte | Spike | *Analyte concentration (µg)* | | | |
		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±0.35
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
Heated 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±0.09b	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 analysis of soil–water slurry preserved with NaHSO₄					
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 analysis of soil–water slurry saturated with NaCl and acidified with H₃PO₄					
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

* See Table 2 for full names.
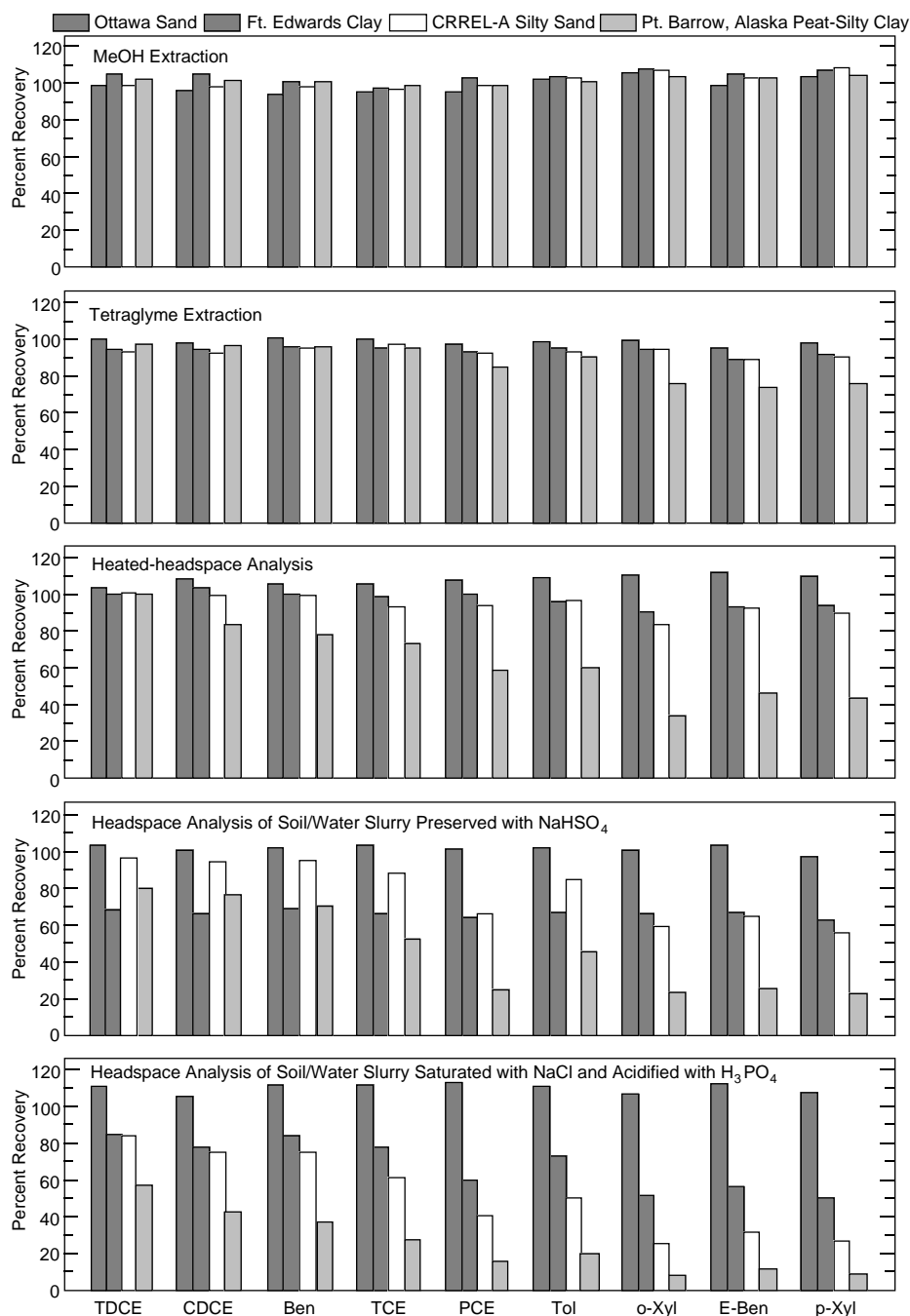
Figure 1. Mean percent recovery from aqueous spiked soils.

chemical transformation, or loss (destruction) trend was seen with chlorinated compounds after 4 days for the tetraglyme extraction from the Ft. E soil. This was particularly striking for TCE and PCE (Fig. 2d and f).

Table 6 also shows the results of the statistical analysis of the comparison of the extraction efficiencies of these two solvents for the 4-day extraction period. The 4-day period was chosen since the highest analyte concentrations often occurred

for this extraction time. This statistical analysis showed that MeOH consistently produced higher concentration estimates for all of the VOCs with the Pt. B and CR-A soils, while there were no significant differences between these two solvents for the Ft. E soil.

Vapor fortification treatment—experiment III

Table 7 shows means and standard deviations for VOC concentration estimates by six different

Table 6. Means and standard deviations of triplicate analyte concentrations established for experiment II with vapor-fortified samples, for various extraction periods.

