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## Preparation and Analysis of Dry VOC-Fortified Soils

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**ABSTRACT:** Studies were performed to assess the practicality of using dry VOC-fortified soils as performance evaluation materials (PEMs) and also to compare the effectiveness of EPA's low- and high-level purge-and-trap procedures [SW-846 Method 5030A (EPA 1992)]. Desiccator-dried soils were fortified in large batches with a combination of eight neat VOCs at 1000 ng each VOC/g soil. Three studies were performed on each of three soil types, namely, Hayesville (0.2% organic carbon, 32% clay), Kyle (0.6% organic carbon, 9% clay), and Charleston (3.8% organic carbon, 8% clay). VOC recoveries by the high-level procedure were good to excellent for all soils and compounds (98% mean recovery) and only fair by the low-level procedure (71% mean recovery). The mean relative standard deviation for all soil/compound/procedure combinations in the first study was 11%. Soil and compound properties influenced the VOC recoveries and rates of vapor losses from dry VOC-fortified soils. The poorest recoveries by the low-level procedure occurred on the soil with the highest proportion of organic matter. Rapid volatilization losses of 1,1,1-trichloroethane, benzene, trichloroethene, toluene, and tetrachloroethene were observed from 1-g samples of Kyle soil. In contrast, only trichloroethene was observed to volatilize from the Hayesville soil and no decreases in VOC concentrations were observed on the Charleston soil from 1-g samples that sat open for 20 min. No volatile losses were observed from any of the soils when dry 20-g soil samples were left open for 20 min. The technique of fortifying large batches of dry soils for PEMs as used in these studies provides good precision, but some modifications are suggested to improve the recoveries of compounds with low GC retention times on some of the soils. Also, further studies are needed to evaluate the influence of soil properties on VOC recoveries.

**KEYWORDS:** volatile organic compounds, soil/solid matrices, methanol extraction, quality assurance samples, performance evaluation materials

The concept of fortifying dry soils with volatile organic compounds (VOCs) to produce quality assurance samples or performance evaluation materials (PEMs) for the analysis of soil VOCs has been advanced by Hewitt et al. (1992) and Hewitt (1993). VOC-fortified dry soils will sustain slow to negligible rates of biodegradation or hydrolysis compared with moist soils. The sorption capacity of a dry soil is generally two to four orders of magnitude greater than that of the moist soil (Chiou and Shoup 1985, Poe et al. 1988, Ong and Lion 1991). Thus research is being conducted by the U.S. Environmental Protection Agency (EPA)

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to determine the stability of VOC-fortified dry soils and the rate of VOC vapor loss from dry soils.

Unlike the partitioning or absorption of (nonpolar) VOCs by organic matter that dominates sorption in moist soil, the mechanism of VOC sorption by dry soil is generally believed to be physical adsorption (Chiou and Shoup 1985, Ong and Lion 1991). Therefore, the capacity of dry soils to adsorb VOCs has been shown to be related to the soil-specific surface area rather than to the organic matter content (Poe et al. 1988, Ong and Lion 1991). Desorption of VOCs from dry soil would be expected to be very rapid for most compounds and to increase with increasing temperature. However, substantive losses from laboratory "piles" of dry soil will be slowed by diffusion through void spaces. Rates of volatile losses following desorption will depend on such factors as the total void space, continuity of void spaces, and the exposed soil surface area to volume ratio.

If homogeneous replicates of dry VOC-fortified soils can be obtained, they can be used not only as PEMs, but also to compare results of various field and laboratory soil VOC analytical methods. The experiments described here include a comparison of the extraction effectiveness of the low- and high-level purge-and-trap procedures, as described in EPA SW-846 Method 5030 (EPA 1992). In the EPA's low-level procedure, 5 mL of water is added to 1 to 5 g of soil or solid waste, and the mixture is purged to extricate VOCs. In the EPA's high-level procedure, 10 mL of methanol is added to 1 to 4 g of soil or solid waste; an aliquot of the methanol extract is added to 5 mL of water and purged as in the low-level procedure. The high-level procedure was designed to provide a method of diluting highly contaminated samples and therefore it was not planned as an equivalent procedure.

The objectives of this work were (1) to investigate the rate of vapor loss from dry, fortified soil during subsampling activities, and (2) to compare the accuracy and precision of EPA low- and high-level purge-and-trap procedures. In this set of experiments, three studies were performed on each of three soils. Dry soils were fortified by spiking with eight compounds (neat) at 1000 ng each VOC/g soil.<sup>3</sup> This rate is the upper end of that which can be analyzed by EPA's low-level procedure. To insure quantification by the high-level procedure at that rate, we used a soil/methanol ratio of 1 g soil/mL methanol. The first study investigated initial vapor losses and compared the low- and high-level procedures for quantifying VOCs in dry soil. The second and third studies provide supplementary data on vapor losses that might be expected while preparing VOC-fortified dry soil for low- and high-level procedures, respectively.

## Materials and Experimental Procedures

### Materials

Soils used in these studies are described in Table 1. The Hayesville soil (clayey, oxidic, mesic Typic Hapludult) came from Fannin County in Georgia's Blue Ridge Mountains. Soils designated "Kyle" (loamy-skeletal, carbonatic, thermic Typic Calciorthid) and "Charleston" (sandy-skeletal, carbonatic, mesic Fluventic Haplustoll) are from an altitudinal transect in the Mojave Desert, Clark County, Nevada; soil series have not been assigned in this region, but extensive soil characterization data and geomorphic descriptions of the areas have been reported (Amundson et al. 1989).

