

Comparison of Soil VOCs Measured by Soil Gas, Heated Headspace, and Methanol Extraction Techniques

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Comparisons of soil volatile organic compound (VOC) measurement techniques and soil properties expected to influence these measurements were performed at two dissimilar sites. A total of 41 soil gas, 52 heated headspace, and 51 methanol extraction/purge-and-trap measurements were obtained on collocated samples. Contaminants present at both sites included cis-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. Heated headspace offered the highest sensitivity, as indicated by the greatest percentage of detections per number of analyses. The statistical regression between headspace concentrations and methanol extraction concentrations was highly significant ($p < 0.001$) with $r^2 = 0.53$. Headspace concentrations (range, 7 to 4250 ng/g) ran approximately 20 to 30% of the methanol extraction concentrations (range, 260 to 7300 ng/g), indicating that the methanol was able to extract significantly more of the chlorinated hydrocarbons (CHCs) than the headspace extraction, even in soils with relatively low organic carbon contents ($< 0.25\%$). None of the soil properties (gravimetric moisture content, organic carbon content, percent sand, and percent clay) significantly improved the regression fit. The soil gas responses were unlike either headspace or methanol extraction data. CHC measurements by vapor extraction/soil gas could not be used to predict soil CHC concentrations at these sites.

KEY WORDS: chlorinated hydrocarbons, 1,1,1-TCA, TCE, PCE, soil properties.

INTRODUCTION □

DIFFICULTIES in measuring soil volatile organic compounds (VOCs) are currently under investigation by the U.S. Environmental Protection Agency's (EPA's) Characterization Research Division in Las Vegas, NV (CRD-LV). These difficulties are exacerbated by the VOCs' multiphase nature and their affinity for the vapor phase. The multiphase problem has led to debates over the use of soil vapor measurements vs. soil extraction techniques for the quantification of VOCs. Soil gas measurements offer an economical and rapid screening method at some sites, but soil gas concentrations cannot be used to predict the total concentration of soil VOCs (vapor, sorbed, dissolved, and nonaqueous-phase liquids). In contrast, soil samples, if properly sealed and preserved, can be used to measure VOCs in all phases. However, unquantifiable VOC losses can occur during sampling and during sample transfer steps prior to analysis (*Siegrist and Jenssen, 1990*).

Sites and depths suitable for soil gas measurements are limited to areas that have relatively high air-filled porosities. In dry, sandy soils, VOCs may be lost so readily during the collection of soil samples that soil gas analyses may be the only technique for measuring the VOC contamination. Alternatively, if the air-filled pore space is low, soil gas is not an option. Soils with high moisture contents, high bulk densities, or high clay contents are generally unsuitable for measuring VOCs by soil gas. Collection of soil samples for analysis of VOCs may then be the only option. In this study, sites were selected where both soil gas and soil sample collection were feasible options.

Studies have shown that large VOC losses occur if samples are not collected and handled prudently (*Siegrist and Jenssen, 1990; Lewis et al., 1991; Hewitt et al., 1992; Hewitt, 1994*). A comparison of in-house purge-and-trap analysis vs. contractor-analyzed collocated samples has shown that preservation and transfer steps were responsible for losses of one to three orders of magnitude (*Hewitt, 1994*). Prudent handling is generally described as (1) sampling by a limited disruptive method or one that limits exposure of soil surfaces, (2) a quick transfer into the sample container with care to provide a complete seal between lid, liner, and container (avoid contact of soil particles with the sealing surfaces of the container), and (3) the use of either methanol extraction or a container/analytical system that requires no further atmospheric exposure during transfer steps. If methanol extraction is used, transfer of the extract into a storage or purging vial can be achieved with a minimal loss of the VOCs. Subsequent transfer steps can be avoided by placing soil into a vial that can be directly analyzed by purge-and-trap or by static headspace systems.

Relatively simple headspace methods have been used as field-screening procedures for a number of years (*Kiang and Grob, 1986; Roe et al., 1989*). *Hewitt et al.* (1992) compared purge-and-trap analysis with headspace analysis of laboratory-prepared samples with VOC concentrations ranging from 0.2 to 3000 pg/g. The correlation between the two techniques was near unity. These two extraction

techniques measured nearly equivalent VOC concentrations (benzene, toluene, trans-1,2-dichloroethene, and trichloroethene) on two different soils at fortification levels below 300 : g/g. At higher VOC concentrations, the purge-and-trap technique had a greater extraction efficiency than the headspace technique.

The use of methanol for extracting soil VOCs serves as a highly favorable partitioning solvent, preservative, and provides the researcher with the ability to perform multiple analyses/dilutions from a single sample. At highly contaminated sites, or in the vicinity of a hot spot, VOCs quantified in methanol extracts are capable of spanning several orders of magnitude. One disadvantage of the methanol extraction technique is a loss of sensitivity at low concentrations due to elevated detection limits. Methanol extraction at a 1:1 soil:methanol ratio is approximately an order of magnitude less sensitive than the low-level purge and trap under the same experimental laboratory conditions (Minnich *et al.*, 1996).