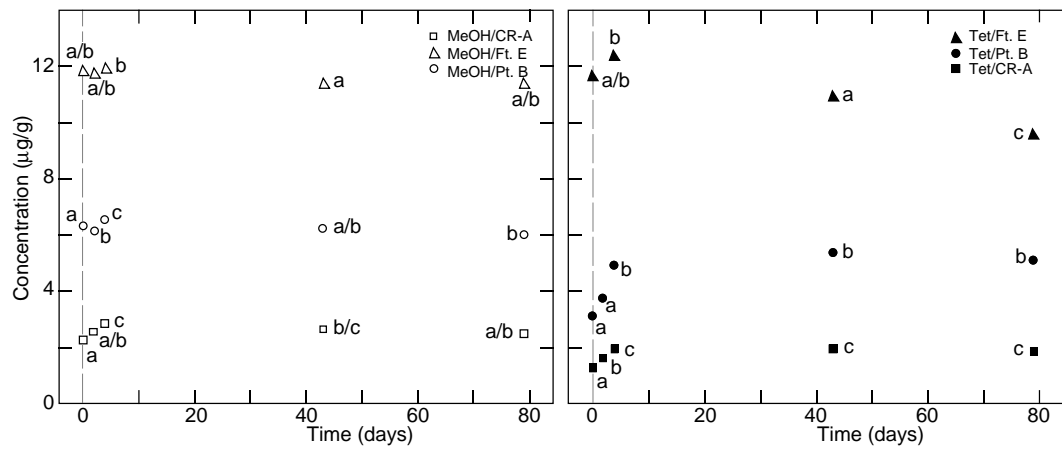| Analyte	*Analyte concentration (µg/g)*				Analyte	*Analyte concentration (µg/g)*			
Analyte	*Ott*	*Ft. E*	*CR*	*Pt. B*	*Analyte*	*Ott*	*Ft. E*	*CR*	*Pt. B*
MeOH extraction, < 2 hours					**Tetraglyme extraction, 4 days**				
TDCE*	ND	3.87±0.06	1.83±0.10	4.91±0.06	TDCE		4.01±0.14	1.57±0.11**	4.14±0.36**
CDCE	ND	11.9±0.25	2.23±0.09	6.30±0.13	CDCE		12.4±0.46	1.86±0.08**	4.86±0.54**
Ben	ND	8.75±0.04	2.18±0.12	6.16±0.10	Ben		9.07±0.24	1.79±0.07**	4.55±0.34**
TCE	ND	7.81±0.14	2.99±0.09	8.19±0.11	TCE		8.15±0.25	2.51±0.12**	6.38±0.49**
PCE	ND	10.9±0.06	4.22±0.12	12.0±0.15	PCE		11.2±0.15	3.85±0.13**	10.1±0.62**
Tol	ND	14.1±0.32	3.60±0.10	9.67±0.08	Tol		14.7±0.40	3.23±0.18**	7.57±0.46**
o-Xyl	ND	15.2±0.46	3.88±0.16	10.8±0.10	o-Xyl		16.1±0.12	3.61±0.21**	8.62±0.48**
E-Ben	ND	17.1±0.35	4.07±0.16	9.81±0.09	E-Ben		18.1±0.30	3.80±0.48**	8.07±0.45**
p-Xyl	ND	16.8±0.21	4.44±0.13	11.2±0.32	p-Xyl		17.5±0.81	4.02±0.34**	8.88±0.36**
Tetraglyme extraction, < 2 hours					**MeOH extraction, 41 days**				
TDCE	0.16±0.25†	3.73±0.05	1.07±0.04	2.89±0.21	TDCE		3.70±0.04	1.94±0.13	4.92±0.09
CDCE	0.082±0.011	11.7±0.23	1.21±0.05	3.17±0.23	CDCE		11.4±0.36	2.58±0.11	6.19±0.06
Ben	0.081±0.004	8.56±0.11	1.11±0.03	3.05±0.19	Ben		8.71±0.38	2.54±0.15	6.02±0.32
TCE	0.092±0.009	7.74±0.11	1.56±0.06	4.45±0.29	TCE		7.63±0.10	3.59±0.10	8.42±0.26
PCE	0.084±0.007	10.8±0.20	2.33±0.04	7.34±0.33	PCE		11.0±0.25	4.89±0.02	12.0±0.45
Tol	0.063±0.009	13.4±0.31	1.92±0.17	5.11±0.27	Tol		14.0±0.25	4.33±0.22	9.59±0.27
o-Xyl	0.040±0.003	14.7±0.26	2.12±0.02	5.57±0.37	o-Xyl		14.8±0.10	4.49±0.09	9.87±0.32
E-Ben	0.037±0.004	16.2±0.26	2.20±0.05	5.36±0.33	E-Ben		17.6±0.15	4.87±0.09	9.80±0.13
p-Xyl	0.045±0.007	16.2±0.15	2.37±0.10	5.94±0.29	p-Xyl		16.6±0.74	5.02±0.15	10.7±0.17
MeOH extraction, 2 days					**Tetraglyme extraction, 41 days**				
TDCE		3.89±0.13	2.04±0.07	4.91±0.13	TDCE		3.05±0.22	1.54±0.04	4.58±0.20
CDCE		11.8±0.26	2.46±0.04	6.07±0.16	CDCE		10.9±0.96	1.88±0.02	5.36±0.32
Ben		8.69±0.26	2.44±0.07	5.87±0.24	Ben		8.47±0.15	1.85±0.11	5.02±0.48
TCE		7.88±0.28	3.38±0.09	8.02±0.29	TCE		3.30±0.24	2.16±0.22	6.98±0.39
PCE		10.6±0.21	4.64±0.15	11.5±0.40	PCE		7.70±0.27	3.75±0.09	11.2±0.68
Tol		13.8±0.50	4.10±0.05	9.19±0.15	Tol		13.4±0.38	3.30±0.07	8.19±0.30
o-Xyl		15.1±0.76	4.18±0.08	9.21±0.27	o-Xyl		14.1±0.80	3.64±0.24	8.90±0.16
E-Ben		16.5±0.36	4.49±0.05	8.88±0.22	E-Ben		16.7±0.81	3.94±0.17	8.87±0.29
p-Xyl		16.6±0.25	4.94±0.20	10.4±0.32	p-Xyl		15.7±0.78	3.94±0.22	9.26±0.43
Tetraglyme extraction, 2 days					**MeOH extraction, 79 days**				
TDCE		3.85±0.11	1.31±0.06	3.45±0.29	TDCE		3.72±0.18	1.73±0.36	4.72±0.11
CDCE		11.8±0.56	1.52±0.05	3.85±0.40	CDCE		11.4±0.32	2.42±0.22	5.98±0.07
Ben		8.65±0.33	1.43±0.07	3.58±0.32	Ben		8.32±0.20	2.35±0.20	5.67±0.12
TCE		7.65±0.34	2.01±0.11	5.09±0.41	TCE		7.63±0.24	3.49±0.13	7.93±0.05
PCE		10.7±0.21	3.21±0.15	8.32±0.69	PCE		10.2±0.21	4.69±0.06	11.1±0.15
Tol		13.4±0.46	2.59±0.13	6.03±0.57	Tol		13.6±0.31	4.34±0.09	9.21±0.12
o-Xyl		14.7±0.26	2.88±0.22	6.32±0.49	o-Xyl		15.4±0.31	4.86±0.17	9.99±0.10
E-Ben		17.0±0.12	3.18±0.16	6.35±0.93	E-Ben		17.5±0.51	4.89±0.16	9.12±0.13
p-Xyl		16.3±0.30	3.38±0.26	7.07±0.67	p-Xyl		16.1±0.78	5.18±0.06	10.7±0.17
MeOH extraction, 4 days					**Tetraglyme extraction, 79 days**				
TDCE		3.88±0.07	2.27±0.13	5.22±0.12	TDCE		1.84±0.21	0.98±0.02	3.53±0.24
CDCE		11.9±0.21	2.79±0.14	6.55±0.10	CDCE		9.58±0.72	1.79±0.10	5.08±0.42
Ben		8.86±0.07	2.73±0.07	6.28±0.10	Ben		7.52±0.50	1.63±0.12	4.53±0.26
TCE		7.95±0.11	3.74±0.05	8.53±0.20	TCE		1.18±0.31	1.42±0.29	6.38±0.44
PCE		10.9±0.10	4.95±0.10	12.3±0.12	PCE		5.01±0.82	2.91±0.26	10.0±0.30
Tol		14.0±0.26	4.47±0.21	9.74±0.33	Tol		12.5±0.87	3.23±0.16	7.86±0.46
o-Xyl		15.9±0.12	4.94±0.24	10.9±0.31	o-Xyl		15.1±1.04	3.98±0.24	9.69±0.43
E-Ben		17.7±0.12	5.06±0.01	9.92±0.19	E-Ben		16.2±1.41	4.07±0.12	8.43±0.32
p-Xyl		17.2±0.60	5.45±0.08	11.2±0.42	p-Xyl		15.9±0.76	4.30±0.32	9.74±0.32

* See Table 2 for full names.