<sup>3</sup> The largest compound in this study, o-xylene, is approximately 1 nm<sup>2</sup>. If only o-xylene were added to the soil at 8000 ng/g, the molecules would occupy approximately  $4.5 \times 10^{-4}$  m<sup>2</sup>/g. This is approximately four orders of magnitude below the 4.3 m<sup>2</sup>/g surface area of the Charleston soil.

TABLE 1—Description of soils.

Soil Designation	Horizon	Sand (%)	Clay (%)	pH Water 1:1(w:v)	pH 0.01M CaCl <sub>2</sub>	EC (dS/m)	Surface Area, <sup>a</sup> (m <sup>2</sup> /g)	Organic Carbon, (%)	Carbonate Carbon, (%)
Hayesville	Bt2	46	32	5.0	4.4	0.018	25.5	0.2	0
Kyle <sup>b</sup>	Bw	45	9	8.1	7.7	0.207	20.2	0.6	2.0
Charleston <sup>b</sup>	A	61	8	7.7	7.3	0.313	4.3	3.8	3.1

<sup>a</sup> Measured by three-point N<sub>2</sub> sorption.

<sup>b</sup> Extended description of these soils can be found in Amundson et al. (1989). Soils collected were from the same pedon and same streamreach as those designated "surface 3 Blackbrush" and "surface 4 fir-pine" for Kyle Canyon and Mt. Charleston soils, respectively.

Target compounds used in these studies, abbreviations for the compounds, and compound properties are listed in Table 2. Two system-monitoring compounds (SMCs), *cis*-1,2-dichloroethene and 1-chloro-2-fluorobenzene, were added to each sample, blank, and standard to monitor the analytical system. SMCs were selected to bracket the retention times of the target compounds without peak interference. The target compounds were purchased neat and the SMCs as 2000 µg/mL standards (Chem Services, West Chester, Pennsylvania).

#### Experimental Procedures

Soils were air-dried and sieved to 2 mm. One kilogram of air-dried soil was placed over indicating anhydrous CaSO<sub>4</sub> in a desiccator for 2 to 7 days just prior to fortification. Desiccator-dried soil was placed in wide-mouthed 2 L glass jars with polytetrafluoroethylene-lined lids. Soil was fortified at 1000 ng each VOC/g soil. Compounds were measured volumetrically, as calculated from liquid densities. The eight target compounds (neat) were added in order of increasing vapor pressure (*o*-xylene through 1,1,1-TCA) by microsyringe, injecting the compounds 4 to 5 cm below the soil surface. The jars were then sealed and tumbled end-over-end for 12 h on a rotary mixer.

Soil was subsampled by pressing the wide end of a glass weighing funnel into the fortified, bulk sample. Subsamples of approximately 1 g and 20 g were collected for the low- and high-level procedures, respectively. Samples to be analyzed by the low-level procedure were placed in preweighed 40 mL vials with modified lids, adapted to fit on the purge-and-trap autosampler (Associated Design & Manufacturing Co., Alexandria, Virginia). Samples to be analyzed by the high-level procedure were placed in 40 mL vials that were weighed after the appropriate quantity of methanol was added.

**Minimum Detection Limits**—Seven 1-g replicates and seven 10-g replicates of unfortified soil were prepared for each soil. The 1-g replicates were spiked with 10 ng of each compound (methanolic solution) in 5 mL water plus SMCs, added just prior to placing samples on autosampler for analysis. These samples were analyzed by the low-level procedure. The replicates analyzed by the high-level procedure were prepared to yield the same quantity (10 ng) on the detector. Methanol (10 mL) and 1000 ng of each compound (in methanolic solution) were added to the 10-g samples (100 ng/g). Aliquots (100 µL) of the extract were

TABLE 2.—Compounds and properties. GC retention times refer to those observed on analytical system described in this report.

Compound	GC Retention Time, min	Molecular Weight, g/mol	Density, (g/mL)	Solubility, 25°C, mg/L	Vapor Pressure, 25°C, mm Hg	Log <i>K<sub>ow</sub></i> <sup>a</sup>
1,1,1-trichloroethane (1,1,1-TCA)	3.9	133.42	1.339	1495 <sup>b</sup>	123.7 <sup>b</sup>	2.49 <sup>b</sup>
Benzene	4.5	78.11	0.879	1791 <sup>c</sup>	95.19 <sup>c</sup>	2.13 <sup>c</sup>
Trichloroethene (TCE)	5.3	131.40	1.464	1100 <sup>b</sup>	69.0 <sup>b</sup>	2.42 <sup>b</sup>
Toluene	7.3	92.13	0.867	534.8 <sup>b</sup>	28.4 <sup>b</sup>	2.73 <sup>b</sup>
Tetrachloroethene (PCE)	8.2	165.82	1.623	150.3 <sup>c</sup>	18.49 <sup>b</sup>	3.40 <sup>b</sup>
Ethylbenzene	10.0	106.16	0.867	161 <sup>c</sup>	9.53 <sup>c</sup>	3.15 <sup>c</sup>
<i>o</i> -xylene	11.0	106.16	0.880	175 <sup>b</sup>	6.6 <sup>c</sup>	3.12 <sup>b</sup>
1,1,2,2-tetrachloroethane (1,1,2,2-TTCA)	12.5	167.85	1.541	1100 <sup>b</sup>	12.03 <sup>c</sup>	3.03 <sup>c</sup>

<sup>a</sup> Log octanol water partition coefficient.