The objective of this study was to compare the method sensitivity and relative concentrations of chlorinated hydrocarbons (CHCs) obtained by soil gas, heated headspace, and methanol-extraction techniques from field samples. Sites were selected that had been previously identified as contaminated with CHCs and offered an opportunity to measure CHCs by active vapor extraction in addition to the soil extraction methods. Variability in soil properties within a site and between sites was desirable to compare extraction techniques over a wide range of soil conditions.

METHODS

Site Descriptions

The study was performed at two Super-fund sites, the San Leandro Plume Superfund Site in San Leandro, CA, and the Southeast Rockford Superfund Site in Rockford, IL. At both sites, numerous discrete areas had been identified as potential sources for VOCs in the local groundwater. Areas of known soil contamination with VOCs were selected. Site characteristics and sampling procedures used at each site are described below.

San Leandro Site

The San Leandro Superfund site is located in a mixed commercial/residential area. Commercial businesses believed to have contributed to the VOC contamination in the area included metal plating and dry cleaning operations. Trichloroethene (TCE), tetrachloroethene (PCE), and other VOCs had been detected in the shallow groundwater aquifer, approximately 5.5 m below ground surface at the location sampled and in various monitoring wells downgradient from the study location.

The local sediments were composed of interbedded marine and continental deposits. The surface 1 to 1.5 m consisted of a high-clay deposit to which gravel had been added and mixed to a depth of approximately 25 cm. Below approximately 1.5 m, sediments had a much lower clay content, with highly variable sand and gravel beds throughout.

Southeast Rockford Site

The Southeast Rockford Superfund site is comprised of 12 source areas, all implicated as contributing to the local groundwater contamination. A source area that had reportedly been used for disposal of industrial and household wastes in the 1950s and 1960s was selected. Previous investigations have shown the area to be highly contaminated with 1,1,1-trichloroethane (TCA), TCE, and xylenes. Groundwater varied from 5 to 30 ft below the soil surface. Peak VOC concentrations generally occurred in the upper portion of the saturated zone or immediately above it. Soils at this site have developed in a high-lime glacial till. A high-lime sand fill covered portions of the site that had been drainage ways at the time dumping was occurring.

Soil Sampling

At the San Leandro site, a cone penetrometer was used to collect soil and soil gas samples at ten locations. The cone penetrometer resistance readings provided information on the soil type (i.e., texture) as a function of depth. Cone penetrometer readings were examined to identify areas with fairly constant soil type over a 25-cm sampling interval and to verify the soil types being sampled. Soil samples were collected by pushing a probe to the top of a sampling depth. A 3.8 cm i.d. split spoon, fitted with brass liners, was then pushed 30 cm further to collect the sample. Samples were collected at two or three depths (ranging from 1.2 to 4.6 m) per hole for a total of 24 discrete samples.

At the Southeast Rockford site, soil and soil gas samples were collected using a Diedrich rig. Fourteen locations were sampled at a depth of approximately 1.2 m below the surface. An elevated water table restricted deeper sampling at many locations, but soils were collected at 2.4 and 3.6 m, where possible. Soil gas collection was hampered by the difficulty of pushing a relatively wide probe (2.5 cm) through a densely packed sand layer encountered below 1.5 m. Therefore, soil gas was only collected at the 1.2-m depth. Soil samples were collected by drilling to within 20 cm of the desired sampling depth. A 6.4-cm i.d. split-spoon sampler, fitted with steel liners, was then pushed 30 cm further to collect the sample. A total of 28 samples were collected for methanol and headspace analyses.

At both sites, soils were carried in the brass or steel liners to minimize atmospheric exposure from the probe to a nearby preparation table where three people quickly divided and sampled the core. Plastic syringes with the tips cut off allowed

for quick removal of the soil subsamples. Samples were collected and treated as follows:

1. 20 ml of soil was placed in a 40-ml vial containing 20 ml of methanol spiked with chlorobenzene (a field-monitoring compound) at 250 ng/ml.
2. 1 and 5 ml soil subsamples were placed in 20-ml headspace vials, 5 ml of water added, and the vials crimp-sealed and weighed.
3. Approximately 20 ml of soil was placed in a soil moisture tin and sealed.
4. The remaining soil was placed in a zip-lock bag for organic carbon and particle-size characterization.

Soil collected for headspace or methanol extraction alternated between the upper and lower portions of the core to achieve a balanced sampling design. Soil moisture and characterization samples were collected after obtaining the VOC samples. Field blanks (vials containing methanol and the field-monitoring compound) were opened every ten samples, left open during the sampling operations, sealed, and processed along with the routine soil methanol samples. Duplicate samples for methanol extraction were collected approximately every ten samples.