† Analyzed after 1 day extraction by transferring 1.0-mL aliquot to VOA vial and adding 9.0 mL of NaCl-saturated solution.
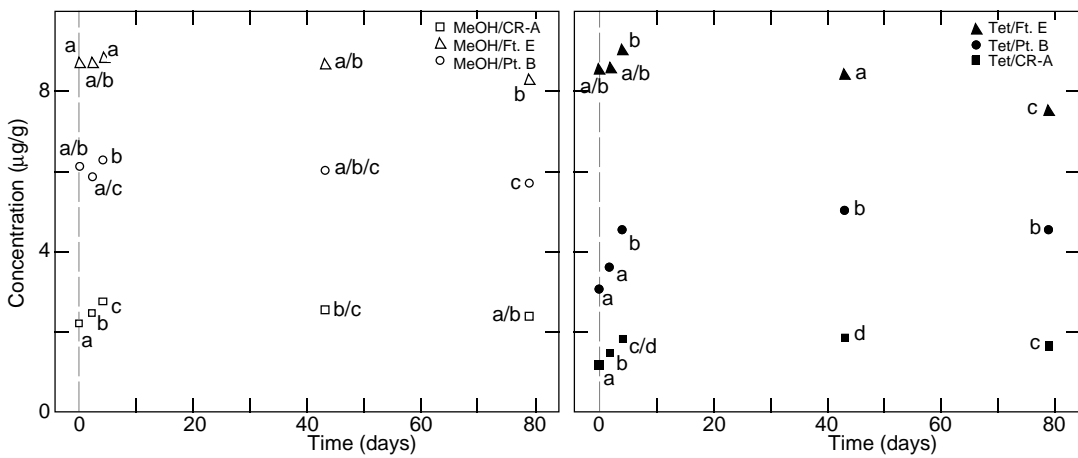
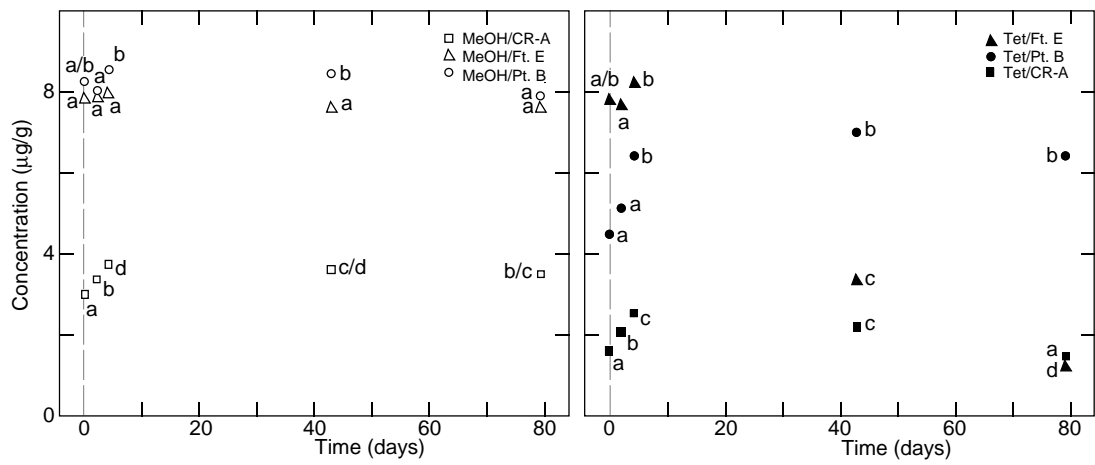** Significantly different at the 95% confidence level, between MeOH and tetraglyme extractions.
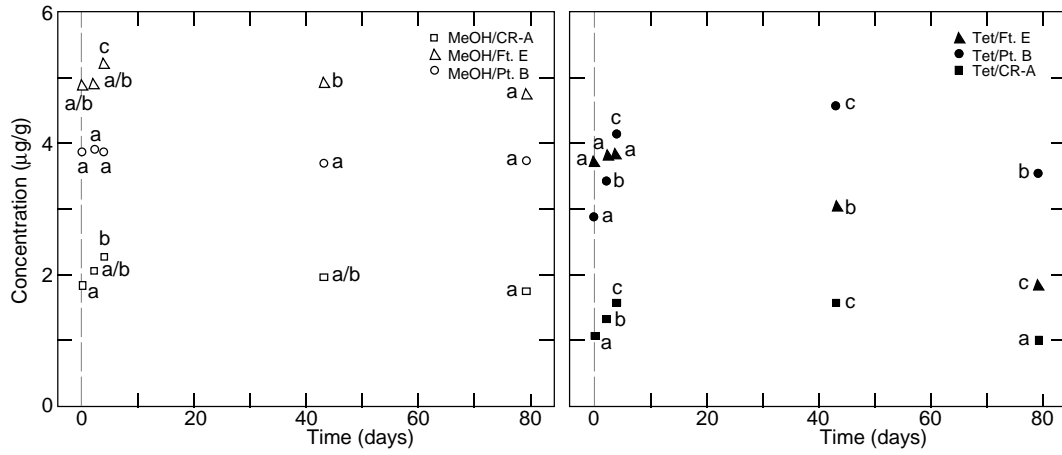
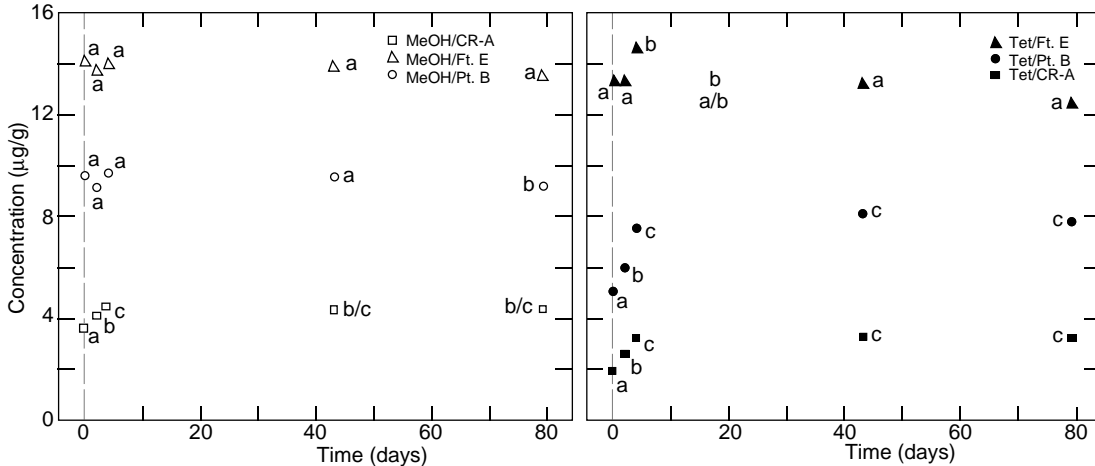*a. TDCE.*

b. CDCE.

c. Ben.

Figure 2. Mean analyte concentrations determined for each extractant and extraction period for the CR-A, Ft. E, and Pt. B vapor-fortified soils with MeOH and tetraglyme. Soils designated with different letters are significantly different at the 95% confidence level.
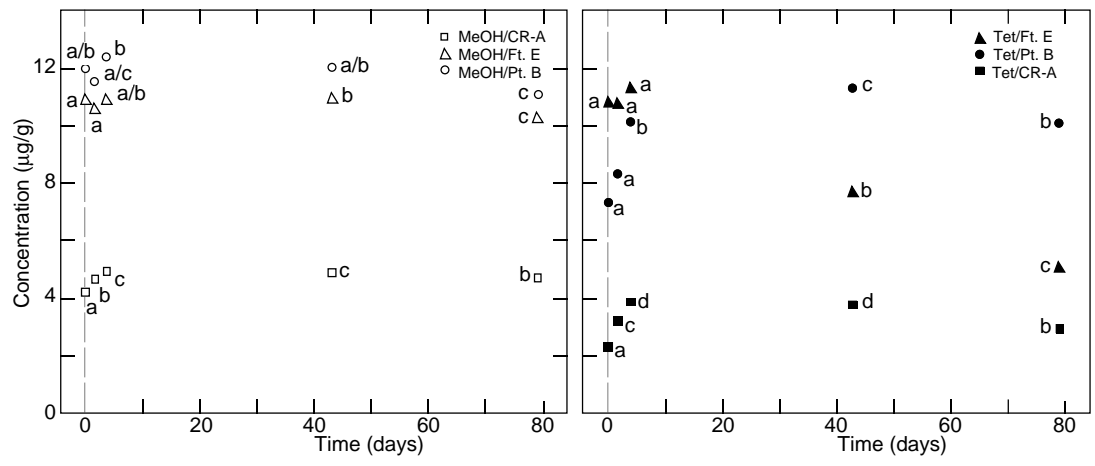
d. TCE.

e. Tol.

f. PCE.