<sup>b</sup> Howard 1990.

<sup>c</sup> Howard 1989.

placed in clean vials, SMCs and water were added, and the replicate extracts were then purged. The minimum detection limit by each procedure for each soil was calculated as the product of the standard deviation of the replicate analyses and the Student's "t" value for a two-sided, 99% confidence level with 6 degrees of freedom. Compound minimum detection limits as determined in this manner are given in Table 3.

*Study 1. Comparison of Low- and High-Level Procedures*—Fourteen samples were collected from the bulk fortified soil, seven to be analyzed by each procedure, taken alternately. As each vial was sealed, the time was noted. Unfortified soils were prepared and analyzed by each procedure as study blanks. Samples were stored in the dark at room temperature until analyzed (within 1 to 10 days).

*Study 2. Volatilization from 1-g Samples*—Quadruplicate 1-g samples were left in open vials in an active fume hood for 0, 5, 10, 20, and 40 min. Each set of replicates was collected in a "round" (four rounds) and the collection of samples by treatment was randomized within each round. After sitting for the specified time, samples were sealed with the modified lids, and soil weights were determined. Two vials of unfortified soil were placed in the middle of fortified samples and left open for 20 and 40 min as study blanks.

*Study 3. Volatilization from 20-g Samples*—Quadruplicate 20-g samples were placed in 0, 5, 10, and 20 mL methanol. A fifth set of replicates, designated "unopened control" was placed in 20 mL of methanol during sampling. Again, each set of replicates was collected in a "round" and the collection of samples by treatment were randomized within each round. Samples were sealed, weighed to determine soil weights, and returned to the hood. The lids were then removed from all but the unopened control samples, and the samples were left open for 20 min. At this point, samples were sealed and weighed to determine any methanol lost. Methanol was added to bring all samples to 20 mL. Thereafter, samples were shaken, stored, and analyzed as described for high-level samples in Study 1. The study blank consisted of 20 mL of methanol, left open for 20 min in the midst of the other open samples.

#### Analytical Procedures

Compounds were analyzed on a Hewlett-Packard Series II Model 5890 gas chromatograph (GC) equipped with a J&W DB 624 30 m, 0.53 mm inside diameter, fused silica column. The purge-and-trap was an O.I. Analytical Model 4460A Sample Concentrator with a MPM-16 multiple purging module autosampler. Detectors were an O.I. Analytical Model 4420 electrolytic conductivity detector and an O.I. Analytical Model 4430 photoionization detector, arranged in series. Operating conditions followed those specified in EPA SW-846 Methods 5030 and 8021 (EPA 1992). Sample concentrations were determined from equations

TABLE 3—Minimum method detection limits (ng/g).

Compound	Low Level			High Level		
	Hayesville	Kyle	Charleston	Hayesville	Kyle	Charleston
Benzene	4.4	3.0	2.3	42	54	45
Toluene	14.4	10.1	9.6	47	157	53
Ethylbenzene	5.8	4.5	3.5	48	101	53
o-xylene	6.9	4.8	2.7	41	129	49
1,1,1-TCA	5.1	2.7	19.1	77	19	81
TCE	4.2	2.3	3.5	32	59	33
PCE	6.1	2.6	5.1	31	62	58
1,1,2,2- <i>TTCA</i>	3.3	2.2	1.6	49	137	77

generated by Turbochrome software using five-point calibration curves (analyzed in triplicate). If the recovery of at least one of the SMCs was  $100\% \pm 25\%$ , the system was assumed to be operating in an acceptable manner.

The analysis of samples by the low-level procedure followed EPA specifications except that the modified lids allowed samples to be placed on the sparger with minimal loss of VOCs. Water (5 mL) plus SMCs (150 ng each cis-1,2-dichloroethene and 1-chloro-2-fluorobenzene in 10  $\mu\text{L}$  methanol) were added by syringe through a three-way valve after the samples were secured on the autosampler.

For the analysis of samples by the high-level procedure, 100  $\mu\text{L}$  of the methanol extract was placed in a clean vial and sealed with a modified lid. Thereafter, the low-level procedure was followed. However, a separate five-point calibration curve was generated, one in which all standards had 110  $\mu\text{L}$  of methanol.

#### Statistical Procedures

The comparison of means between low- and high-level procedures for each compound on each soil were t-tested for the two-tailed hypotheses:  $H_0: \bar{x}_1 = \bar{x}_2$ , and  $H_a: \bar{x}_1 \neq \bar{x}_2$ . The ratio of the variances associated with each procedure was first compared with the appropriate F-ratio to determine the homogeneity of variances. Variances that were not significantly different at the 95% level were t-tested using a pooled variance,  $s_p^2$  (following Zar 1984, p. 129). Variances that were significantly different were tested using an alternate t-test (following Zar 1984, p. 131).

