

Long-Term Study of Volatile Organic Compound Recovery from Ampulated, Dry, Fortified Soils

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ABSTRACT

Our objective was to evaluate the stability and extractability of volatile organic compounds (VOCs) when fortified on dry soils and stored in sealed ampules. Two desiccator-dried soils were fortified with eight neat VOCs, benzene, toluene, ethylbenzene, o-xylene, 1,1,1-trichloroethane (TCA), trichloroethene (TCE), tetrachloroethene (PCE), and 1,1,2,2-tetrachloroethane (TTCA) at 800 ng each VOC/g soil. The fortified soil was portioned into ampules, sealed, and stored in the dark at 25°C for up to 56 wk. Replicate ampules were analyzed after 2 d and 2, 4, 8, 13, 34, and 56 wk by two extraction procedures modified from the U.S. Environmental Protection Agency's (USEPA's) low- and high-level purge-and-trap procedures (SW-846 Methods 5030/8021). The modified high-level procedure (1-h methanol extraction at 25°C prior to purge-and-trap analysis) yielded significantly higher recoveries of all compounds on both soils as compared with the low-level procedure, with the exception of benzene on the Charleston soil. Moreover, when measured by the high-level procedure, concentrations of benzene, toluene, ethylbenzene, and o-xylene (BTEX) remained relatively unchanged during the 56-wk study. The results indicate that the 1-h, 25°C methanol extraction was sufficient for extraction of the BTEX compounds from these soils. For the chlorinated compounds, regression analysis demonstrated significant trends of changing concentrations over time. Recoveries of TCA decreased at a rate of 3 and 4 n%/week and recoveries of TTCA decreased at rates of 8 and 17 ng/g/week on the Hayesville and Charleston soils, respectively. PCE concentrations did not show any significant concentration changes, while TCE concentrations increased at 6 and 7 ng/g/week for the Hayesville and Charleston soils, respectively. We submit that the 1-h, 25°C methanol extraction was inadequate for removal of the chlorinated compounds. Additionally, we postulate that dehydrochlorination of TTCA to form TCE occurred in desiccator-dried soil.

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Characterization Research Division, Las Vegas (EPA CRD-LV), NV, is seeking ways to develop quality assurance samples or performance evaluation materials to verify analytical accuracy during routine soil VOC analyses. Currently, analytical accuracy is verified through the analysis of liquid performance evaluation materials, samples that do not reflect the difficulties of VOC extraction from a soil matrix. Dry soils can be fortified with VOCs to provide relatively stable and reliable quality assurance samples (Minnich et al., 1996a; Hewitt et al., 1992; Hewitt, 1994). Dry soil adsorbs two to four orders of magnitude more compound than moist soil, depending on the soil and compound characteristics (Chiou and Shoup, 1985; Ong and Lion, 1991) and VOC degradation rates are markedly reduced in dry soil (Hewitt, 1994). From a research perspective, the generation of relatively stable samples will increase the accuracy and precision of numerous studies involving VOCs in soil.

Fortification of dry soil with VOCs can be accomplished by injection of neat compounds (Minnich et al., 1996a) or by vapor sorption in a closed system (Hewitt et al., 1992; Hewitt, 1994). By the former method, the initial fortification level is specified *a priori*, while with the latter method, the fortification level is dependent on soil and chemical properties, time of exposure, and relative concentrations of the VOCs in the fortification solution. By either method, the resulting concentration must be verified by analyzing subsamples.

The purpose of this study was to explore the feasibility

Abbreviations: VOC, volatile organic compound; TCA, 1,1,1-trichloroethane; TCE, trichloroethene; PCE, tetrachloroethene; TTCA, 1,1,2,2-tetrachloroethane; USEPA, U.S. Environmental Protection Agency; BTEX, benzene, toluene, ethylbenzene, and xylene; CRD-LV, Characterization Research Division, Las Vegas; SMC, system monitoring compound.

Table 1. Description of soils.

| Soil designation | Sand† | Clay† | pH | pH | Electrical conductivity | Surface area‡ | Organic C§ | Carbonate C§ |
|------------------|-------|-------|---------------|-------------------------|-------------------------|---------------|------------|--------------|
| | | | Water 1:1 w/v | 0.01M CaCl ₂ | | | | |
| | | % | | | | % | | |
| Hayesville | 46 | 32 | 5.0 | 4.4 | 0.018 | 23.5 | 0.2 | 0 |
| Charleston¶ | 61 | 8 | 7.7 | 7.3 | 0.313 | 4.3 | 3.8 | 3.1 |

† Determined by pipette method after pretreatment for removal of organics and carbonates.