Figure 2 (cont'd). Mean analyte concentrations determined for each extractant and extraction period for the CR-A, Ft. E, and Pt. B vapor-fortified soils with MeOH and tetraglyme. Soils designated with different letters are significantly different at the 95% confidence level.
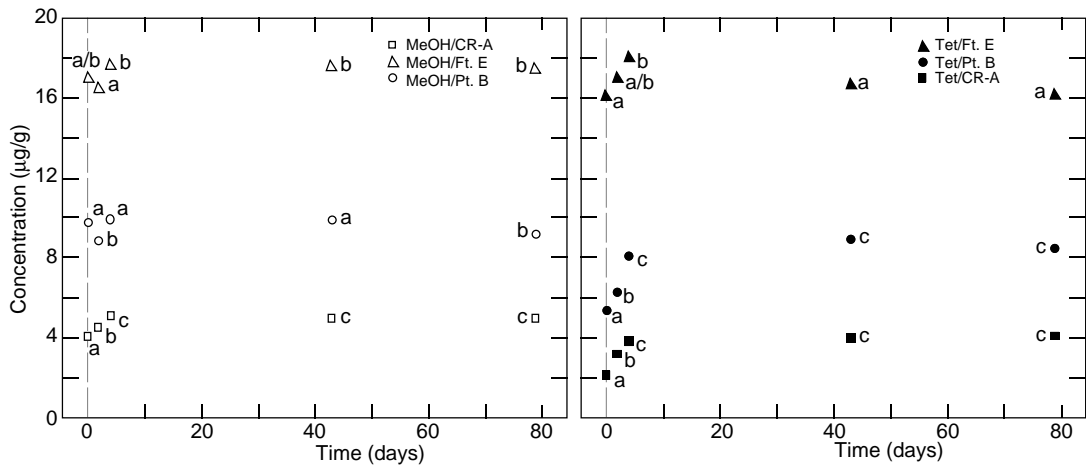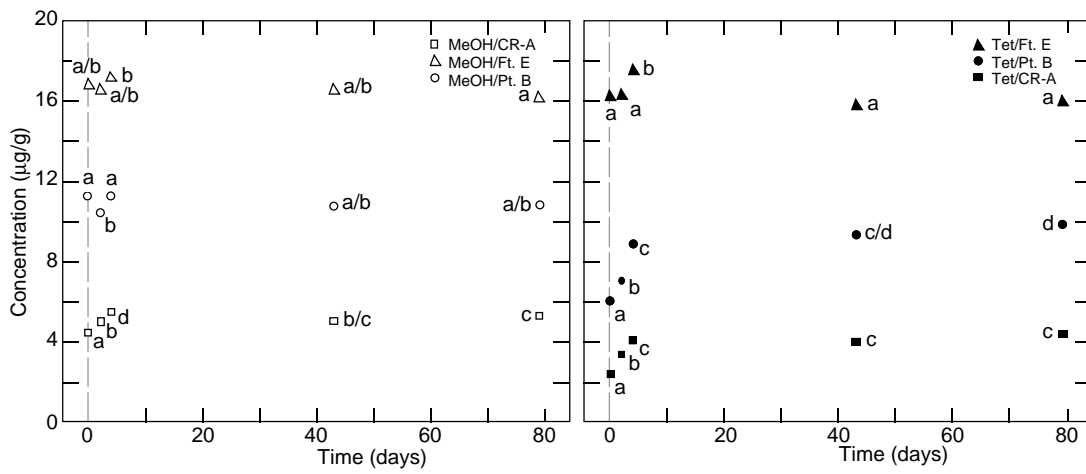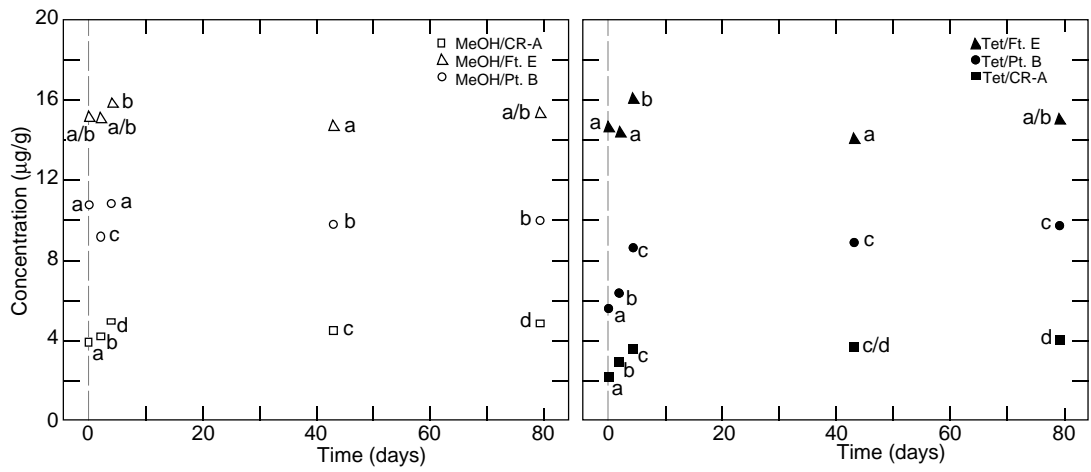
g. E-Ben.

h. p-Xyl.

i. o-Xyl.

Figure 2 (cont'd).

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Table 7. Means and standard deviations of triplicate analyte values for experiment III performed with vapor-fortified CR-B soil. 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.
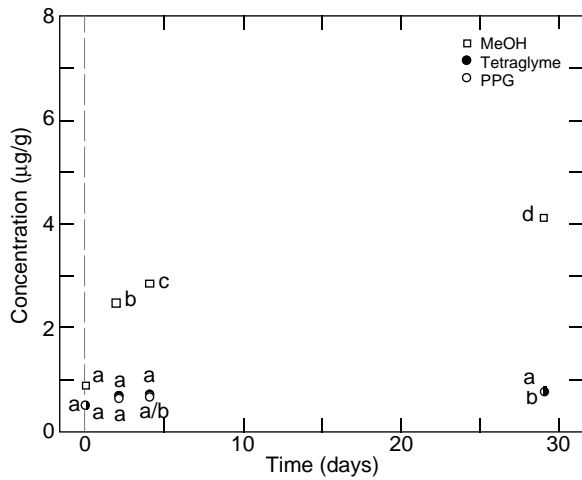
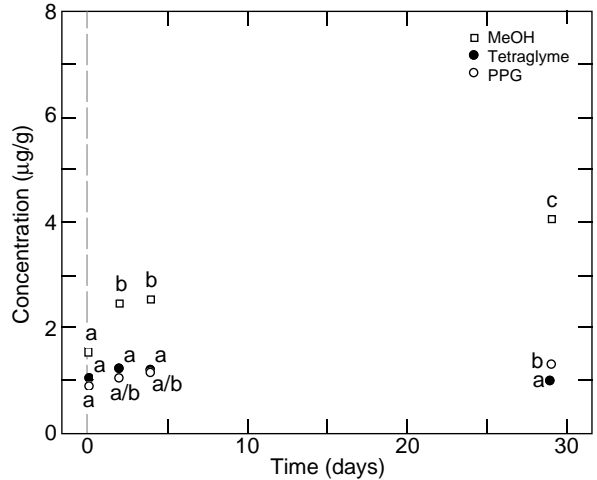| Method	Time	Analyte concentration (μg/g)								
		TDCE	CDCE	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl
HS-NaHSO$_4$	1–2 hr	0.68c ±0.05	1.53a ±0.12	1.40a ±0.08	1.64a ±0.07	2.54a ±0.05	2.49a ±0.07	2.56a ±0.12	2.41b ±0.06	2.36b ±0.05
HS-NaCl/H$_3$PO$_4$	1–2 hr	0.45d ±0.02	1.15b ±0.01	0.99c ±0.01	1.05c ±0.02	1.61c ±0.01	1.62c ±0.03	1.58c ±0.02	1.40d ±0.03	1.37b ±0.05
Heated HS	1–2 hr	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 hr	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 hr	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 hr	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 ±.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

* See Table 2 for full names.

sample preparation methods for vapor-fortified samples. For this six-method comparison, samples were either prepared and analyzed within 2 hours or a solvent aliquot was removed within 2 hours of the ampoule contents being dispersed. This table also shows the results for three additional solvent extraction periods. The CR-B soil was the only matrix, and this was the only experiment that included PPG as an extraction solvent. Two ANOVA tests were performed at the 95% confidence level with this data set. One evaluated changes in analyte concentration relative to extraction period for each of the three solvents, the other compared the analyte concentrations established among the six sample preparation methods. In each case the Fisher's Protected LSD was used to determine which values were significantly different.