#### Results

In Study 1, the chronological order of sampling was expected to demonstrate VOC losses during sampling. The time required to collect 14 samples in the first study was 5 to 10 min, depending mainly on the ease with which the soil slid through the sampling funnel. Benzene, 1,1,1-TCA, and TCE concentrations appeared to decrease during sample collection of the Kyle soil (Fig. 1). No other decreases in VOC concentrations corresponding to sample order were observed, indicating no significant losses during the 5 to 10 min sample collection time (data provided for Kyle and Charleston soils, Fig. 1).

Generally higher concentrations of the VOCs were measured by the high-level procedure as compared to the low-level procedure (Fig. 2). The differences between VOC concentrations obtained by the two methods were greater for compounds with larger GC retention times, whereas results for compounds with the lowest retention times (1,1,1-TCA and benzene) were comparable by either extraction procedure. Differences between VOC concentrations obtained by the two methods were not statistically significant (95%) for many compound/soil combinations (Table 4). Significant differences (at least 95% level) were observed for toluene on the Hayesville soil, ethylbenzene and o-xylene on the Kyle soil, and toluene, ethylbenzene, o-xylene, TCE, PCE, and 1,1,2,2-TTCA on the Charleston soil.

Recovery of the nominal fortification level of 1000 ng each VOC/g soil provided a basis for comparing the Study 1 means across compounds and soils (Fig. 2). The mean recovery of all compounds from all soils was 71% by the low-level procedure (range 25% to 149%) and 98% by the high-level procedure (range 69% to 143%). Relative standard deviations (RSDs) among replicates ranged from 2% to 24%, with an overall mean RSD of 11.0%. Data for 1,1,2,2-TTCA on the Hayesville was excluded from the above means because, for the low-level procedure, only one of the replicates was within the calibration range.

In Study 2, soil left open for up to 40 min exhibited considerable variation in VOC concentrations among the compound/soil combinations. Substantial decreases in VOC con-

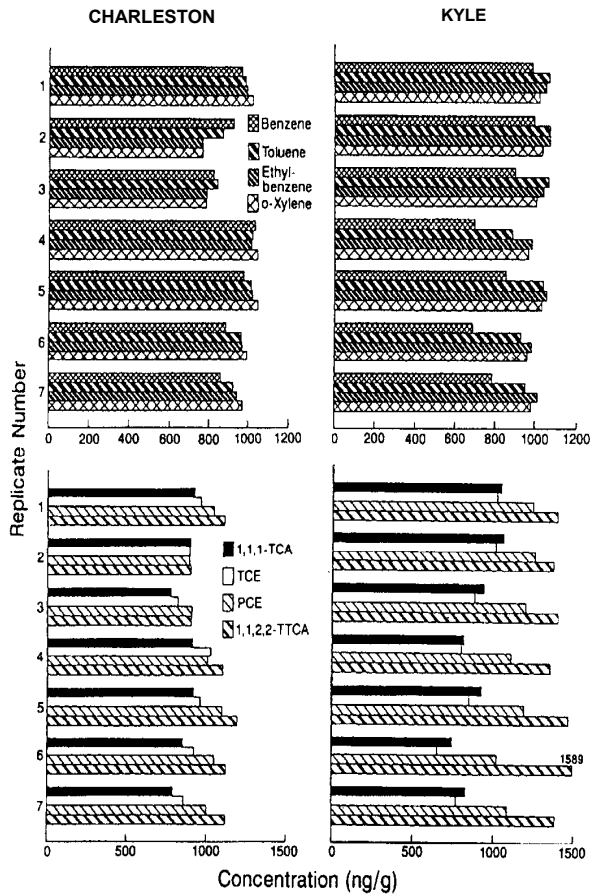


FIG. 1—VOC concentrations (in methanol extracts) of seven replicate samples of Charleston and Kyle soils, presented in the chronological order in which samples were collected. Samples were collected in 9.5 and 5 min for the Kyle and Charleston soils, respectively.

centrations were evident for benzene, toluene, 1,1,1-TCA, TCE, and PCE on the Kyle soil (Fig. 3). On the Hayesville soil, a considerable decrease in concentrations of benzene, 1,1,1-TCA, and TCE was noted between 20 and 40 min. In contrast, a marked increase in VOC concentrations with time for all compounds except 1,1,1-TCA was observed on the Charleston soil and for ethylbenzene, o-xylene, and 1,1,2,2-TTCA on the Hayesville soil. Subsequent studies indicated that the increase in VOC concentrations was an experimental artifact, related to the extraction time (Minnich et al., in review). While queued on the autosampler, the samples sat in water for up to 8 h, and an increasingly improved extraction by the low-level purge-and-trap resulted. Therefore, for some of the soil/compound combinations, if vapor loss occurred in Study 2, it could not be discerned because the samples were analyzed in the same order that vials were sealed, and VOC recoveries were increasing during the time samples soaked.