‡ Measured by three-point N₂ sorption.

§ Organic C calculated as difference between total C (dry combustion) and carbonate C (manometric method).

¶ Extended description of this soil can be found in Amundson et al., 1989. Soil was collected from the same streamreach as that designated surface 4 fir-pine.

of storing VOC-fortified soil in sealed ampules over many months. We postulated that the concentration of the VOCs would remain constant, but the extractability of the VOCs from the soil might decrease, depending on the rigor of the analytical procedure. To test the hypothesis, we monitored the recovery of VOCs from fortified soils during many months by two analytical procedures, which were slightly modified from USEPA's purge-and-trap low- and high-level SW-846 Method 5030 (USEPA, 1992). Previous studies have demonstrated that the high-level procedure, methanol extraction prior to purge-and-trap analysis, is superior to the low-level procedure for recovery of VOCs from dry soils (Minnich et al., 1996a,b).

MATERIALS AND METHODS

Materials

Two soils were used in this study, the Hayesville series and Charleston (Table 1). The Hayesville soil (clayey, kaolinitic, mesic Typic Kanhapludult) came from Fannin County in Georgia's Blue Ridge Mountains. Soil designated "Charleston" (sandy-skeletal, carbonatic, mesic Fluventic Haplustoll) is 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 rePotted (Amundson et al., 1989).

Eight target compounds were used in the study, four components of gasoline and four chlorinated solvents (Table 2). Two system monitoring compounds (SMCs), cis-1,2-dichloroethene and 1-chloro-2,4-dichlorobenzene, were added to each sample, blank and standard to insure the purge and detector systems were operating properly. The target compounds were purchased neat, and the SMCs were purchased as 1000 µg/mL standards (Chem Services, West Chester, PA).

Sample Preparation

Soils were air-dried and sieved to 2 mm. One kilogram of air-dried soil was placed over indicating anhydrous CaSO₄ in a desiccator for 2 to 7 d prior to fortification. This dried the Hayesville and Charleston soils to within 3 and 7%, respectively, of the oven-dried weights (105°C). Desiccator-dried soil was placed in wide-mouthed 2-L glass jars with polytetrafluore ethylene-lined lids. Soil was fortified at 800 ng each VOC/g soil*. Compounds were measured volumetrically as calculated

¹ The combined rate of VOCs added to the soil did not exceed the surface area of these soils. If o-xylene, the largest compound in this study at approximately 1 nm², was added to the soil at 8000 ng/g (10 times the actual rare), the molecule, would occupy approximately 5.2 x 10⁻² m²/g. This is approximately two orders of magnitude below the surface area of the Charleston soil (4.3 m²/g. Table 1).

from liquid densities. The eight target compounds (neat) were added in order of increasing vapor pressure (o-xylene through 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. Approximately 1 and 5 g were sampled alternately for the low- and high-level procedures, respectively, and poured into 10-mL ampules via a glass funnel. Ampules were sealed, weighed, and stored at 25°C in the dark until analysis.

The subsampling and ampulation took approximately 3-h per soil to complete. Therefore, the ampules were divided into seven blocks, or rounds, based on the consecutive order in which they were filled. Ampules were randomly assigned to an analysis date within each round. In this manner, five replicates at each analytical date encompassed the time required to ampulate the samples. Sample analyses occurred at 2 d and 2, 4, 8, 13, 34, and 56 wk. Some replicates were accidentally broken during storage and, therefore, only two replicates were analyzed by the low-level procedure at 56 wk.

Analytical Procedures

Compounds were analyzed on a Hewlett-Packard Series II Model 5890 gas chromatograph (Hewlett-Packard Co., Palo Alto, CA) equipped with a J&W DB 624 30 m, 0.53 mm ID, fused silica column (J&W Scientific, Folsom, CA). The purge-and-trap unit was an 0.1. Analytical Model 4460A Sample Concentrator with an MPM-16 multiple purging module autosampler (01 Analytical, College Station, TX). Detectors were an 0.1. Analytical Model 4430 photoionization detector and an 0.1. Analytical Model 4420 electrolytic conductivity detector, arranged in series. Procedures were essentially as specified in USEPA SW-846 Methods 5030/8021 (USEPA, 1992), with calibration only for the analytes of interest. Sample concentrations were determined using live-point calibration curves: one for the low level procedure containing no more