Figure 3 gives plots of the mean concentrations established for the three solvents for each extraction period. In each figure, points designated with a different letter 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 caused an increasing concentration trend for all of the analytes. The slow rate of extraction for this soil with MeOH was surprising since this trend was not observed in experiment II using the CR-A soil. Both the CR-A and CR-B soils were obtained the same general area and at the same approximate depth. Although not reported here, the MeOH extraction kinetics
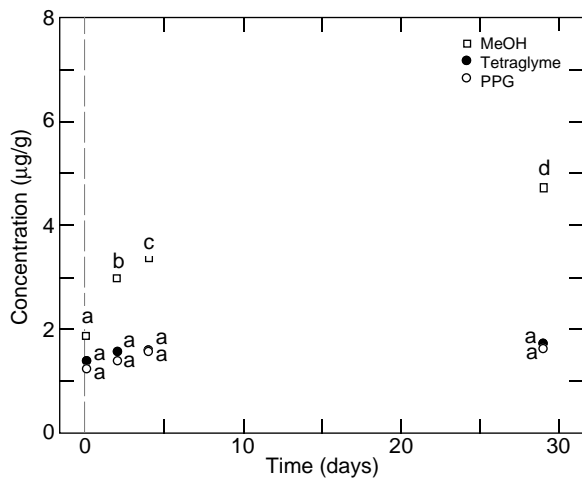
Figure 3. Mean analyte concentrations determined for each extractant and extraction period for the CR-B vapor-fortified soil with MeOH, tetraglyme, and PPG. Soils designated with different letters are significantly different at the 95% confidence level.
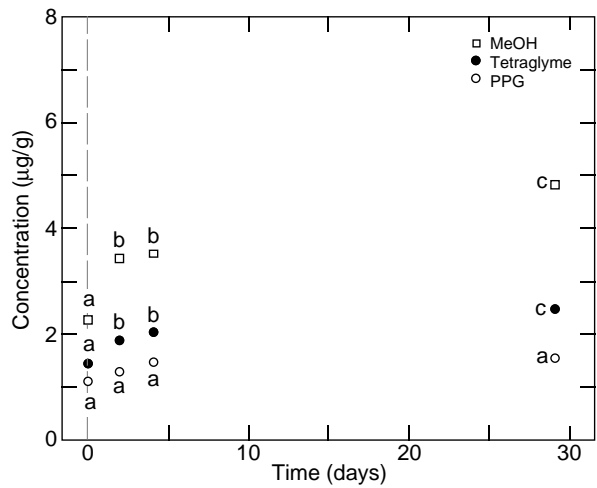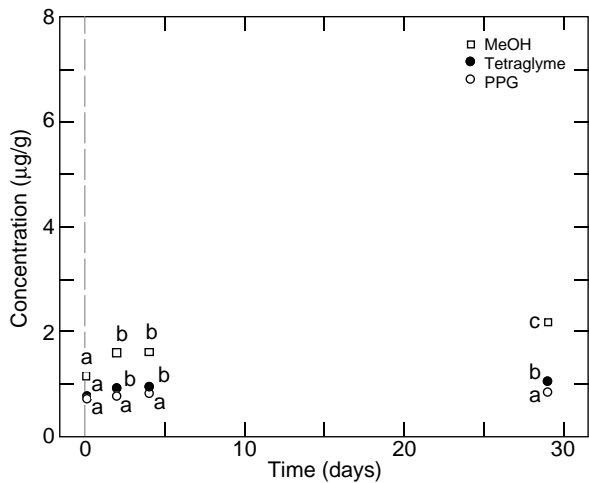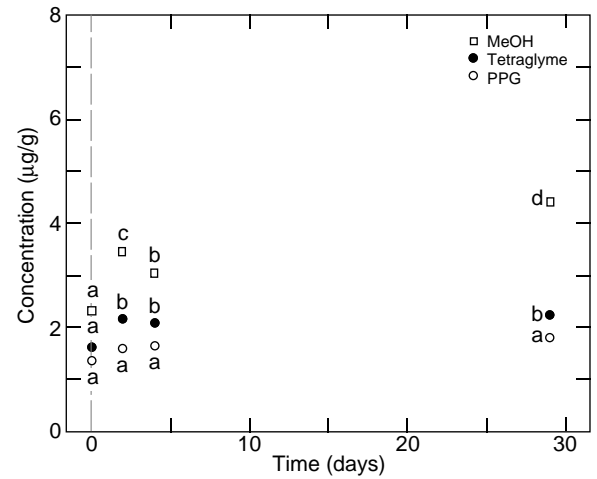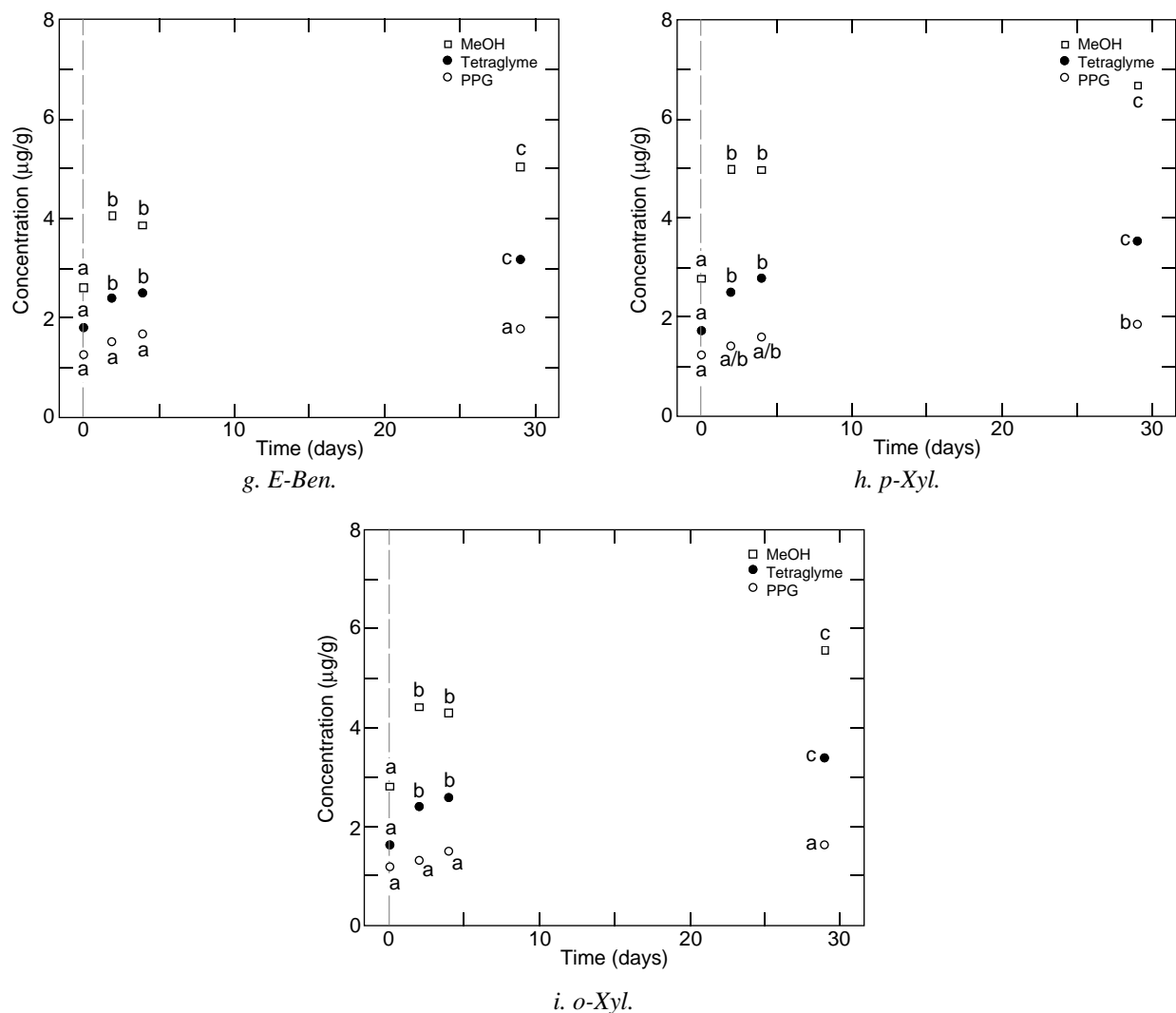
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g. E-Ben.

h. p-Xyl.

i. o-Xyl.