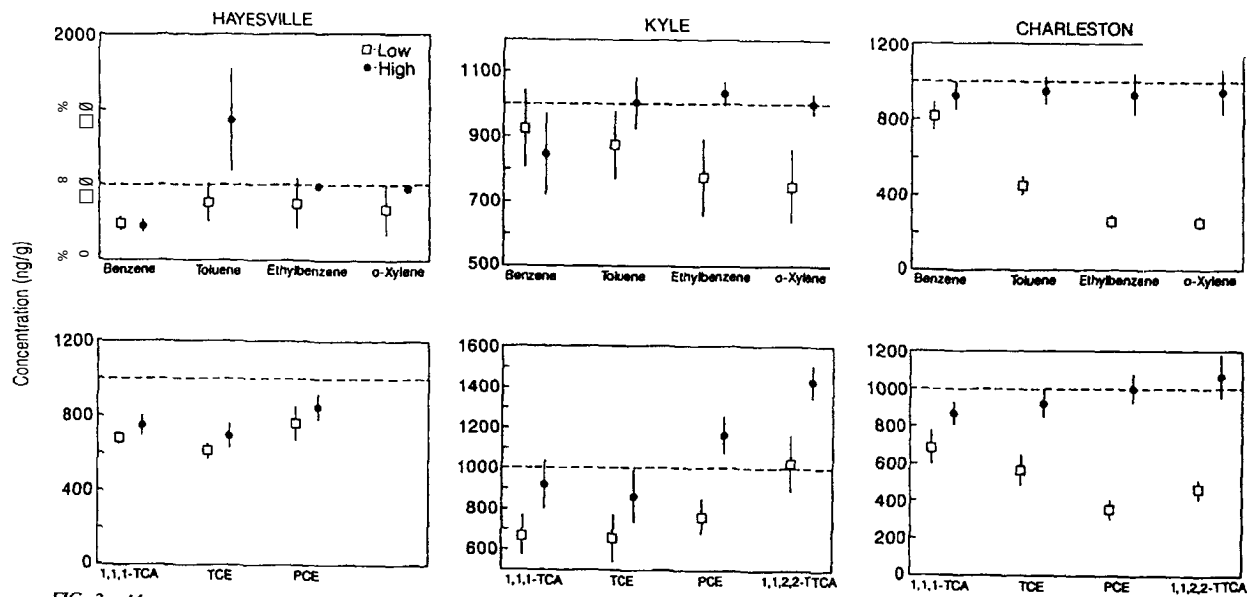


FIG. 2—Mean concentration and one standard deviation about the mean ( $n = 7$ ) of VOCs on three soils using EPA's low- and high-level purge-and-trap procedures. Note the nominal fortification level (1000 ng/g) plotted on each graph. Data for 1,1,2,2-TCFA by the low-level procedure on the Hayesville soil exceeded the calibration curve for six of the seven replicates and, therefore, the comparison for this compound was deleted.



TABLE 4—Variance ratios and *t*-test results from Study 1.

Soil	Compound	Variance Ratio <sup>a</sup>	<i>t</i> <sub>1</sub> <sup>b</sup>	<i>t</i> <sub>2</sub> <sup>c</sup>	Degrees of Freedom	Critical <i>t</i> <sub>(α/2)=0.05</sub>
Hayesville	benzene	1.13	0.15	...	6	2.447
	toluene	7.70	...	3.98**	8	2.306
	ethylbenzene	60.53	...	1.84	6	2.447
	o-xylene	51.51	...	2.30	6	2.447
	1,1,1-TCA	2.53	0.81	...	6	2.447
	TCE	2.17	0.86	...	6	2.447
	PCE	1.94	0.60	...	6	2.447
	1,1,2,2-TTCA	18.97	...	0.06	7	2.365
Kyle	benzene	1.11	0.34	...	6	2.447
	toluene	1.78	0.75	...	6	2.447
	ethylbenzene	9.84	...	5.55***	7	2.365
	o-xylene	13.18	...	5.69***	7	2.365
	1,1,1-TCA	1.46	1.22	...	6	2.447
	TCE	1.26	0.88	...	6	2.447
	PCE	1.03	2.43	...	6	2.447
	1,1,2,2-TTCA	2.93	1.95	...	6	2.447
Charleston	benzene	1.09	0.81	...	6	2.447
	toluene	2.35	4.57**	...	6	2.447
	ethylbenzene	12.06	...	16.00***	7	2.365
	o-xylene	14.06	...	14.73***	7	2.365
	1,1,1-TCA	2.18	1.25	...	6	2.447
	TCE	1.40	2.48*	...	6	2.447
	PCE	2.21	5.32**	...	6	2.447
	1,1,2,2-TTCA	4.86	...	12.57***	8	2.306

<sup>a</sup> Ratio of variance of the seven replicates by each method. Largest variance used as numerator; values compared to critical values of  $F_{0.05,6,6}$  (after Zar 1984, p. 123).

<sup>b</sup> Used where variance ratio less than 4.28. Significance denoted as \*, \*\*, and \*\*\* for  $p = 0.05$ ,  $p = 0.01$ , and  $p = 0.001$ , respectively.

<sup>c</sup> Used where variance ratio greater than 4.28. Significance levels as noted above.

Study 3 showed no significant effect of treatment (amount of methanol) on recovery of VOCs after 20 g samples were left open 20 min. Moreover, there was no difference greater than one standard deviation around the mean between an unopened control and the zero level of methanol for any compound, even on the Kyle soil. Although Kyle soil showed volatile losses of benzene, 1,1,1-TCA and PCE in Study 2 (1-g soil samples), statistically significant volatilization was not observed in Study 3 (20-g samples). A statistically insignificant but perceptible decrease in benzene, ethylbenzene, and o-xylene concentrations at 5 mL of methanol as compared to samples with no methanol was seen on the Kyle soil (Fig. 4).