Table 2. Compounds and properties.

| Compound | Molecular | | Solubility, 25°C | Vapor pressure, Log K _{ow} † | |
|-----------------------------|-----------|---------|------------------|---------------------------------------|-------|
| | weight | Density | | 25°C | 25°C |
| | g/mol | g/mL | mg/L | mm Hg | |
| Benzene | 78.11 | 0.879 | 1791‡ | 95.19‡ | 2.13‡ |
| Toluene | 92.13 | 0.867 | 534.8‡ | 28.4‡ | 2.73‡ |
| Ethylbenzene | 106.16 | 0.867 | 161‡ | 9.53‡ | 3.15‡ |
| o-Xylene | 106.16 | 0.880 | 175‡ | 6.6‡ | 3.12‡ |
| 1,1,1-Trichloroethane (TCA) | 133.42 | 1.339 | 1495‡ | 123.7‡ | 2.49‡ |
| Trichloroethene (TCE) | 131.40 | 1.464 | 1100‡ | 69.0‡ | 2.42‡ |
| Tetrachloroethene (PCE) | 165.82 | 1.623 | 150.3‡ | 18.49‡ | 3.40‡ |
| 1,1,2,2-Tetrachloroethane | 167.85 | 1.541 | 1100‡ | 12.03‡ | 3.03‡ |

† Log octanol water partition coefficient.

‡ Howard, 1990.

§ Howard, 1989.

than 50 μL of methanol per standard and one for the high-level procedure containing exactly 110 μL of methanol per standard. A mid-point continuing calibration standard bracketed every 14 samples on the autosampler. SMCs were selected to bracket the retention times of the target compounds without peak interference. Data was accepted if continuing calibration standards and the SMCs fell within $\pm 25\%$.

The analysis of samples by the low-level procedure followed SW-1346 Methods 5030/8021 with minor modifications. Soil was placed in 40-mL vials with modified lids, adapted to fit on the purge-and-trap autosampler (Associated Design and Manufacturing Co., Alexandria, VA). The modified lids allowed samples to be placed on the sparger with minimal loss of VOCs. Water (5 mL) plus SMCs (150 ng each of *cis*-1,2-dichloroethene and 1-chloro-2-fluorobenzene in 10 μL methanol) were added by syringe through a sample-valvesyringe port once the samples were secured on the autosampler.

Samples to be analyzed by the high-level procedure were placed in 40-mL VOA vials that contained 5 mL of methanol. Vials were shaken and allowed to sit at 25°C for at least an hour to extract the VOCs. A 100 μL aliquot of the methanol extract was placed in a clean vial and sealed with a modified lid. At this point, the analysis followed the low-level procedure, as described above.

Minimum Detection Limits

Seven replicates of each soil were prepared and analyzed by each procedure. The low level replicates were spiked with 10 ng of each compound (in methanol) just prior to analysis. The replicates analyzed by the high-level procedure were prepared to yield the same quantity on the detector as the low-level replicates; these were spiked with the compounds at 100 ng/g, "diluted" 1:1 in methanol, and the extract analyzed. The minimum detection limits by each procedure for each soil (Table 3) were 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 six degrees of freedom.

RESULTS AND DISCUSSION

The effect of the extraction procedure was significant for every soil/compound combination except benzene in the Charleston soil (Table 4). The high-level procedure recovered greater amounts of the VOCs than the low-level procedure during every sampling event, except for Charleston soil/benzene (Fig. 1 and 2). Measured concentrations of the BTEX compounds were more consistent over time than those of the chlorinated solvents. Differences due to time were significant for every compound on the Charleston soil, but for only one-half of

Table 3. Minimum method detection limits (n/g for the low level and high level analytical procedures on the Hayesville and Charleston soils.

| Compound | Low level | | High level | |
|-----------------------------|------------|------------|------------|------------|
| | Hayesville | Charleston | Hayesville | Charleston |
| Benzene | 1.7 | 2.7 | 27 | 43 |
| Toluene | 12.1 | 6.9 | 86 | 75 |
| Ethylbenzene | 1.7 | 2.8 | 61 | 61 |
| <i>o</i> -Xylene | 2.9 | 4.6 | 70 | 84 |
| 1,1,1-Trichloroethane (TCA) | 2.1 | 2.4 | 25 | 79 |
| Trichloroethene (TCE) | 1.9 | 3.1 | 27 | 107 |
| Tetrachloroethene (PCE) | 2.7 | 3.9 | 23 | 88 |
| 1,1,2,2-Tetrachloroethane | 5.0 | 4.0 | 53 | 139 |

the compounds on the Hayesville soil (Table 4). The compound TTCA was inadvertently deleted from the dataset at Week 56 because newer studies initiated at that time had replaced this compound with another and therefore, TTCA had been deleted from the calibration standards mixture.