Figure 3 (cont'd). Mean analyte concentrations determined for each extractant and extraction period for the CR-B vapor-fortified soil with MeOH, tetraglyme, and PPG. Soils designated with different letters are significantly different at the 95% confidence level.

of this soil was repeated. The results of this additional experiment confirmed those shown in Figure 3.

In contrast, after the initial extraction period, tetraglyme failed to show an increase in analyte concentration for TDCE, CDEC, Ben, TCE, and PCE, but did for the other four analytes. PPG only showed an increasing analyte concentration for TDCE after the initial extraction period. In all cases, MeOH extraction showed the highest yields among the three solvents throughout this experiment.

Table 7 also shows the results of the statistical analysis of the six sample preparation (extraction) and analyses performed on samples within a 2-hour period. Under these conditions, MeOH extraction and Aq-NaHSO$_4$-HS usually produced

the highest analyte concentrations for eight of the nine VOCs tested. H-HS gave the highest recovery for TDCE, the most volatile analyte. However, recoveries tended to decline relative to MeOH extraction with increasing analyte boiling point, to the extent that it obtained the lowest recovery among the six methods for E-Ben, p-Xyl, and o-Xyl. Tetraglyme and Aq-NaCl sat'd-HS gave similar recoveries that were significantly below MeOH and Aq-NaHSO$_4$-HS but above PPG solvent extraction.

DISCUSSION

When developing analytical methods for environmental samples, one of the most important things that we must consider is method robust-

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ness: consistent accuracy despite inevitable variations in the sample matrix. The experiments performed here included four soil types, and several of the most frequently identified constituents at hazardous waste sites (Plumb and Pitchford 1985), 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 criteria. Recovery of VOCs from these laboratory-fortified soil samples with MeOH extraction was found to be quantitative for all soils tested (Table 5), and it ultimately achieved the greatest analyte concentrations for vapor-fortified samples (Tables 6 and 7). In the case of the vapor-fortified soil samples, where concentrations could only be operationally defined (spiked levels were not controlled), several days of room temperature (22°C) extraction with MeOH provided the maximum values. The only surprising result was that, with the CR-B soil, the recovery of VOCs continued over a very long period (29 days, Fig. 3). This slow extraction kinetics is consistent with the recent findings of Askari et al. (1996). Therefore, the extraction kinetics of VOCs from soil with MeOH can be an important variable.

Of the two other solvents studied, tetraglyme often failed to show extraction efficiencies equivalent to those of MeOH (Tables 5–7); however, the results were generally better than those achieved with the HS techniques. In two cases MeOH and tetraglyme achieved similar results for some of the extraction periods used with the Ott and Ft. E soils. In general, the discrepancies between the tetraglyme and MeOH, which had been previously observed by Jenkins and Schumacher (1987), were found to increase with percent organic carbon in the test matrix, and with analyte octanol–water partition coefficients. In general, solvent extraction was independent of the laboratory-spiking method and matrix–analyte residence time. However, an unanticipated finding was the loss of chlorinated compounds from the tetraglyme extraction solution in the presence of a soil with a high clay content (Fig. 1, 2a, d, and f).

Initially, we thought that these compounds were adsorbed back onto the matrix, since rapid dechlorination processes are not likely under these conditions and no degradation products were observed (i.e., increases in CDCE, or formation of tri- or dichloroethanes or vinyl chloride). This assumption was based on the hypothesis that, with time, tetraglyme caused the clay lattice to swell, opening sites where chlorinated compounds, such as TDCE, CDCE, TCE, and PCE, could be preferentially sorbed. However, this theory could not be substantiated by introducing MeOH (20%), sonicating, or adding $CaCl_2$ to the sample to extract or exchange sorption sites with these chlorinated compounds. Thus, destruction through an alternate path, or a chemical transformation, remain distinct possibilities.

The other solvent tested, PPG, which was used in only one experiment, failed to show extraction efficiencies equivalent to those of MeOH (Table 7). Moreover, tetraglyme achieved significantly higher concentrations than PPG with five of the nine analytes for the extraction period that was less then 2 hours and beyond.

The low vapor pressure of tetraglyme and PPG make these solvents far less likely to interfere with instrumental analysis procedures, and these solvents do not raise the flammability, toxicity, and regulatory concerns associated with MeOH. A Method Detection Limit (MDL, Federal Register 1984) study was performed using seven 4-g soil subsamples, each spiked with 44 ng/g of nine VOCs and allowed to equilibrate for 2 days. These aqueous spiked soils were then extracted with 8 mL of tetraglyme. MDL values obtained are presented in Table 8. To achieve this level of detection for HS analysis of soil extracts, 1 mL of the solvent extract was transferred to a VOA vial (22 mL) and 9 mL of NaCl-saturated solution was added just before the vial was capped. With this preparation and analysis procedure, the soil sample only experiences 20× dilution (a 2-fold dilution during analyte extraction from the soil matrix and a 10-fold dilution of the extraction solvent during the analysis step). With MeOH, often only a 0.100-mL aliquot of the extraction solvent can be taken for analy-

Table 8. Method detection limit (MDL) study of soil extracted with tetraglyme.

				MDL (ng/g)				
TDCE*	CDCE	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl
7.25	8.97	4.53	14.4	7.72	10.4	9.72	14.1	12.5

* See Table 2 for full names.

sis without compromising the analysis (or analysis system). In this case, the sample dilution would be 200×, thus the corresponding MDLs would be some 10× greater.

In this study, all three equilibrium HS methods provided lower estimates for VOCs than those obtained after several days of MeOH extraction (Tables 5 and 7). In general, the differences between estimates using HS methods and those obtained after several days of MeOH extraction increased with organic carbon content in the soil matrix and with analyte octanol–water partition coefficient. Furthermore, unlike the comparison between tetraglyme and MeOH, the method of sample preparation did appear to have an influence on the equilibrium HS methods.

H-HS showed better recoveries of VOCs from the aqueous spiked samples than did Aq-NaHSO$_4$-HS preparation and analysis (Table 5). However, the opposite tended to take place for a vapor-fortified sample (Table 7). These two experiments used different residence times for analyte–matrix interactions and used two different soils from the same location. Another possible explanation for the change in recovery efficiency between these two equilibrium HS procedures is the difference in soil moisture. For the vapor-fortified laboratory treatment procedure, most of the bulk water was removed by desiccation; thus, very little water was present during the H-HS analysis. In the absence of soil moisture, organic matter could perhaps play a much greater role in analyte partitioning. Future experiments have been planned that will address the role of soil moisture and the use of higher equilibration temperatures (100°C or higher), as recommended by Markelov and Guzowski (1993) and Kolb et al. (1994) for a full evaporation approach to H-HS VOC analysis in soil.

A feature common to all of the equilibrium HS methods is that analytes are removed from a vessel that still contains the soil matrix, which is not present in the standards. The presence of soil has two potential effects. First, the soil plus the broken glass ampoule occupies about 2 cm^3 of space (reducing the HS from about 12 to 10 cm^3); thus, samples have a smaller amount of HS. Secondly, the soil is available for analyte partitioning.

To determine if the reduced headspace volume for the samples had an effect on analyte response by HS/GC analysis, we did the following experiment. For each of the three HS sample procedures, triplicate VOA vials with and without 2 cm^3 of glass beads were prepared and spiked. Analysis of these three HS sample preparation procedures was consistent with that of the samples. An ANOVA performed at the 95% confidence level on the results of these comparisons (Table 9) showed that often the mean responses for the VOA vials with beads for both the H-HS and for the Aq-NaCl sat'd-HS procedures were significantly enhanced. This effect is apparent for the spike recoveries obtained for the Ott sand in Table 5, where the values for this matrix are greater than spike values. This enhancement of analyte signal by changing the headspace volume is consistent with theoretical considerations (Roe et al. 1989).

The magnitude of differences caused by variations in the headspace volume between samples and standards, however, are small in comparison to the potential for analyte loss because of partitioning with the soil matrix. Table 5 shows that the headspace volume that was decreased by the Ott soil appears to cause as much as an 11% increase in analyte response, while reductions in analyte recoveries for the other three soils ranged from inconsequential to more than 90%. Clearly, losses attributable to analyte partitioning can result in very poor recoveries of VOCs for certain soils when an equilibrium sample preparation and analysis method is used.