## Discussion

### Vapor Loss During Sampling

To achieve preservation in moist soil, loss of VOCs due to both biodegradation and volatilization must be prevented. In dry soil, the problem is largely confined to preventing vapor loss. Disturbance during sampling (that is, scooping and pouring) is likely to increase vapor losses, conceivably even more than short periods of time with soil sitting in open vials (Studies 2 and 3). For the most part, replicate samples in Study 1 demonstrated that the differences in sample concentrations were not related to sampling order (Fig. 1).

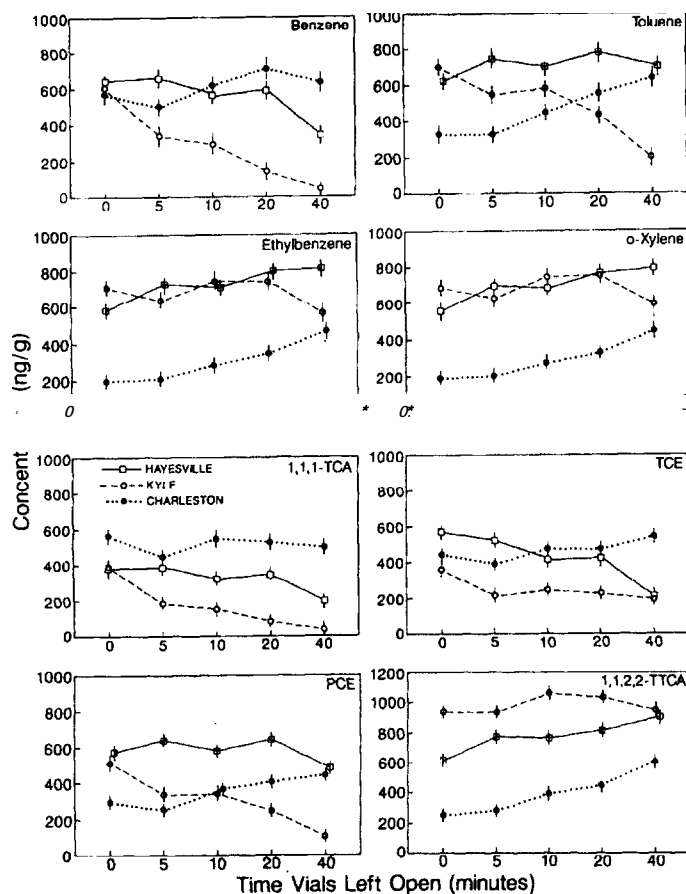


FIG. 3—Mean VOC concentration and one standard deviation about the mean ( $n = 4$ ) observed in 1-g fortified soil after samples sat open in hood for time indicated.

It is assumed, however, that the headspace VOCs—the proportion of VOCs present in the vapor phase above the soil—are readily lost upon opening the jar. This initial loss of headspace VOCs is certainly followed by a continuous diffusion of VOCs from the soil to the atmosphere. Jars of fortified soil were resealed after sampling for Study 1, and then sat for up to 2 h before being opened a second and third time to obtain samples for Studies 2 and 3. Mean VOC concentrations in the control samples of Study 3 (unopened control) are compared with Study 1 concentrations in Table 5. (The Hayesville soil has been excluded because a different batch of fortified soil was used in the first study.) On the Kyle soil, the mean concentrations of all compounds except 1,1,2,2-TTCA were lower in the Study 3 control, indicating that vapor loss was occurring from the Kyle soil. On the Charleston soil,

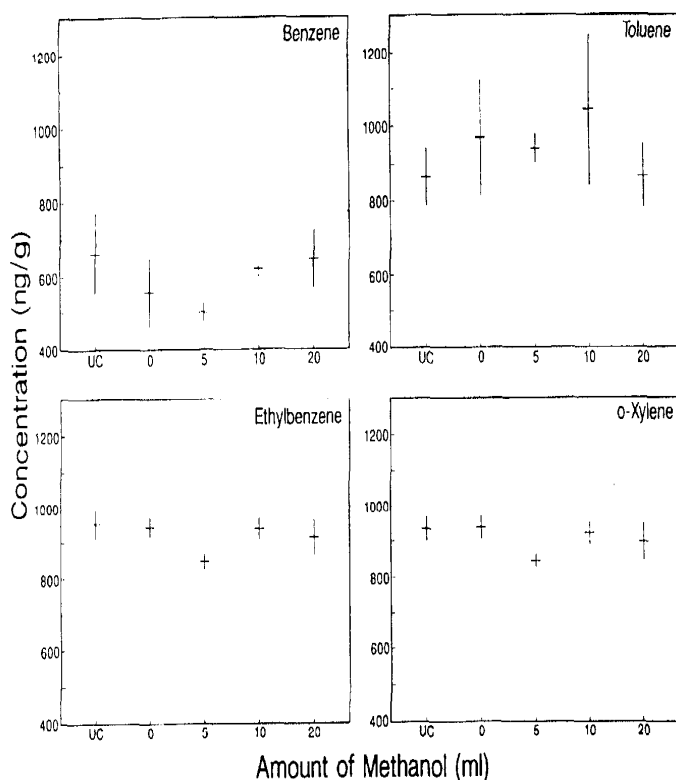


FIG. 4—Mean VOC concentration and one standard deviation about the mean ( $n = 4$ ) after fortified Kyle soil (20-g) sat open 20 min in the amount of methanol specified. Unopened control (UC) samples were placed in 20 mL of methanol and sealed immediately.