The experimental design allowed for a disparity in the initial soil volumes by treatment, which may have influenced the results. The 1-g soil sample had a larger headspace in the ampule than the 5-g soil sample, and therefore, a proportionately larger loss of analyte probably occurred in the 1-g sample when the ampules were broken open for analysis. While the volume discrepancy introduced some degree of bias, evidence from previous studies indicate that the headspace loss was small relative to other factors. Previous studies have indicated volatile losses of these VOCs, with the exception of benzene and possibly TCA, are very low from dry soil. Minnich et al. (1996a) report on initial studies of the discrepancies between the low- and high-level procedures. Using the same compounds and soils, but without the intermediate step placing and sealing the soil in the container used for the low-level analysis (no transfer steps to or from ampules), large differences between the low- and highlevel procedures were observed on the Charleston soil, and lesser differences were seen on the Hayesville soil. Furthermore, in replicate 1-g samples of Charleston soil that sat open for 40 min before sealing, there were no apparent differences in concentration between the open set and samples that were sealed immediately. On the Hayesville soil, volatile losses over the first 20 min were not observed, but decreases in benzene, TCA, and TCE were seen after 20 min. **Therefore, any bias introduced by the headspace volume discrepancy in the**

Table 4. Analysis of variance (ANOVA) results from the long-term study. The ANOVA for each soil or compound combination included 67 observations; degrees of freedom (df) represent two treatments (extraction procedures) and seven discrete times when the analyses were repeated.

| Compound | Source | df | F ratio | |
|-----------------------------|-------------|----|------------|------------|
| | | | Hayesville | Charleston |
| Benzene | extraction | 1 | 10.82*** | 0.84 |
| | time | 6 | 0.44 | 7.30*** |
| | interaction | 6 | 0.75 | 2.27* |
| Toluene | extraction | 1 | 33.72*** | 66.20*** |
| | time | 6 | 1.17 | 3.98** |
| | interaction | 6 | 2.03 | 0.60 |
| Ethylbenzene | extraction | 1 | 42.22*** | 242.6*** |
| | time | 6 | 3.28** | 4.74*** |
| | interaction | 6 | 3.49** | 0.34 |
| <i>o</i> -Xylene | extraction | 1 | 32.36*** | 265.0*** |
| | time | 6 | 1.97 | 3.14** |
| | interaction | 6 | 2.07 | 0.40 |
| 1,1,1-Trichloroethane (TCA) | extraction | 1 | 25.45*** | 4.26* |
| | time | 6 | 2.91* | 5.71*** |
| | interaction | 6 | 4.72*** | 1.81 |
| Trichloroethene (TCE) | extraction | 1 | 65.76*** | 34.75*** |
| | time | 6 | 5.17*** | 9.16*** |
| | interaction | 6 | 6.98*** | 3.51** |
| Tetrachloroethene (PCE) | extraction | 1 | 46.54*** | 43.30*** |
| | time | 6 | 0.64 | 3.59** |
| | interaction | 6 | 4.32*** | 6.98*** |
| 1,1,2,2-Tetrachloroethane | extraction | 1 | 7.10** | 79.01*** |
| | time | 5 | 7.62*** | 21.15*** |
| | interaction | 5 | 2.08 | 20.09*** |

*, **, and *** Significant at $P \leq 0.05$, 0.01, and 0.001, respectively.

present study would certainly be greatest for the most volatile compounds, benzene, and TCA, while least for the less volatile compounds, o-xylene, and ethylbenzene. As the effect does not follow the previously documented vapor losses, the extraction factor is held largely responsible for the observed treatment differences.

Regression analysis of the BTEX compounds indicated that no significant decrease through time occurred in compound concentrations on either soil as measured by the high-level procedure (Table 5). This result indicates that BTEX compounds remained stable (did not degrade) in dry soils when held in sealed ampules at 25°C. More-

over, the 1-h, 25°C methanol extraction (modified SW-846 Method 5030 high-level procedure) achieved mean recoveries of toluene, ethylbenzene, and o-xylene that ranged from 84 to 99% when averaged during the 56 wk study. Mean recoveries of the same VOCs by the low-level procedure averaged across the entire study time ranged from 49 to 83%.

In the Charleston soil, however, linear decreases in BTEX concentrations measured by the low-level procedure were observed (Table 5). These decreases are interpreted as an extraction difference between the low- and high-level procedures. Sawhney et al. (1988) showed

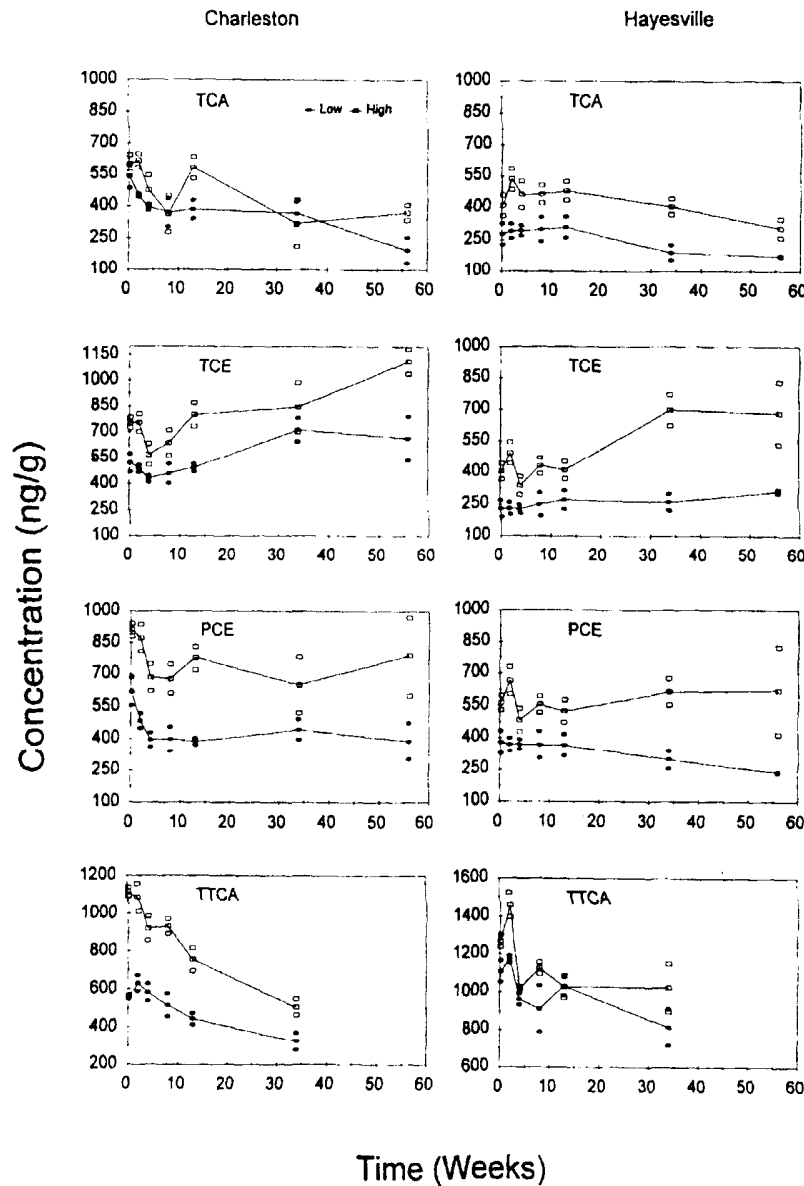


Fig. 1. Concentrations of chlorinated compounds measured in Charleston and Hayesville soils (fortified at 800 ng each VOC/g soil). Data are the means and one standard deviation about the mean of five replicate ampules analyzed by each procedure (SW-846 Method 5030/8021) at the times shown.

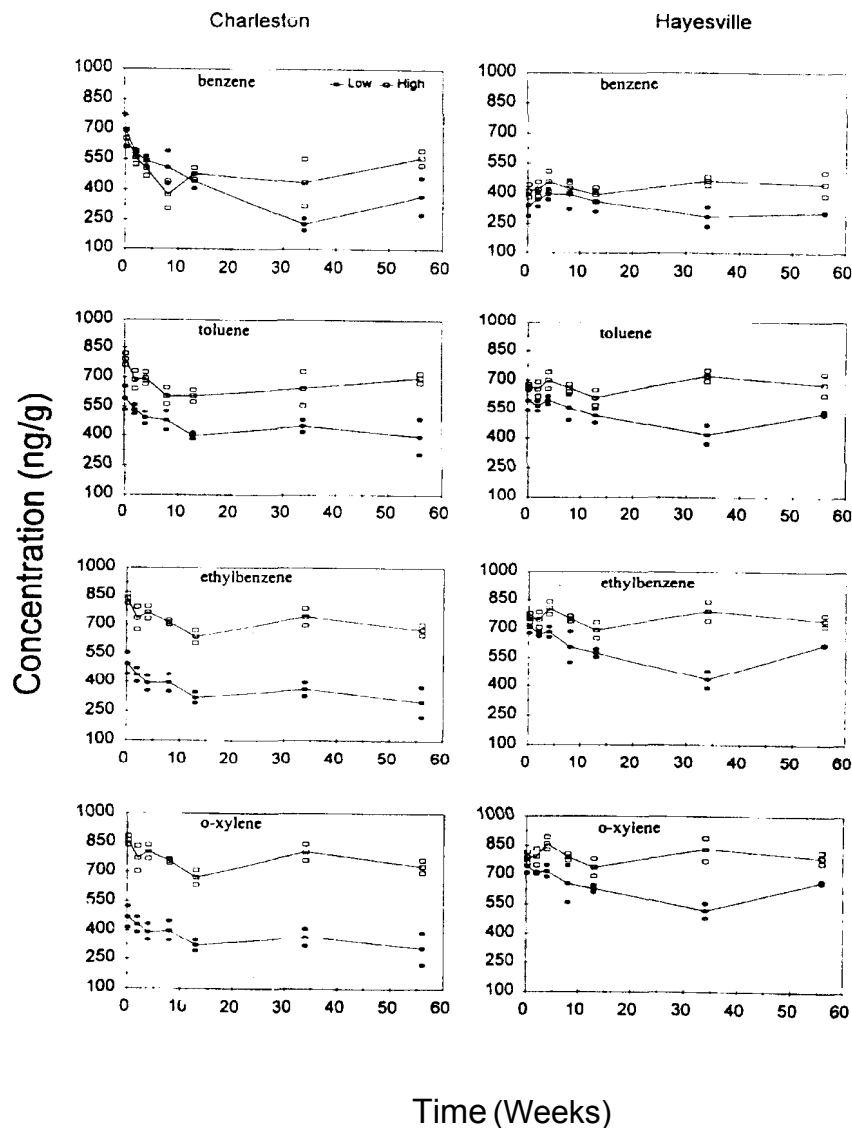


Fig. 2. Concentrations of BTEX compounds measured in Charleston and Hayesville soils (fortified at 800 ng each VOC/g soil). Data are the means and one standard deviation about the mean of five replicate ampules analyzed by each procedure (SW-846 Method 5030/8021) at the times shown.

that standard purge-and-trap extraction recovered less than 10% of the 1,2-dibromoethane (EDB) that could be solvent extracted from soils that had received applications of this pesticide 5 to 25 yr prior to measurement. Further evidence of difficulty in extracting VOCs has been documented by Pignatello (1990) and Pavlosthathis and Jaglal (1991). Given time, the BTEX compounds diffuse into remote soil microsites or into the soil organic matter and, consequently, the extraction efficiency of the low-level procedure decreases. Benzene extraction by the low-level procedure decreased at a rate of 7 ng/g/week. Decreases in extractability of toluene, ethylbenzene, and o-xylene

by the low-level procedure were observed at approximately 2 ng/g/week.

Results of the chlorinated compounds presented a complex picture (Table 5; Fig. 2). Statistically significant decreases in TCA concentrations occurred on both soils by both extraction procedures during 56 weeks, while statistically significant increases in TCE concentrations were observed on both soils by both extraction procedures. Changes in PCE concentrations were highly erratic and not statistically significant, except for a decrease on the Hayesville soil by the low-level extraction procedure. Significant decreases of TTCA were observed on

the Charleston soil by **both** procedures. Slope factors ranged from approximately 2 to 8 ng/g/week, except for a TTCA decrease of 17 n/g/week for the high-level extraction in the Charleston soil.

These erratic and unpredicted results in chlorinated compound concentrations by the high-level procedure while the concentrations of the BTEX compounds remained fairly constant suggest an interaction of at least two factors. incomplete extraction procedures and surface-catalyzed reactions of the chlorinated compounds. First, not only was the low-level extraction deficient for removal of the chlorinated compounds, the extraction of these compounds in methanol for approximately 1 h at 25°C was insufficient after long exposure times. Sawhney et al. (1988) achieved the best recovery of EDB by heating the soil in methanol at 75°C for 24 h. Initial experiments with heated methanol extraction of these soils showed no significant change in recoveries of the compounds 10 d after fortification. Subsequent to the initiation of this study, data was generated in our laboratory that showed the chlorinated compounds, particularly TCE and PCE, were more difficult to extract than the BTEX compounds 90 d after the soils were fortified. Extracting in methanol at 65°C for 24 h was significantly superior to a room temperature extraction for recovery of TCE from both soils and for recovery of PCE from the Hayesville soil (Minnich et al., 1996b).

Second, we **suspect** surface-catalyzed reactions were occurring on the soils. Clay and **oxide** surfaces possess both Bronsted acidity (the ability to donate protons) and Lewis acidity (the ability to accept electrons). Both types of acidity are strongest under desiccating conditions. Numerous reactions of organics on clay and oxide surfaces have **been** documented, including oxidation, alkene formation, polymerization, dechlorination, and addition to double bonds (Voudrias and Reinhard, 1986; Mortland and Boyd, 1989). In previous studies, repeated attempts to fortify Hayesville soil with TTCA resulted in measured concentrations at 1.2 to 1.5 times the nominal fortification level. TCE and, to a lesser extent, PCE concentrations were below the nominal fortification level (Minnich et al., 1996a). The same neat standards **used to fortify the** soils were used to prepare the stock calibration mixture. Therefore, the changes in compound composition observed in the presence of a soil, but not seen in the standard methanol mixture, were likely induced by the soil.

In the current study, the initial TTCA level was measured as approximately 1100 ng/g on both soils and the TTCA concentration increased further to approximately 1450 ng/g on the Hayesville soil during the first week. On the Hayesville soil, TCE and PCE were correspondingly low at the initiation of the experiment, while on the Charleston soil, decreases in the concentrations of all the chlorinated compounds were observed after 4 **wk**. The **use of** five replicate samples give us some measure of confidence that the results are not artifacts of a spurious instrument response or an aberrant soil sample. The data indicate an initial reduction of PCE to TTCA, or the addition of HCl to TCE to form TTCA.

Following the initial generation of TTCA, both soils

Table 5. Slope statistics from the regression of mean values ($n = 7$), VOC concentration (ng/g) = $a + b \times \text{time (wk)}$ where a is the intercept and b is the slope. Confidence in the slope estimate was tested against Student's t distribution for rejection of the null hypothesis: slope equals zero.

| | Low-level extraction | | High-level extraction | |
|-----------------------------|----------------------|------------|-----------------------|-----------|
| | Slope | t value† | Slope | t value |
| Charleston soil | | | | |
| Benzene | -6.95 ± 1.69 | 5.45** | -0.38 ± 1.96 | 0.26 |
| Toluene | -2.45 ± 1.08 | 2.97* | -0.39 ± 1.38 | 0.38 |
| Ethylbenzene | -2.49 ± 0.98 | 3.39* | -1.42 ± 1.20 | 1.56 |
| <i>o</i> -Xylene | -2.09 ± 0.82 | 3.40* | -0.95 ± 1.24 | 1.01 |
| 1,1,1-Trichloroethane (TCA) | -4.38 ± 1.09 | 5.34** | -3.98 ± 2.03 | 2.60* |
| Trichloroethene (TCE) | 4.40 ± 1.26 | 4.64** | 7.31 ± 1.83 | 5.28** |
| Tetrachloroethene (PCE) | -1.70 ± 1.66 | 1.36 | -1.29 ± 2.08 | 0.82 |
| 1,1,2,2-Tetrachloroethane | -8.35 ± 1.43 | 7.84** | -17.35 ± 2.46 | 9.47*** |
| Hayesville soil | | | | |
| Benzene | -1.58 ± 0.60 | 3.52* | 0.57 ± 0.48 | 1.56 |
| Toluene | -1.76 ± 1.07 | 2.18 | 0.59 ± 0.72 | 1.08 |
| Ethylbenzene | -2.35 ± 1.71 | 1.82 | -0.06 ± 0.79 | 0.11 |
| <i>o</i> -Xylene | -1.91 ± 1.36 | 1.86 | -0.04 ± 0.84 | 0.07 |
| 1,1,1-Trichloroethane (TCA) | -2.47 ± 0.51 | 6.49** | -2.93 ± 0.91 | 4.27** |
| Trichloroethene (TCE) | 1.31 ± 0.26 | 6.61** | 5.89 ± 1.53 | 5.10** |
| Tetrachloroethene (PCE) | -2.53 ± 0.17 | 19.60*** | 1.13 ± 1.25 | 1.19 |
| 1,1,2,2-Tetrachloroethane | -8.14 ± 3.29 | 0.93 | -7.86 ± 5.94 | 0.69 |