Losses from 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 solutions acidified with NaHSO$_4$ were 0.21 M for the Aq-NaHSO$_4$-HS procedure and at least 6.2 M for the Aq-NaCl sat'd-HS procedure. Lower analyte recoveries ascribable to this salting-out effect are apparent in both Tables 5 and 7 for the CR-A/B and Pt. B soils by comparing results obtained by the two procedures.

When HS/GC is used to analyze water, the partitioning of VOCs into the vapor phase from solution is more strongly increased by salt addition than by increases in temperature (Friant and Suffet 1979). Usually, in the analysis of aqueous solutions by equilibrium HS/GC, both parameters are managed in concert for optimal partitioning. Accordingly, the standards prepared for equilibrium Aq-NaCl sat'd-HS had analyte responses some two to four times greater than those prepared without added salt (Table 9). Enhanced analyte responses, obtained when a miscible organic–aqueous solution was salted-out, were used several times in this study (for estimating MDLs, estimating analyte concentrations on aqueous-treated soil and, likewise, the Ott vapor-fortified soil).

Table 9. Instrument responses to HS equilibrium standards with and without glass beads occupying 2 cm^3 of space.

Method	TDCE*	CDCE	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl
	*Analyte response (peak height or area)*
HS-NaHSO$_4$									
No beads	302	151	547	274	816	365	859	876	615
	±21	±10	±27	±11	±42	±16	±51	±44	±27
Beads	309	153	566	286	854	387	883	901	628
	±10	±4.5	±17	±10	±28	±13	±21	±47	±26
HS-NaCl/H$_3$PO$_4$									
No beads	674	527	1730	630	2580	624	2470	2600	2460
	±13	±7.5	±20	±10	±50	±15	±38	±75	±26
Beads	759[†]	575[†]	1870[†]	712[†]	2850[†]	704[†]	2730[†]	2970[†]	2750[†]
	±27	±12	±66	±30	±57	±20	±95	±61	±65
Heated HS									
No beads	541	553	1460	476	2030	455	1800	1960	2010
	±6.0	±6.4	±25	±9.0	±10	±7.2	±26	±29	±81
Beads	573[†]	576[†]	1550[†]	507[†]	2140[†]	476[†]	1900[†]	2040	2120
	±10	±9.0	±5.8	±4.2	±35	±7.5	±17	±51	±51

* See Table 2 for full names.

† Standards with beads had significantly greater responses than without beads.

However, this salting-out approach for preparing soil samples for equilibrium HS analysis failed to achieve a similar enhanced analyte response. Instead, the matrix–analyte interactions cited previously increased. A possible explanation for this phenomenon is that organic carbon, which can be thought of as a separate phase into which hydrophobic VOCs can partition, is a more favorable repository than the vapor state under salting-out conditions. Indeed, a study by Jenkins and Miyares (1991) demonstrated how organic compounds could be efficiently salted-out of a large volume of aqueous solution and into a small volume of an organic solvent as a preconcentration procedure.

Flores and Bellar (1993a,b) have also studied, in the laboratory, Aq-NaCl sat'd-HS sample preparation and analysis. Their experiments used four soil matrices and some 57 VOCs. Very similar trends for recoveries relative to organic carbon content of the matrix and analyte octanol–water partition coefficient were found. They concluded that lower (49 to 1%) "recoveries were not due to inefficient headspace analysis, but to stronger adsorption capacity of soil." Furthermore, they stated that "the results obtained with the 7000-HA are equivalent or better than current methodology for volatiles in soil."

The results reported here are contrary to both of these statements. Using a salting-out approach enhances matrix effects, resulting in a reduced amount of analyte being available to partition with the headspace phase. Therefore, headspace methods become less effective with salting-out. For preparing samples, MeOH extraction, and perhaps many other solvents, would achieve much greater analyte recoveries than the headspace method that Flores and Bellar (1993a,b) used.

To correct for these matrix effects, Flores and Bellar (1993a,b) have recommended introducing as many as seven surrogates that have similar chemical and physical properties as the compounds most affected. To achieve realistic correction factors, analytes that are introduced as surrogates must be allow to achieve a similar equilibrium (partition) as the contaminants. As recently noted by both Pignatello and Xing (1996) and Grant et al. (1996), spiked analytes are unlikely to ever replicate the characteristics of contaminants.

To illustrate this concept, the following comparison was made. Recoveries estimated when surrogates were added to slurries of 2 g of the Pt. B soil in 10 mL of the Aq-NaCl sat'd-HS solution were used to correct the estimates shown in Table 5, for the same soil and solution. The discrepancies shown in Table 10 between the corrected and spiked values, while improved, still are far from accurate (19 to 59%, low). Here, the only difference between the two sets of samples are a 2–4 hour analyte–slurry contact vs. a 2-day aqueous sorption period followed by a 2-day dispersion–extraction at 4°C. Differences between surrogate spikes and environmental samples will typically

Table 10. Correction factors based on two exposure conditions and periods between analytes and the Pt. B soil as prepared for Aq-NaCl sat'd-HS analysis.

	TDCE*	CDCE	Ben	TCE	Tol	PCE	E-Ben	p-Xyl	o-Xyl
Correction factors†	1.47	1.92	2.00	2.36	3.19	3.00	4.67	5.20	7.10
Corrected values**	6.73	6.57	4.18	5.92	3.76	3.72	2.90	2.81	3.76
Spiked values††	8.26	8.45	5.83	9.98	6.54	9.10	6.23	6.22	6.71

  * See Table 2 for full names.
  † Correction factors based on analytes added to aqueous slurry 2–4 hours prior to analysis.
 ** Corrected analytes estimates (µg) from Table 5 of the aqueous treated Pt. B soil.
 †† Analyte concentrations (µg) in aqueous spike.

be much greater with regard to residence times and methods of analyte–contaminant introduction.

Proposed Methods 5021 and 5035 both recommend in-vial methods to solve the volatilization and preservation issues that plague VOC determinations in solid waste matrices. These two loss mechanisms have been shown to often cause more than a 90% reduction in VOCs between collection and analysis (Hewitt et al. 1995, Hewitt and Lukash 1996). Clearly, in-vial methods are necessary for obtaining site-representative VOC concentrations from vadose-zone samples. These two methods, along with the currently used Method 5030, recommend an aqueous dispersion–extraction method for low-level (less than 0.2 mg/kg) VOC determinations in soils and MeOH extraction for high-level (more than 0.2 mg/kg) determinations. The water-based sample analysis procedures for Methods 5030 and 5035 are performed by dynamic purging, while static headspace is used for Method 5021.

As shown here and previously, MeOH is a superior solvent in comparison to water for recovering VOCs from soils (Hewitt et al. 1992, Askari et al. 1996, Minnich et al. 1996), and because of mass transfer, dynamic purging may be more efficient than the static equilibrium methods (Hewitt et al. 1992). With regard to establishing representative VOC values for soil samples, the discrepancies among sample preparation methods found here and elsewhere (Flores and Bellar 1993a,b) can rival the error associated with volatilization and biological degradation losses incurred during collection and handling.

SUMMARY

This comparison of different sample preparation methods for the analysis of VOCs in soils was made on samples that exclude the systematic error associated with sample collection and handling. Investigators who have taken precautions to eliminate confounding effects all have concluded that MeOH extraction is the most robust method of recovering VOCs from soil. To my knowledge, papers that report contrary findings either made no attempt to or failed to limit the error associated with sample handling. Except in the case where there are no matrix effects (i.e., little or no organic carbon or clay content) such as was shown for Ott sand, yields less than what can be obtained using MeOH extraction will often be obtained when either purging a soil–water slurry or performing an equilibrium HS analysis of a soil or soil–water slurry. In general, soil matrix effects will increase with the analyte octanol–water partition coefficient and the organic carbon content of the soil. Furthermore, because analyte–organic carbon matrix effects increase with increasing solution electrolyte concentrations, using a salting-out approach with soils can create more problems than advantages.