Soil Gas Collection

Soil gas samples were collected from separate holes within 25 cm of the original soil sampling locations 1 or 2 d after the soil samples were collected. The probe was inserted to a depth corresponding to the middle of the soil collection depth, then retracted slightly to open the probe, allowing soil gas to be pumped through Tetlon™ tubing. Calculations based on the dead volume and gas flow rate were used to determine the pumping time necessary to purge three volumes of air. After approximately 2 min of vacuum pumping to purge the tubing, a valve was shut to isolate the tubing between the probe and pump, the pump was turned off, and the vacuum in the line was observed to dissipate as soil gas filled the vacated tubing. Evacuated 20-ml headspace vials were filled by piercing a small section of Tygon™ tubing with one end of a double-end needle, and then piercing the crimped, septum-sealed vial with the other end. Duplicate soil gas samples were collected by placing a second evacuated vial on the needle immediately after the first vial was removed.

Analytical Procedures

Methanol/soil mixtures were shaken by hand until thoroughly mixed (visual inspection). After sitting for 24 h at ambient temperatures, the vials were opened and subsampled by pipette to remove the clear methanol extract. Extracts were stored cold (4°C) in 10-ml vials with Teflon™ lined rubber septa and metal crimp-seals

until analyzed. Methanol aliquots (100 µl) were analyzed for VOCs essentially following EPA SW-846 method 5030 high-level purge-and-trap procedures and quantified following SW-846 method 8010 (EPA, 1992). A five-point calibration curve was generated prior to analysis of routine samples. An instrument blank (water) and midrange calibration standard preceded and followed every fifteenth sample. Two system-monitoring compounds, fluorobenzene and 1-chloro-2-bromopropane, were added to every sample, standard, and blank as a means of evaluating the consistency of the detector response and effectiveness of each purge. Data are reported on a dry soil basis calculated from the sample wet weight and percent moisture found in the corresponding moisture content subsample.

Headspace samples were analyzed on-site in a mobile laboratory at the San Leandro site. At the Southeast Rockford site, samples were shipped on ice, stored at 4°C, and analyzed at the Lockheed Analytical Laboratory in Las Vegas, NV, within 8 days of sample collection. Samples were equilibrated at least 60 min at 60°C before analysis. The injection loop volume was 100 µl. Quantification of VOCs followed the gas chromatograph (GC) operating conditions specified in SW-846 method 8010 (EPA, 1992). A five-point calibration curve was generated prior to analysis of routine samples. A distilled water instrument blank and midrange calibration standard preceded and followed every twentieth sample. Again, data are reported on a dry weight basis calculated from the wet soil weight and soil moisture content found in the corresponding moisture content subsample.

Soil gas samples were analyzed via the autosampler. A 100-µl aliquot was withdrawn from the crimp-sealed soil gas vials (maintained at 26°C) and injected into the GC. Quantitation of VOCs followed the GC operating conditions specified in SW-846 method 8010 (EPA, 1992). A five-point gas calibration curve was generated prior to analysis of routine samples. Gas standards were made by injecting microliter amounts of a stock mixture of the analytes into headspace vials. A blank and midrange calibration standard preceded and followed every twentieth sample.

All samples were analyzed on two identical GCs, Hewlett-Packard (HP) Series 11 Model 5890, equipped with J&W DB 624 30 m x 0.53 mm i.d. fused silica columns and 0.1 Model 4420 electrolytic conductivity detectors. Two sample introduction systems were fitted on separate GCs: (1) an 0.1 Model 4460A sample concentrator and Model MPM-16 multiple purging module for purge-and-trap introduction and (2) an HP Model 19395A Headspace Sampler for the soil gas and heated headspace sample injections. Detector signals were analyzed through a PE Nelson Series 900 Interface using Turbochrome 3.1 software.

RESULTS AND DISCUSSION

Soil properties at the sites and sampling depths varied widely (Table 1). The variability allowed us to test the relationships between measurement techniques over a wide range of soil conditions.

TABLE 1
Description of Variability in Soil Properties of Study Samples

	Molsture (%)	Organic carbon (%)	Sand (%)	Clay (%)
Mean	10.9	0.23	54.4	14.2
Median	10.5	0.15	53.1	9.1
Range	3.2-24.8	0-1.18	18.3-97.5	2.5-36.8

Sensitivity and Detection Limits

For each analytical technique - methanol extraction, heated headspace, or soil gas - the number of detects as a percent of the total number of analyses performed by each method was tallied to determine method sensitivity (i.e., the capability of the technique to detect and quantify VOCs in the samples). Because there were fewer soil gas analyses performed than soil extraction analyses, the number of detects per number of analyses were also calculated using only the sampling locations where soil was collected for all three quantitation methods (i.e., the limited dataset).