however, no trend of vapor losses from multiple sampling events was observed. The key difference between these soils was the organic carbon content which was relatively high in the Charleston soil and relatively low in the Kyle soil. The results imply that organic carbon was capable of sorbing the VOCs and only released the VOCs slowly.

#### Surface Area and Volatilization Rates

Observations on these three soils indicate that  $N_2$  Brunauer-Emmett-Teller (BET) surface area is a poor predictor of volatilization rate, although other studies have shown that specific surface area is correlated to sorption capacity (Poe et al. 1988, Ong and Lion 1991). Note that the Hayesville and Kyle soils had similar surface areas, as measured by 1-point  $N_2$  BET sorption (Table 1). The Hayesville soil (25.5  $m^2/g$ ) contains 32% clay (predominantly gibbsite, goethite, and kaolinite) as compared with the Kyle soil (20.2  $m^2/g$ ), which contains 9% clay (predominantly smectite, quartz, and mica). Qualitative differences between the oxides and sheet silicates could account for the similar surface areas with such dissimilar clay contents. However, the rate of vapor loss from the Kyle soil, particularly for benzene, toluene, 1,1,1-TCA, and PCE, appears much greater than the rate of vapor loss from the Hayesville soil (Fig. 3).

TABLE 5—Comparison of mean VOC concentrations between Studies 1 and 3.

Soil	Compound	Concentration, ng/g	
		Study 1 High	Study 3 Control
Kyle	benzene	843	662
	toluene	1001	865
	ethylbenzene	1028	954
	o-xylene	999	934
	1,1,1-TCA	914	733
	TCE	860	675
	PCE	1163	1079
	1,1,2,2-TTCA	1429	1588
Charleston	benzene	924	904
	toluene	946	943
	ethylbenzene	928	952
	o-xylene	947	983
	1,1,1-TCA	866	809
	TCE	919	942
	PCE	998	1034
	1,1,2,2-TTCA	1064	1206

In the third soil, Charleston, organic carbon was high (3.8%), but the measured surface area was only 4.3 m<sup>2</sup>/g. The specific surface of dehydrated organic matter is generally low. For example, Jurinak and Volman (1957) reported that the surface area of a Staten peaty muck soil was 11.7 m<sup>2</sup>/g by dry N<sub>2</sub> versus 264 m<sup>2</sup>/g by glycol retention. For this study, surface area was measured by N<sub>2</sub> BET sorption on dry soil (dried at 80°C), selected to closely resemble the actual experimental conditions. However, two experimental observations on the Charleston soil, (1) the low VOC volatilization rate and (2) poor VOC recovery by the low-level procedure, indicated that VOCs were sorbed by, or had diffused into dehydrated organic matter. Desiccator-dried Charleston soil contained 0.7% moisture and perhaps this residual moisture content was sufficient to explain why these sorption results differ from studies that use oven dry materials. Therefore, the BET surface area measurement of soil dried at 80°C did not correspond to either the VOC desorption rate or the volatilization rate from the Charleston soil.

#### *Vapor Loss via Minimal Amounts of Methanol*

In Study 3, an interesting effect was noted for the 5 mL methanol treatment of the Kyle soil. Our intention was to investigate whether or not small amounts of methanol were sufficient as an absorbent for VOC vapors (fortified soil left open for 20 min in various amounts of methanol). The mean concentration recovered in the 5-mL methanol treatment was lower than that of all other treatments, including the treatment with no methanol present. Figure 4 presents the results for benzene, ethylbenzene, and o-xylene on the Kyle soil. We suggest that methanol vapor was displacing these compounds, similar to displacement of VOCs by water vapor observed in other studies (Chiou and Shoup 1985, Ong and Lion 1991). However, the effect was not noted on Hayesville and Charleston soils. This is further evidence

that desorption/volatilization was more rapid on the Kyle soil and that sorption sites on Kyle soil were qualitatively different from the other soils.

#### *Dry Soils as PEMs*

Quality soil VOC PEMs will require: (1) homogeneous (precise) replicates, (2) slow rates of vapor loss, and (3) long-term stability. Replicate variability could arise from soil heterogeneity, differences in the amount of disturbance during sampling, and analytical noise. In these studies, RSDs were similar for both low- and high-level procedures. This indicates that 1-g soil samples were no more heterogeneous than 20-g samples for sieved, air-dried soil or, that the soil "noise" contributed less than the analytical noise. It may be possible to reduce the analytical noise by careful selection of internal standard(s) that mimic the target compounds, or perhaps, by use of one of the newer, redesigned purge-and-trap instruments that eliminate port-to-port variability and use uniform internal diameter on all fittings, valves, and tubing to avoid dead volume.

Compounds with low GC retention times are difficult to retain, particularly on soils that are low in both clay and organic matter. Chilling the soil prior to subsampling will be investigated to deter the vapor losses. The greatest losses we observed were decreases of approximately 50% for benzene and 1,1,1-TCA on the Kyle soil during the first five minutes that the 1-g samples sat unsealed (Fig. 3). However, we found no apparent difference on the Hayesville soil (for toluene, ethylbenzene, o-xylene, PCE, and 1,1,2,2-TTCA) between 1-g samples sealed immediately and replicate samples that sat open for 40 min before sealing. On the Charleston soil, it appears that any vapor losses that occurred were slight relative to the loss in extraction efficiency when samples were analyzed too quickly (within a few hours) by the low-level procedure.

The third concern, the stability of VOCs over extended periods of time, was not addressed in these studies, but is currently being investigated. Two issues should be considered: losses that may occur (degradation or slow vapor losses through leakage) and changes in extractability. Preliminary data have indicated that some of the compounds exhibit decreased recoveries by the low-level procedure with increased storage times.

#### **Conclusions**

VOC-fortified dry soils can be prepared by addition of neat compounds to achieve good reproducibility among replicates (RSDs of eight compounds on three soils ranged from 2% to 24%). VOC recoveries from the dry, fortified soils were influenced by the compound properties (for example, vapor pressure), soil properties (for example, organic carbon content), and extraction method. The most volatile compounds in this study, 1,1,1-TCA and benzene, were readily lost from the Kyle soil; that is, losses of up to 50% were observed from 1-g samples left unsealed for five minutes. In contrast, excellent recoveries of all eight VOCs in the study resulted from the methanol extraction of Charleston soil (after the EPA Method 5030 high-level procedure). Vapor losses from the Charleston soil were negligible, even in samples that sat open for 40 min. To more accurately generate VOC-fortified PEMs on all soil types by the procedure described herein, improved retention of the most volatile compounds is needed.

The EPA Method 5030 low-level purge-and-trap extraction was not as rigorous as the high-level extraction. The high-level procedure extracted a significantly greater amount of VOCs for nine soil/compound combinations and never resulted in significantly lower VOC concentrations

Recovery by the low-level method was impeded by slow desorption of some compounds from the Charleston soil as shown by the increased concentrations of many VOCs as the soil soaked in water prior to purging. From the limited perspective of only three soils, the results implied that *dry* organic matter was capable of sorbing VOCs and only slowly released the VOCs, a conclusion that conflicts with other studies that report vapor sorption to be related to the dry soil surface area (Poe et al. 1988, Ong and Lion 1991). Unlike studies where solids are oven-dried before performing sorption tests, soil was desiccator-dried in the present study, which we believe left sufficient water to maintain a natural structure in the soil organic matter and thus the organic matter absorbed VOC vapors.

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#### References

- Annundson, R. G., Chadwick, O. A., Sowers, J. M., and Donner, H. E., 1989, "Soil Evolution Along an Altitudinal Transect in the Eastern Mojave Desert of Nevada," *Geoderma*, Vol. 43, pp. 349-371.
- Chiou, C. T. and Shoup, T., 1985, "Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanism and Capacity," *Environmental Science and Technology*, Vol. 19, pp. 1196-1200.
- EPA, 1992, *Test Methods for Evaluating Solid Waste. SW-846*, 3rd ed., Final Update I. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC.
- Hewitt, A. D., Miyares, P. H., Leggett, D. C., and Jenkins, T. F., 1992, "Comparison of Analytical Methods for Determination of Volatile Organic Compounds in Soils," *Environmental Science and Technology*, Vol. 26, pp. 1932-1938.
- Hewitt, A. D., 1993, "Vapor Fortification: A Method to Prepare Quality Assurance Soil Samples for the Analysis of Volatile Organic Compounds," Abstract from the *National Symposium on Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs*, Jan. 12-14, Las Vegas, NV, U.S. Environmental Protection Agency, Las Vegas, NV.
- Howard, P. H., Ed., 1989, *Handbook of Environmental Fate and Exposure Data*, Vol. I, Lewis Publishers, Chelsea, MI.
- Howard, P. H., Ed., 1990, *Handbook of Environmental Fate and Exposure Data*, Vol. II, Lewis Publishers, Chelsea, MI.
- Jurinak, J. J. and Volman, D. H., 1957, "Application of Brunauer, Emmett and Teller Equation to Ethylene Dibromide Adsorption by Soils," *Soil Science*, Vol. 83, pp. 487-496.
- Minnich, M. M., Zimmerman, J. H., and Schumacher, B. A., in review, "Extraction Methods for Recovery of VOCs from Fortified, Dry Soils."
- Ong, S. K. and Lion, L. W., 1991, "Mechanisms for Trichloroethylene Vapor Sorption onto Soil Minerals," *Journal of Environmental Quality*, Vol. 20, pp. 180-188.
- Poe, S. H., Valsaraj, K. T., Thibodeaux, L. J., and Springer, C., 1988, "Equilibrium Vapor Phase Adsorption of Volatile Organic Chemicals on Dry Soils," *Journal of Hazardous Materials*, Vol. 19, pp. 17-32.
- Zar, J. H., 1984, *Biostatistical Analysis*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 781 pp.