† Calculated t values are shown. Significance level designated by *, **, and *** corresponding to the critical values of $t_{(0.05,5)} = 2.57$, $t_{(0.01,5)} = 4.03$, and $t_{(0.001,5)} = 6.86$, respectively. For 1,1,2,2-tetrachloroethane, critical t values ($t_{(0.05,6)}$) were 2.78, 4.60, and 8.61 for significance at the same levels.

showed a trend of TTCA loss. On the Hayesville soil, the loss of TTCA was inconsistent, resulting in a statistically insignificant slope, but the trend of TTCA losses after 2 wk was apparent (Fig. 1). Dehydrochlorination of TTCA to form TCE under anaerobic conditions has **been** reported as an abiotic process (Macalady et al., 1986; Kiecka and Gonsior, 1984) and as a microbial degradation (Smith and Dragun, 1984; **Bouwer and McCarty**, 1983). The ampules of dry soil were unlikely to have become anaerobic, but the plausibility of surface catalyzed degradation reactions is well established (Voudrias and Reinhard, 1986; Mortland and Boyd, 1989). The statistically significant increase in TCE concentrations on **both** soils by both extraction procedures provides fairly credible evidence for the generation of TCE. Increases in TCE concentrations ranged from 4.6 to 6.5 ng/g/wk while TTCA concentrations decreased 7.9 to 17 ng/g/wk. Based on the assumption that extraction in methanol for 1-h at 25°C was insufficient, we may infer that some of the TCE generated by the degradation of TTCA was not extracted. **M*CA**, we conclude, is unstable in dry soil and cannot be used in a compound spiking mixture, designed to produce performance evaluation standards. Indeed, reactions of chlorinated compounds on a given soil must be explored prior to the generation of soil performance evaluation materials.

CONCLUSIONS

The high-level purge-and-trap procedure of SW-846 Method 5030 provided a more thorough extraction for recovery of the VOCs than the low-level procedure. The effect of extraction efficiency was highly significant on all but one of the soil-compound combinations (Charleston soil-benzene). Based on the relatively stable concentrations of BTEX compounds measured by the high-level procedure, we have no evidence that BTEX compounds degraded or were lost over 56 wk when stored in sealed ampules of dry, fortified soil. The results imply that the 1-h, 25°C methanol extraction (modified SW-846 Method 5030 high-level procedure) was sufficient for extraction of the BTEX compounds from these soils.

In contrast, evidence for an increase in the difficulty of extracting BTEX from the Charleston soil by the low-level procedure was observed. Statistically significant negative slopes in the BTEX concentrations over time were observed by the low-level procedure only. Rates of decrease were less than 6 rig/g/k. On the Hayesville soil, only benzene exhibited a loss in concentration over time (less than 2 ng/g/k) and only by the low-level procedure, indicating a possible loss in extractability over time. No statistically significant change in the concentrations of toluene, ethylbenzene, or xylene were noted on the Hayesville soil. The critical difference between these soils was the higher organic carbon content of the Charleston soil, providing a greater capacity for absorption of BTEX than found in the Hayesville soil.

Concentrations of the chlorinated compounds TCA, PCE, and TTCA tended to decrease with time by both extraction methods, although losses were not always significant. The results indicate a combination of decreases in extractability with time and surface-catalyzed degradation were occurring. Not even a 1-h methanol extraction (25°C) was sufficient for recovery of the chlorinated compounds following long exposure times (more than 7 d).

TCE increased in concentration during the 56 wk by both extraction procedures on both soils. The increase in TCE concentration is believed to be real and has tentatively been postulated to result from the dehydrochlorination of TTCA. These results preclude the use of TTCA in dry, fortified soil standards.

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