Heated headspace provided the highest ratio of VOC detects using either the full dataset or limited dataset (Table 2). From this result, we deduce that headspace was the most sensitive technique for the detection of each compound regardless of soil type and detection limit differences (discussed below). Methanol extraction was the second most sensitive technique for all compounds. Somewhat surprisingly, soil gas provided the poorest detection record for all the compounds except TCA, where soil gas measurement was the second most sensitive detection technique.

Heated headspace detection limits varied slightly at each site and with each compound, ranging from 4 to 12 rig/g.. Detection limits for the methanol extraction varied by site and compound and were markedly affected by individual soil:methanol ratios. The soil:methanol ratio, dependent on the dry soil weight added to each vial, varied between samples and sites. At the San Leandro site, the quantity of dry soil added to the vials was generally higher than the intended 1:1 ratio, and thus the detection limits by methanol extraction were approximately 30 ng of VOC per gram of soil. At the Southeast Rockford site, a lower dry soil weight per vial than collected at the San Leandro site resulted in detection limits of approximately 200 ng of VOC per gram of soil. Therefore, particularly at the Southeast Rockford site, methanol extraction was not able to detect VOCs present at the low concentrations due to its elevated detection limit.

The units of soil gas concentration are expressed as the mass of the compound per unit volume of soil air. These numbers cannot be converted to a soil volume or soil mass basis. Soil gas had detection limits of 0.5 to 1.5 ng/ml, varying slightly by VOC and site. This limited number of comparisons indicates that soil gas

TABLE 2
Number Of Detects per Number of Analyses Found by Each Analytical Technique

	<i>cis</i> -1,2-DCE ^a			1,1,1-TCA			TCE			PCE		
	M ^b	HS	V	M	HS	V	M	HS	V	M	HS	V
A. No. detects	5	6	1	10	21	14	16	23	10	27	33	9
A. No. analyses	28	28	17	51	52	41	51	52	41	51	52	41
A. Ratio	0.18	0.21	0.06	0.20	0.40	0.34	0.31	0.44	0.24	0.53	0.63	0.22
B. No. detects	2	3	1	4	16	13	14	19	9	24	28	8
B. No. analyses	17	17	17	40	40	40	40	40	40	40	40	40
B. Ratio	0.12	0.18	0.06	0.10	0.40	0.33	0.35	0.48	0.23	0.60	0.70	0.20

^a *cis*-1,2-DCE was measured only at the Rockford, IL, site.

^b M, methanol extraction/purge and trap; HS, heated headspace; V, soil gas.

Part A includes all data. Part B limits the dataset to those points where all three methodologies could be compared.

measurement was less sensitive than either soil extraction technique for VOCs when the collected soil samples were handled quickly and carefully.

Regressions between Headspace and Methanol Data

Linear regression between VOC concentrations determined by heated headspace and methanol extraction methods demonstrated close agreement between the collocated samples (Table 3). Data included in the regression were only those data pairs that had VOC concentrations above detection limits. The regression analysis included one extremely high point, cis-1,2-dichloroethene (DCE) at 7300 ng/g by methanol extraction and 4250 ng/g by heated headspace, which is believed to have unduly influenced the regression results. Excluding this point from the regression equation resulted in a lower coefficient of determination, r^2 , but the slope of the regression line was comparable to the slopes of the regression lines for TCE or PCE individually (Figures 1 and 2, Table 3).

Although the r^2 values ranged from 0.4 to 0.9, an analysis of variance (ANOVA) demonstrated a highly significant relationship between heated headspace and methanol extractions in all cases ($p < 0.001$). Overall, headspace concentrations were approximately half of the concentrations determined using methanol extraction (Table 3). When the highest DCE concentration data were removed (due to its strong influence on the ANOVA), headspace concentrations were only 21 to 27% of the concentrations in comparable methanol extractions.

Multiple regression was used to explore whether any of the measured soil properties were contributing to the remaining variability in the headspace vs. methanol extraction regression. Soil properties investigated included moisture content, organic carbon content, percent clay, and percent sand. None of these factors improved r^2 values more than a few hundredths of a unit. Further, the influence of which site was sampled did not cause any significant differences in the headspace vs. methanol extraction regression results (Figure 3), indicating that the

TABLE 3
Regression Analyses on Combined Dataset

	No. observations	Slope (SE) ^a	Intercept (SE)	r^2 ^a	F	$p <$
All data	50	0.50 (0.03)	-55.3 (39.7)	0.9	281	0.001
Exclude high point	49	0.27 (0.04)	65.0 (31.5)	0.5	53	0.001
TCE only	15	0.21 (0.03)	18.9 (8.1)	0.8	62	0.001
PCE only	24	0.22 (0.06)	142.8 (63.3)	0.4	15	0.001

Note: Regression line formula: headspace concentration = slope × methanol concentration + intercept.

^a SE, standard error; r^2 , coefficient of determination.

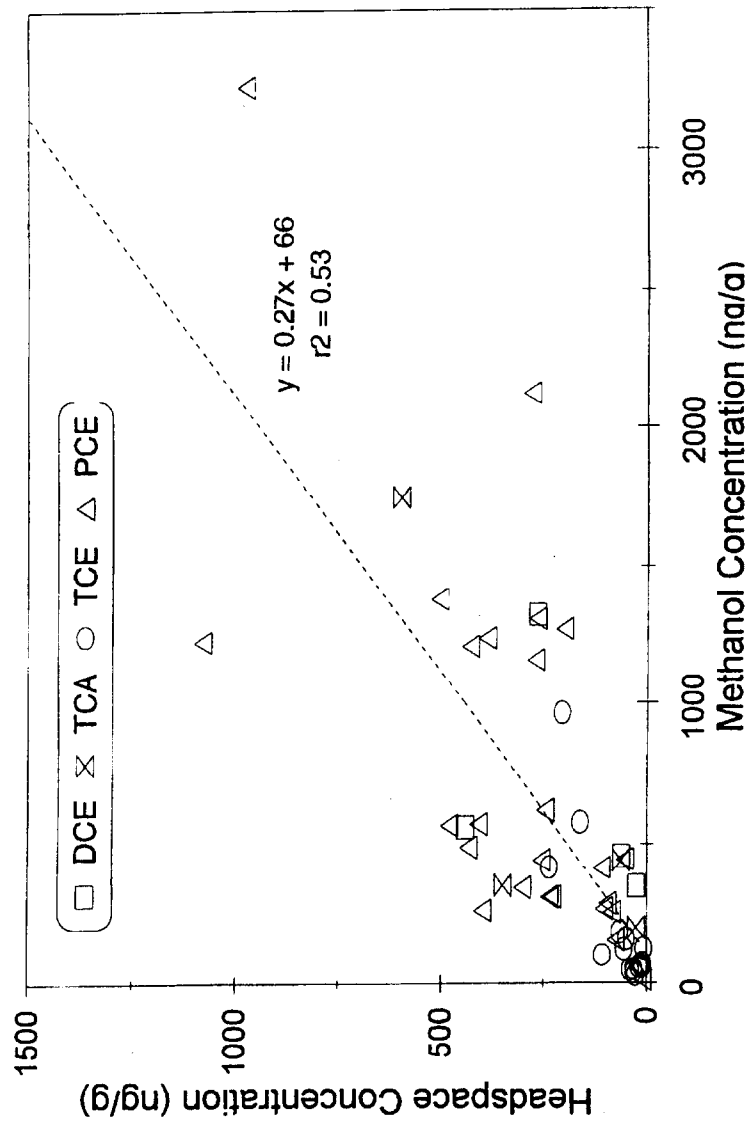


FIGURE 1

Regression of collocated sample pairs, heated headspace vs. methanol extraction concentrations, all data excluding the highest point (n = 49).

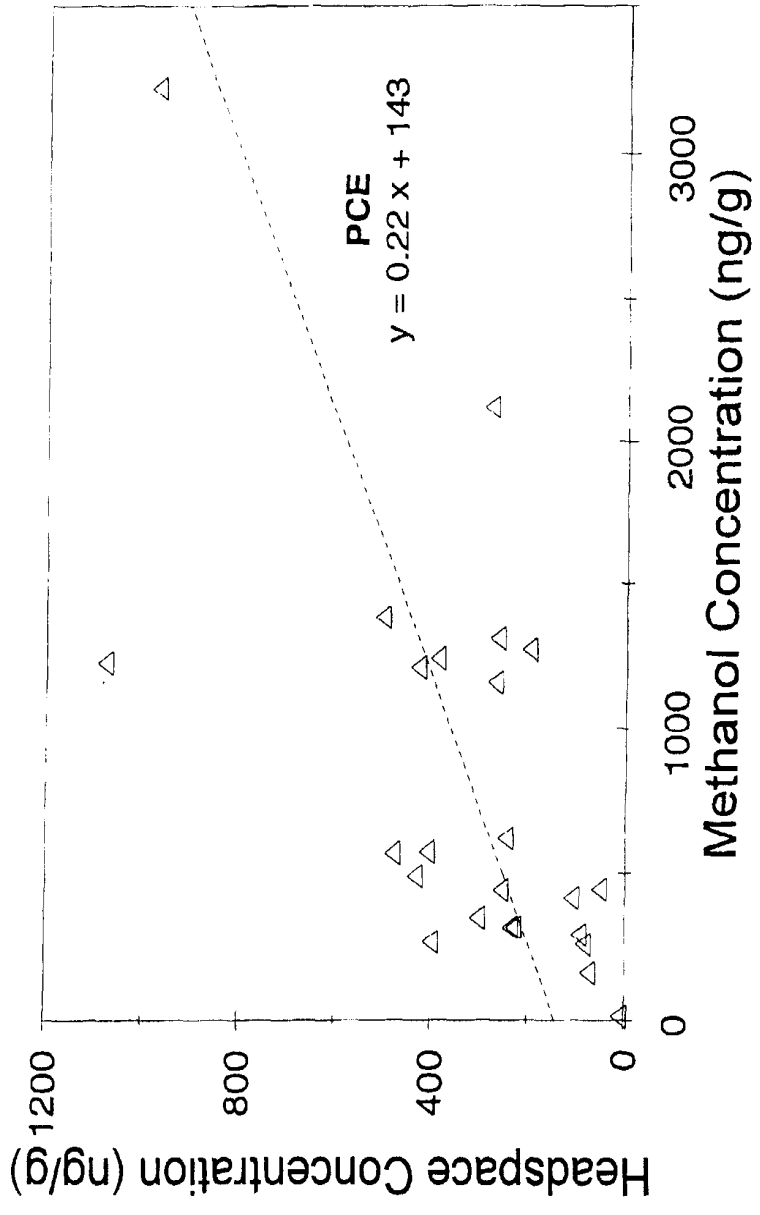


FIGURE 2

Regression of collocated sample pairs, heated headspace vs. methanol extraction concentrations, PCE data only (n = 24).

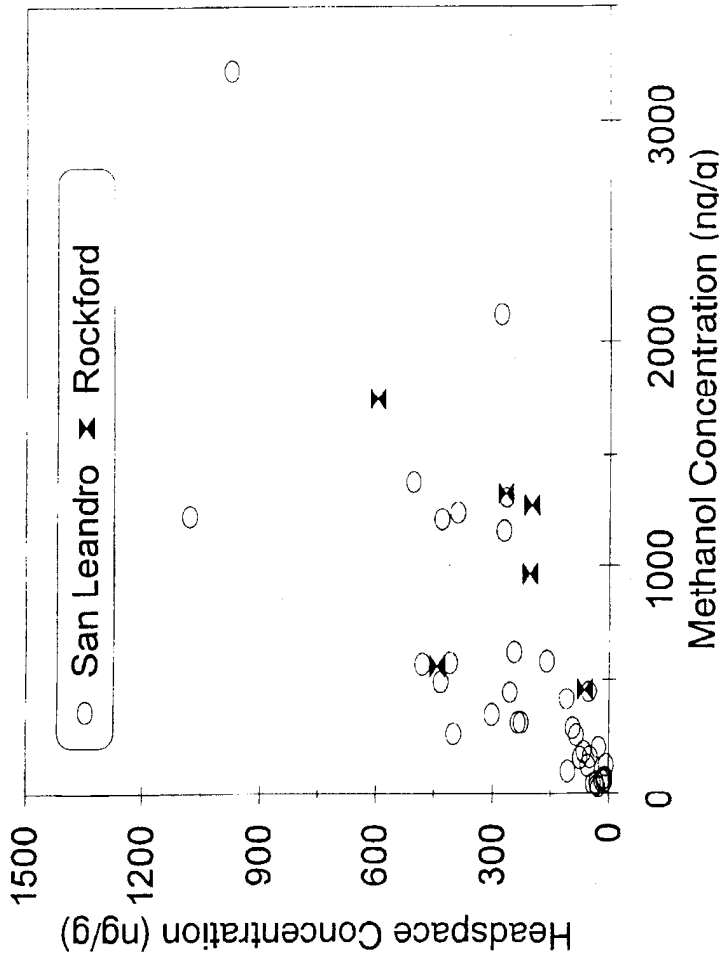


FIGURE 3

Scatterplot of collocated sample pairs, heated headspace vs. methanol extraction concentrations. Data identified by field site.

different climatic conditions and parent materials at the two sites had negligible influence on the extraction and quantification of the VOCs in the soils.

Regressions between Soil Gas and Soil Extraction VOC Data

Twenty-seven nonzero data pairs were generated between the soil gas and soil headspace data. The relationship between soil gas and soil headspace analyses was random regardless of analyte or field site examined (Figures 4 and 5). Multiple regression analyses between soil gas and soil headspace methods were explored to determine if any soil property influenced the variability between the two analytical techniques. Regression analyses that included the influence of organic carbon contents resulted in the best correlation coefficient of 0.43 ($r^2 = 0.186$) among the soil parameters examined. This observation is interesting, but the correlation is not particularly strong and therefore indicates a lack of correlation between soil gas and soil headspace-measured VOC concentrations.

Only 16 nonzero data pairs were generated between soil gas measurements and methanol extraction data. Similar to the relationship between soil gas and soil headspace techniques, no correlation was evident from this technique comparison (Figure 6).

CONCLUSIONS

Soil VOCs can be measured by heated headspace or methanol extraction with a high degree of correlation between the results. No significant correlations between soil properties and VOC concentrations were identified. The headspace technique had lower detection limits than determined for methanol extraction, was generally easier and less expensive to perform, but extracted only about 25% of the VOCs recovered by methanol. Methanol extraction offered the advantage of sample preservation and of providing a more complete extraction than headspace analyses.

Soil gas measurements did not correlate with either headspace or methanol extraction results. The fetch or volume of soil air sampled is not known and cannot be controlled during soil gas sampling. Moreover, equilibrium between the vapor phase and the other phases cannot be assumed.

NOTICE

The U.S. Environmental Protection Agency, through its Office of Research and Development (ORD), funded and collaborated in the research described here. It has been subject to the Agency's peer review and has been approved as an EPA

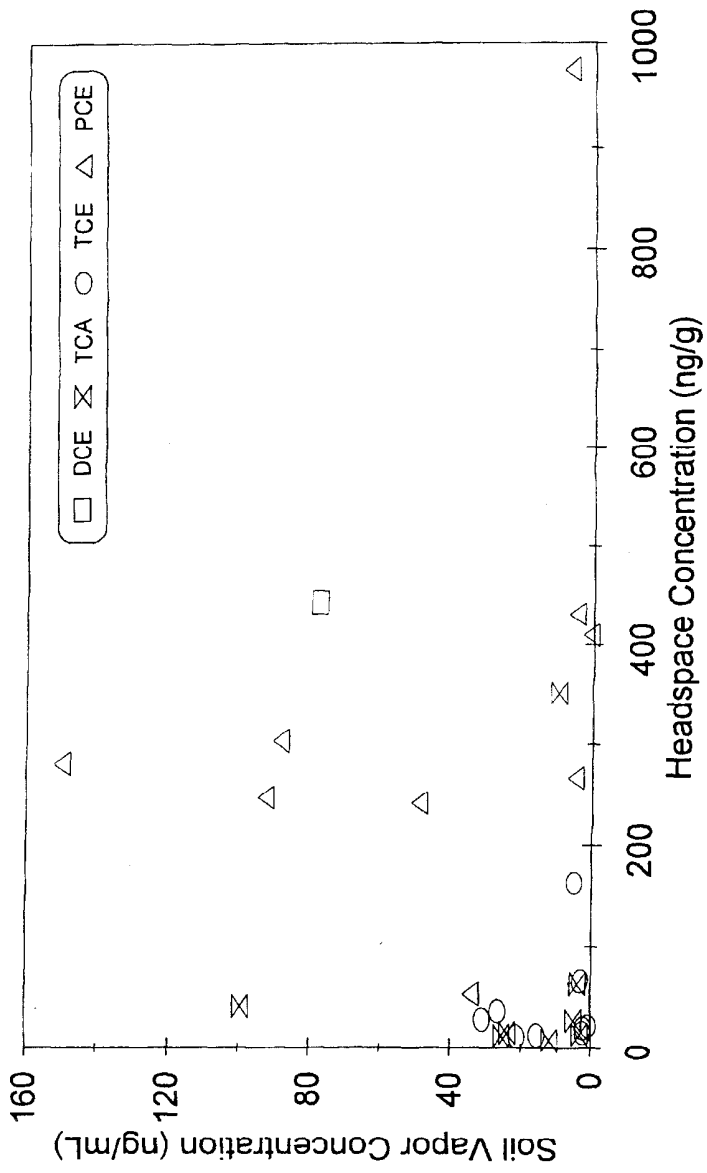


FIGURE 4

Scatterplot of collocated sample pairs, soil vapor vs. heated headspace concentrations. Data identified by analyte.

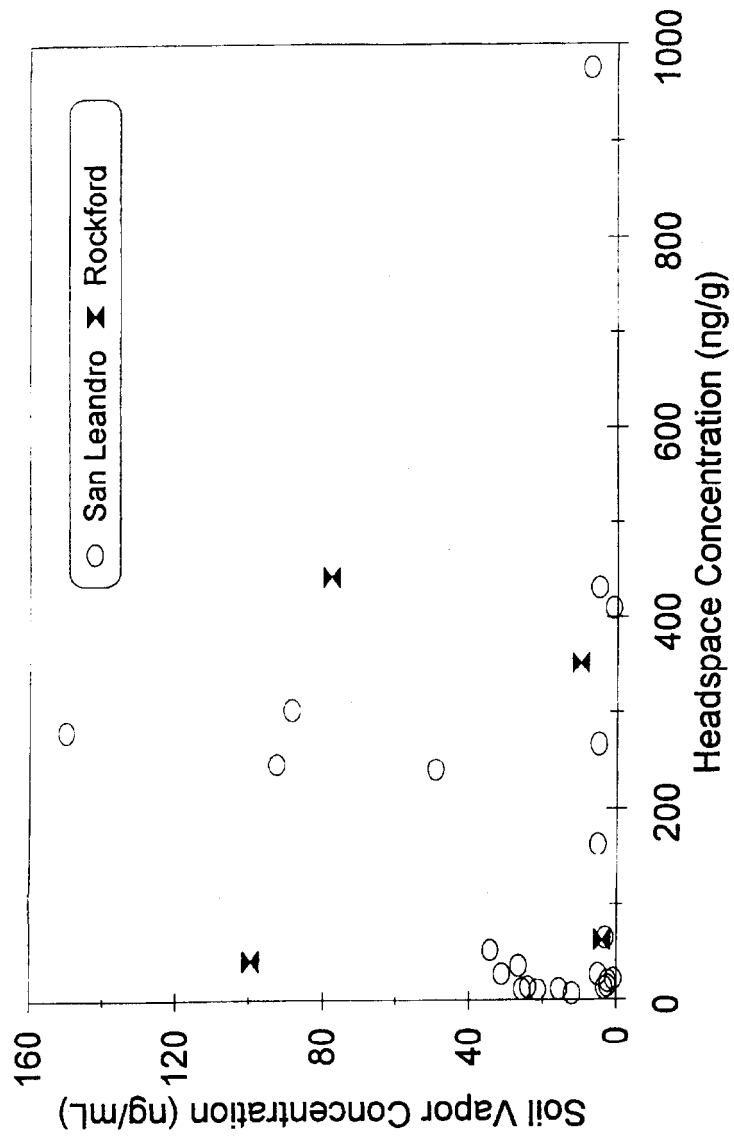
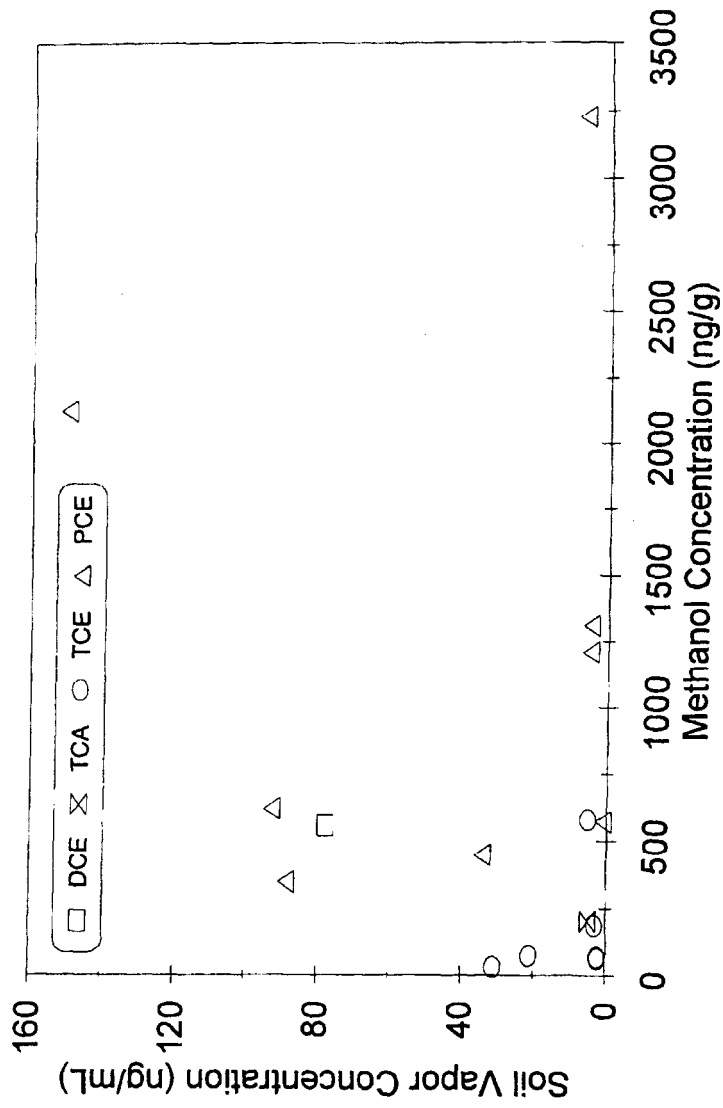


FIGURE 5

Scatterplot of collocated sample pairs soil vapor vs. heated headspace concentrations. Data identified by field site.



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