Any of the equilibrium HS methods described here would be adequate for on-site screening applications, where the number of samples that can be inexpensively processed is of greater importance than the certainty of any single value. In addition, alternative solvents could be used to reduce regulatory agency concerns and achieve lower detection limits than currently can be

obtained with MeOH. The intent of this study was to make users of equilibrium HS/GC methods and alternative solvents aware of potential matrix–analyte interactions. As stated before, on a site-per-site basis, these interactions can easily be identified as a potential concern by the assessment of surrogate or matrix spike recoveries. Often, these interactions will be small, perhaps even insignificant, because vadose-zone soils rarely have high (>1%) organic carbon contents.

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, MeOH extraction and matrices other than quartz sand (a single low organic carbon soil) should be included in the performance evaluation study.

LITERATURE CITED

Askari, M.D.F., M.P. Maskarinec, S.M. Smith, P.M. Beam, and C.C. Travis (1996) Effectiveness of purge-and-trap for measurement of volatile organic compounds in aged soils. *Analytical Chemistry*, **68**: 3431–3433.

Federal Register (1984) Definition and procedure for the determination of the method detection limit. Code of Federal Regulations, Part 136, Appendix B, October 26.

Flores, P., and T.A. Bellar (1993a) Determination of volatile organic compounds in soils using equilibrium headspace analysis and capillary column gas chromatography/mass spectrometry. Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-93/032.

Flores, P., and T.A. Bellar (1993b) Determination of volatile organic compounds in soils using equilibrium headspace analysis and capillary column gas chromatography/mass spectrometry—Evaluation of the Tekmar 700 HA Analyzer. Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-93/032.

Friant, L.F., and I.H. Suffet (1979) Interactive effects of temperature, salt concentration, and pH on headspace analysis for isolating volatile organics in aqueous environmental samples. *Analytical Chemistry*, **51**: 2167–2172.

Grant C.L., T.F. Jenkins, K.F. Myers, and E.F. McCormick (1995) Holding-time estimates for soil containing explosives residues: Comparison of fortification vs. field contamination. *Environmental Toxicology and Chemistry*, **14**: 1865–1874.

Hewitt, A.D. (1994) Comparison of methods for sampling vadose zone soils for determination of trichloroethylene. *Journal of the Association of Analytical Chemistry, 77*: 458–463.

Hewitt, A.D. (1995a) Preservation of soil subsamples for the analysis of volatile organic compounds. USA Cold Regions Research and Engineering Laboratory, Special Report 95-5.

Hewitt, A.D. (1995b) Enhanced preservation of volatile organic compounds in soil with sodium bisulfate. USA Cold Regions Research and Engineering Laboratory, Special Report 95-26.

Hewitt, A.D. (1996) Methods of preparing soil samples for headspace analysis of volatile organic compounds: Emphasis on salting out. In *Proceedings of 12th Annual Waste Testing and Quality Assurance Symposium, July 23–26, Washington D.C.,* p. 322–329.

Hewitt, A.D. (1997) Chemical preservation of volatile organic compounds in soil. *Environmental Science and Technology*, **31**: 67–70.

Hewitt, A.D., and C.L. Grant (1995) Round robin study of performance evaluation soils vapor-fortified with volatile organic compounds. *Environmental Science and Technology*, **29**: 769-774.

Hewitt, A.D., and N.J.E. Lukash (1996) Sampling for in-vial analysis of volatile organic compounds in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 96-5.

Hewitt, A.D., P.H. Miyares, D.C. Leggett, and T.F. Jenkins (1992) Comparison of analytical methods for determination of volatile organic compounds. *Environmental Science and Technology*, **26**: 1932–1938.

Hewitt, A.D., T.F. Jenkins, and C.L. Grant (1995) Collection, handling, and storage: Keys to improved data quality for volatile organic compounds in soil. *American Environmental Laboratory*, Jan–Feb.

Illias, A.M., and C. Jaeger (1993) Evaluation of sampling techniques for the analysis of volatile and total recoverable petroleum hydrocarbons (GC) by IR, GC, and GC/MS methods. In *Hydrocarbon Contaminated Soils,* vol. 3. Chelsea, Michigan: Lewis Publishers, p. 147–165.

Jenkins, T.F., and P.H. Miyares (1991) Nonevaporative preconcentration techniques for volatile and semivolatile solutes in certain polar solvents. *Analytical Chemistry*, **63**: 1341–1343.

Jenkins, T.F., and P.W. Schumacher (1987) Comparison of methanol and tetraglyme as extraction solvents for determination of volatile organics in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 87-22.

Kolb, B., C. Bichler, M. Auer, and T.C. Voice (1994) Simultaneous determination of volatile aromatic and halogenated hydrocarbons in water and soil by dual-channel ECD/PID equilibrium headspace

analysis. *Journal of High Resolution Chromatography,* **17**: 299–302.

Lewis, T.E., A.B. Crockett, R.L. Siegrist, and K. Zarrabi (1994) Soil sampling and analysis for volatile organic compounds. *Environmental Monitoring and Assessment,* **30**: 213–246.

Markelov, M., and J.P. Guzowski, Jr. (1993) Matrix independent headspace gas chromatographic analysis. The full evaporation technique. *Analytica Chimica Acta,* **276**: 235–245.

Merry, R.H., and L.R. Spouncer (1988) The measurement of carbon in soils using a microprocessor-controlled resistance furnace. *Soil Science and Plant Analysis,* **19**(6): 707–720.

Minnich, M.M., J.H. Zimmerman, and B.A. Schumacher (1996) Extraction methods for recovery of volatile organic compounds from fortified, dry soils. *Journal of the Assoc. Off. Analytical Chemistry,* **79**: 1198–1204.

Pignatello, J.J., and B. Xing (1996) Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology,* **30**(1): 1–11.

Plumb, R.H., Jr., and A.M. Pitchford (1985) Volatile organic scans: Implications for ground water monitoring. In *Proceedings of National Water Well Association/American Petroleum Institute Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, 1315 November 1985, Houston, Texas,* p. 13–15.

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

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

Turriff, D., C. Reitmeyer, L. Jacobs, and N. Melberg (1995) Comparison of alternatives for sampling and storage of VOCs in soil. In *Proceedings of 11th Annual Waste Testing and Quality Assurance Symposium, July 23–28, Washington D.C.,* p. 51–58.

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

U.S. Environmental Protection Agency (1986) *Test Methods for Evaluating Solid Waste.* Vol. 1B. SW-846.

U.S. Environmental Protection Agency (1993) Draft statement of work for quick turnaround analysis. Analytical Operations Branch, Washington, D.C., EPA/540/R/94/086.

Voice, T.C., and B. Kolb (1993) Static and dynamic headspace analysis of volatile organic compounds in soils. *Environmental Science and Technology,* **27**: 709–713.

REPORT DOCUMENTATION PAGE

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

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 1997	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

Preparing Soil Samples for Volatile Organic Compound Analysis

5. FUNDING NUMBERS

6. AUTHORS

Alan D. Hewitt

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER

Special Report 97-11

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Environmental Center
Aberdeen Proving Ground, Maryland

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

SFIM-AEC-ET-CR97014

11. SUPPLEMENTARY NOTES

For conversion of SI units to non-SI units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-93, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Three equilibrium headspace and three solvent extraction methods of preparing soil samples for determining volatile organic compounds (VOCs) were compared. Soil samples were spiked with five gasoline range aromatic compounds and four chlorinated compounds using two different laboratory procedures that limit volatilization and biodegradation losses. All comparisons were made with sample triplicates of one or more soil types. Recovery efficiencies for the preparation methods depended on soil organic carbon content, octanol–water partition coefficients of specific analytes, length of solvent extraction, and the spiking procedure used. In general, methanol extraction was the most robust method for recovering spiked VOCs. Recovery efficiencies for VOCs with tetraethylene glycol dimethyl ether and poly(propylene)glycol, as well as three equilibrium headspace methods, varied with the parameters tested.

14. SUBJECT TERMS

Recovery efficiency   Vapor partitioning
Sample preparation   Volatile organic compounds
Solvent extraction

15. NUMBER OF PAGES
24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL