Solid sorbent method for the collection and analysis of volatile halogenated organic compounds in soil gas

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Abstract

A solid sorbent technique was developed to measure volatile halogenated organic compounds (VHOCs) in soil gas. The VHOCs were preconcentrated onto graphitized carbon black (Carbotrap) and analyzed by thermal desorption/high-resolution gas chromatography with electron-capture detection. The method detection limit (MDL) for trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4) in soil gas was approximately 1 $\mu g\ m^{-3}$ for a 60-ml sample volume. A thermal-desorption temperature of 200°C was sufficient to recover more than 90% of the VHOCs from the sorbent. Breakthrough volumes for $CHCl_3$ and CCl_4 were at least 1000 ml when soil gas was drawn through the sample cartridge at a rate of 30 ml min^{-1}. Sorbent cartridges stored at 20°C were sufficiently stable for at least 30 days. Application of the method in the field indicated that the measured concentration of VHOCs in soil-gas monitoring wells was sensitive to the volume of soil gas that was withdrawn.

Keywords: Soil gas; Sampling methods; Environmental analysis; Volatile organic compounds; Halogenated compounds; Tetrachloromethane; Trichloromethane

1. Introduction

Soil gas monitoring has been widely used to indicate the extent of subsurface contamination and to evaluate the progress of remediation at sites contaminated with volatile organic compounds (VOCs). The characterization of a contaminated site may require a technique that is capable of measuring VOCs in soil gas at levels that are orders of magnitude greater than those observed in ambient air while the demonstration of a successful remediation

effort may require accurate analysis of VOCs in soil gas at concentrations comparable to those observed in ambient air [1]. Samples of soil gas are typically collected by methods similar to those used to sample ambient air. Methods that have been successfully used to sample VOCs in ambient air include (1) collection of whole air samples in metal canisters, glass bulbs, or polymeric bags or (2) preconcentration onto solid sorbents (e.g., Tenax, XAD-2, charcoal and Carbotrap). The samples are analyzed by some combination of cryogenic preconcentration or thermal desorption with high-resolution gas chromatography.

The advantages and disadvantages of the ambient air methods have been described in detail [2,3]. VOCs in Summa canisters are stable over long

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periods [4] and multiple aliquots can be analyzed from the same container. Water may have to be removed from the sample to eliminate interferences, especially when using electron capture detection. The canisters are rugged and reusable but expensive. Polymeric bags are relatively inexpensive and multiple aliquots can be analyzed from the same bag. Sorption of some analytes to the bags can be a problem, and holding times are limited by their permeability. The need to remove water from the sample is dependent upon its water content and the volume to be analyzed. One of the major advantages of using solid sorbents for ambient air sampling is their hydrophobicity [5,6]; however, if thermal desorption is used for analysis, only one analysis per sample can be made. Interferences and artifacts created during thermal desorption can also be a problem.

The objective of this investigation was to adapt an ambient air method to accurately quantify a wide range of concentrations of trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4) concentrations in soil gas. Sample stability over a period of at least two weeks was also critical to our application because analyses were to be performed at an off-site laboratory. The aim of this study was to develop a solid sorbent technique in which graphitized carbon black (Carbotrap) is used for the collection and analysis of volatile halogenated organic compounds (VHOCs) in soil gas. The VHOCs are analyzed by thermal desorption/high-resolution gas chromatography (HRGC) with electron-capture detection (ECD). Results from experiments to determine (1) thermal desorption efficiencies, (2) breakthrough volumes of the analytes and (3) the stability of the samples during storage are described. The technique is compared with whole air sampling methods in which samples are collected in Summa passivated stainless-steel canisters and Tedlar bags. A preliminary evaluation of the method of sampling soil gas in monitoring wells is also presented.

2. Experimental

The soil-gas monitoring wells consisted of polyvinyl chloride pipe (1.58 cm I.D.) that was inserted into the ground to depths of 1.7–6.8 m. Each well

pipe was threaded at the surface and capped with a combination of iron pipe and stainless-steel fittings. A manifold consisting of a 300-ml type 304 stainless-steel gas-sampling cylinder (Parker Hannifin, Huntsville, AL, USA) with three stainless-steel ports was attached to the well to facilitate the collection of replicate samples.

Soil gas was preconcentrated on Carbotrap (Supelco, Bellefonte, PA, USA) or collected in Tedlar bags (PMC, Oak Park, IL, USA) or Summa passivated stainless-steel canisters (Scientific Instrumentation Specialists, Moscow, ID, USA). Stainless-steel sample cartridges (7.62 cm$\times$0.635 cm O.D.) were packed with 300–325 mg of 20–40 mesh Carbotrap and attached to a sample holder containing a critical orifice (SKC, Eighty Four, PA, USA) for sample collection. Soil gas was drawn through the cartridges by using SKC personal sampling pumps (SKC). The Tedlar bags were filled from the manifold by using a Teflon PTFE low-flow diaphragm pump (Cole-Parmer, Niles, IL, USA). Summa-passivated stainless-steel canisters (250 ml) were filled to a pressure of 15 p.s.i.g. from the manifold by using an air sampler described in detail by Doskey and Gaffney [7].

The sorbent tubes were cleaned by purging them with helium at 200 ml min^{-1} in an oven at 315°C for 1 h. The cleaned cartridges were placed in glass containers containing a cushion of untreated glass wool and sealed with screw-top caps lined with soft septa (Supelco). The sample containers were put in 40-ml glass vials with septum-lined caps and stored in a refrigerator prior to shipment for sample collection. Tedlar bags were cleaned by filling them with humidified ultra zero air and emptying the contents a total of three times. The bags were then filled with air and shipped to the field. Canisters were cleaned in a series of pressurization/evacuation cycles with humidified ultra zero air.

Samples were analyzed by a cryogenic preconcentration/high-resolution gas chromatographic technique [8]. The instrumentation included a Chemical Data Systems (CDS) Model 330 sample concentrator (Autoclave, Oxford, PA, USA) that was interfaced to a Hewlett-Packard 5890 HRGC system (Palo Alto, CA, USA) with ECD. The Carbotrap cartridges were thermally desorbed and purged with 150 ml of ultra high-purity helium that flowed through the sample

cartridge at 30 ml min^{-1}. Whole air samples from the Tedlar bags were injected with a 10-ml Hamilton Gastight syringe (Alltech Associates, Deerfield, IL, USA) into a stream of ultra high-purity helium. The purge gas flowed through a stainless-steel tee that was connected to the empty thermal-desorption probe of the CDS 330. Whole air samples from the canisters were injected into the preconcentrator through a glass-lined stainless-steel inlet by a procedure described in detail by Doskey [8].

The VHOCs were separated on a 60 m×0.32 mm I.D. fused-silica capillary column coated with a 1.0-μm film of DB-1 (J & W Scientific, Folsom, CA, USA). The column was held at $-50°C$ for 2 min while the sample was being desorbed from the trap and then was increased at 8 C° min^{-1} to 135°C and then was increased at 20 C° min^{-1} to 250°C and held for 5 min to clean the column of high-molecular-mass compounds.

Neat liquid standards (99% purity) were purchased from Alltech (Deerfield, IL, USA) and Aldrich (Milwaukee, WI, USA) and included tetradecafluorohexane (C_6F_{14}), $CHCl_3$, 1,1,1-trichloroethane (CH_3CCl_3), CCl_4, octafluorotoluene (C_7F_8), trichloroethene ($CHClCCl_2$), and tetrachloroethene (C_2Cl_4). Gas standards were prepared by the static dilution method [9] and were stable for a period of 5 days. All seven compounds exhibited calibration curves with narrow linear ranges that extended to approximately 2–20 ng (Table 1). For experiments in which the analytes and internal standards had to be added to the cartridges, a standard was prepared in a static dilution bottle and injected through a

stainless-steel tee containing a septum adapter at room temperature into a stream of helium gas flowing through the tee and sample cartridge at 30 ml min^{-1} for 5 min.

A gaseous mixture of the five analytes and two internal standards was added to 36 cartridges to examine the stability of soil gas samples collected on Carbotrap. A total of eight clean cartridges were used as blanks; and three sets of cartridges, each set consisting of three spiked cartridges and a blank, were stored at three different temperatures: -20, -9 and 20°C. A fourth set was analyzed on the same day that the cartridges were prepared, while the other sets were analyzed after being stored for 5, 15 and 30 days.

3. Results and discussion

We compared recoveries for analytes in soil gas that had been preconcentrated on sorbent cartridges in the field with recoveries for gas standards that had been added to sorbent cartridges in the laboratory. The cartridges were thermally desorbed at temperatures of 200, 250 and 300°C. Each soil gas sample was desorbed and purged two or three times in succession with 150 ml of helium at 30 ml min^{-1} to determine the recoveries. An injection of 6.4 ng of C_7F_8 into the helium purge gas stream during the first desorption was used as an internal standard. For the soil gas samples, $CHCl_3$ and CCl_4 were completely desorbed during the first desorption at temperatures as low as 200°C (Table 2); however, a desorption temperature of 300°C was needed to recover more than 90% of the C_7F_8 that had been added during the first thermal desorption of the cartridges. The mean recovery of C_7F_8 for 77 soil gas samples in which the internal standard was added during thermal desorption was 88±15%, with a range of 50–100%.

We also injected a gaseous mixture of the five target analytes and two internal standards into 150 ml helium that entered the rear of the sorbent cartridges (in the same direction that VOCs enter the sample cartridge during sample collection) at 30 ml min^{-1}. The cartridges were then attached to the thermal-desorption probe and desorbed at temperatures of 200, 250 and 300°C. Recoveries for C_6F_{14},

Table 1
Instrument calibration and method parameters

Analyte	Linear range[a] (ng)	MDL[b] (ng)	Precision[c] (%)
C_6F_{14}	18	0.05	±1.9
$CHCl_3$	11	0.05	±4.6
C_7F_8	4	0.03	±2.4
CH_3CCl_3	5	0.05	±5.2
CCl_4	1.5	0.01	±5.4
$CHClCCl_2$	11	0.06	±1.8
C_2Cl_4	1.5	0.09	±4.4

[a] Estimated maximum.
[b] Method detection limit (MDL)=3×standard deviation of the laboratory blank ($n=5$).
[c] Injection of gas standard at a level 5×MDL ($n=5$).

Table 2
Recoveries (%) for analytes in a soil gas sample that was collected in triplicate and thermally desorbed a total of two or three times in succession at three different temperatures

Analyte	Amount (ng)	300°C[b]		250°C			200°C		
		Cycle		Cycle			Cycle		
		1	2	1	2	3[c]	1	2	3[c]
$CHCl_3$	4.8	100	0	100	0	0	100	0	0
CCl_4	24	100	0	100	0	0	100	0	0
$C_7F_8^a$	6.4	97	3.0	38	37	25	28	0.70	72

[a] Gas standard of the analyte was directly injected during thermal desorption.

[b] Temperature of thermal desorption.

[c] Thermal desorption at 300°C.

CH_3CCl_3, CCl_4 and $CHClCCl_2$, relative to a direct injection of the standard into the instrument, were nearly 100% at each temperature (Table 3); however, recoveries of $CHCl_3$, C_7F_8, and C_2Cl_4 decreased as the thermal desorption temperature increased, indicating that these analytes were thermally decomposed. Thermal decomposition of toluene, hexane and some oxygenated compounds on graphitized carbon black at 300°C has been observed [10]. We also determined recoveries of C_7F_8 and C_6F_{14} for 110 sample cartridges to which the internal standards were added to the rear of the cartridges prior to being shipped to the field. During sample collection, 60 ml of soil gas was preconcentrated onto the cartridges. The mean recovery of C_7F_8 in 110 cartridges that were thermally desorbed at 300°C was 99±7.1%, with a range of 72–120%. Recoveries of C_6F_{14} were consistently greater than 100%. An unidentified compound in the soil gas was found to coelute with C_6F_{14}, making it unsuitable as an internal standard. These experiments indicated that, if an internal standard method is going to be used for quantitation, it would be best to add the internal standard to the cartridge prior to collection of the sample. For our soil gas matrix C_7F_8, was a suitable internal standard.

The recoveries of the analytes were also examined as a function of the depth to which they penetrated the sorbent bed during sample collection. A gaseous standard was added through the rear (the same direction that analytes enter the cartridge during sampling) and front (opposite to the direction that analytes enter the cartridge during sampling) of the cartridges before they were attached to the thermal-desorption probe and desorbed at 200°C. Analytes added to the front of the cartridge must traverse the entire sorbent bed during thermal desorption. A gaseous standard was also directly injected into empty stainless-steel cartridges and cartridges filled with sorbent while they were being thermally desorbed at 200°C. Analytes added to the rear of the cartridges before they were attached to the thermal-

Table 3
Recoveries (%) for analytes on sorbent cartridges desorbed at three different temperatures

Analyte[a]	Amount (ng)	200°C[b]	250°C	300°C
C_6F_{14}	4.0	98.8±3.16	99.7±3.94	100±3.47
$CHCl_3$	3.6	101±9.76	93.7±5.71	90.4±4.31
C_7F_8	4.0	96.1±5.84	89.4±5.44	85.3±7.17
CH_3CCl_3	3.2	101±5.32	97.7±5.69	98.7±4.98
CCl_4	3.8	100±3.07	98.7±2.78	98.0±2.98
$CHClCCl_2$	3.5	117±13.3	120±12.7	111±14.1
C_2Cl_4	3.9	101±4.1	98.0±4.36	93.5±4.49

[a] A gas standard containing a mixture of the analytes was injected into a stream of helium flowing through the rear of five sorbent cartridges before they were attached to the thermal-desorption probe.

[b] Temperature of thermal desorption.

Table 4
Recoveries for analytes in a gas standard that was (1) directly injected into empty cartridges ($n=5$) and cartridges filled with Carbotrap ($n=5$) during thermal desorption at 200°C and (2) injected into a helium gas stream flowing through the rear and front of sorbent cartridges ($n=5$) before they were thermally desorbed at 200°C

Analyte	Amount (ng)	Recovery (%)			
		Method 1[a]		Method 2[b]	
		Empty	Filled	Rear	Front
C_6F_{14}	4.0	97.6±3.19	101±8.56	98.8±3.16	102±3.73
$CHCl_3$	3.6	89.4±4.18	100±8.10	101±9.76	98.9±6.17
C_7F_8	4.0	91.3±6.77	29.6±7.17	96.1±5.84	1.6±0.99
CH_3CCl_3	3.2	96.9±5.11	93.9±4.93	101±5.32	61.0±36.0
CCl_4	3.8	97.4±2.73	93.9±3.58	100±3.07	92.7±3.55
$CHClCCl_2$	3.5	94.8±6.46	94.9±7.61	117±13.3	112±13.4
C_2Cl_4	3.9	93.1±3.79	86.8±12.4	101±4.11	71.8±29.6

[a] Direct injection of standard into cartridge during thermal desorption.
[b] Standard added before thermal desorption.

desorption probe exhibited recoveries of greater than 95% (Table 4); however, recoveries of C_7F_8 and C_2Cl_4 were incomplete when the gas standard was added during thermal desorption, and the recoveries were even lower for these two analytes and also CH_3CCl_3 when they were added to the front of the cartridges before they were attached to the thermal-desorption probe. Of the seven analytes that were investigated, C_7F_8 and C_2Cl_4 are the least volatile, and their recoveries were the most sensitive to their depth of penetration into the sorbent bed. CH_3CCl_3 did not fit this pattern even though its vapor pressure is similar to that of CCl_4, an analyte that did not exhibit this sensitivity; however, the highly variable recoveries for CH_3CCl_3 that were obtained when it was added to the front of the cartridge prior to thermal desorption may explain the discrepancy.

We examined the breakthrough volumes of $CHCl_3$

and CCl_4 for the sorbent by withdrawing soil gas volumes of 60, 600 and 1000 ml from two different monitoring wells at a rate of 30 ml min^{-1} through a set of two sorbent cartridges connected in series. Less than 5% of the total amount of $CHCl_3$ and CCl_4 that was recovered was found on the second cartridge in the series for sample volumes as large as 1000 ml (Table 5). The retention of VOCs by organic sorbents is related to their volatility [11] and the concentration of VOCs in the gas stream [12]. Consequently, the least volatile organic analytes typically exhibit the largest breakthrough volumes. $CHCl_3$ was the most volatile of the analytes we tested. Consequently, breakthrough volumes for the other analytes, although not present in the soil gas matrix, are expected to be similar to or greater than the breakthrough volume exhibited by $CHCl_3$. The breakthrough volumes for $CHCl_3$ and CCl_4 reported

Table 5
Fraction of the analytes that was recovered on the second cartridge of a two-cartridge series that was used to collect two different soil gas samples

Analyte	Concentration ($\mu g\ m^{-3}$)	Fraction[a] (%)		
		60 ml sample	600 ml sample	1000 ml sample
Well 1				
$CHCl_3$	77	0	0.17	1.9
CCl_4	240	0	0	0
Well 2				
$CHCl_3$	420	0	0.42	3.5
CCl_4	1700	0	0	0

[a] Fraction of total amount recovered that was found on the second sorbent cartridge.

here are for actual soil gas samples. These field-determined breakthrough volumes take into account the competition between target analytes and other VOCs in the soil gas matrix for sorbent sites. Thus, breakthrough volumes for VOCs in actual sample matrices will be smaller than those derived in clean gas streams and more accurately reflect the volume that should be used for sample collection.

Hazard and Brown [13] examined the preservation of VOC samples collected on Carbotrap and recommended that they be stored in a freezer prior to analysis. Because freezing samples during shipment is cumbersome, we decided to further investigate the storage characteristics of the sorbent. We found that VHOC levels in blanks at all temperatures (-20, -9 and $20°C$) over the 30-day period were the same as those found initially, with the exception of CH_3CCl_3, which increased non-linearly at an average of 0.44 ng above the initial levels. In cartridges to which the gas standard was added, $CHCl_3$, CCl_4 and C_2Cl_4 levels remained constant; CH_3CCl_3 and $CHClCCl_2$ levels increased; and C_6F_{14} levels decreased at all

temperatures over the 30-day period (Table 6). Increases in CH_3CCl_3 levels were attributed to contamination from ambient air because levels in blank cartridges also increased. The reason for the increase in $CHClCCl_2$ levels with time is uncertain because $CHClCCl_2$ levels in blank cartridges did not increase. C_6F_{14} is the most volatile of the analytes, and losses during storage can probably be attributed to evaporation. In general, the stability of all five analytes and C_7F_8 on Carbotrap was the same for samples stored at temperatures from $-20°C$ to $20°C$ for 30 days. Heavner et al. [14] also found that $CHClCCl_2$ and C_2Cl_4 were stable on a mixed sorbent bed of Tenax TA and Carbotrap at room temperature for a period of four weeks. Contrary to results obtained by Hazard and Brown [13], our data indicate that the most critical factor in sample storage on Carbotrap is not temperature or time but rather the elimination of contamination from ambient air.

A comparison of three different sample collection methods was performed by preconcentrating soil gas

Table 6
Recovery of analytes that were added to sorbent cartridges ($n=3$) and stored at three different temperatures before analysis

Analyte	Amount (ng)	Temperature (°C)	Recovery (%)		
			5 days storage	15 days storage	30 days storage
C_6F_{14}	2.4	20	93.0±1.69	94.8±0.79	0
		-9	92.7±0.78	98.4±4.50	0
		-20	92.6±1.35	95.6±1.13	0
$CHCl_3$	2.1	20	94.2±4.05	99.0±2.59	98.0±9.86
		-9	95.2±1.02	100±2.73	99.5±2.77
		-20	94.1±2.62	99.1±0.94	98.4±4.47
C_7F_8	2.4	20	98.1±1.48	96.6±5.76	100±2.07
		-9	98.2±0.49	100±2.76	101±1.08
		-20	98.4±0.64	101±1.70	101±1.72
CH_3CCl_3	1.9	20	108±46.6	118±18.0	131±10.7
		-9	122±21.3	121±18.3	102±1.08
		-20	100±4.76	114±16.2	109±46.4
CCl_4	2.3	20	95.8±3.14	95.9±0.51	99.4±2.81
		-9	101±1.49	100±2.78	101±1.13
		-20	98.8±2.17	99.0±1.24	99.7±5.91
$CHClCCl_2$	2.1	20	107±2.22	109±3.35	118±2.01
		-9	105±4.54	108±3.41	106±4.40
		-20	101±2.39	107±4.65	110±10.7
C_2Cl_4	2.3	20	106±3.27	105±2.17	108±2.78
		-9	104±2.95	102±1.69	104±3.24
		-20	102±1.77	106±4.34	105±4.40

on Carbotrap while simultaneously collecting samples in Tedlar bags and Summa passivated stainless-steel canisters. Levels of $CHCl_3$ were lower in Carbotrap samples than in the Summa canisters, but the levels were similar to those in the Tedlar bags (Fig. 1A). The concentration of $CHCl_3$ in one of the Tedlar bag samples was below the MDL and could not be used in the comparison. The disparity in the $CHCl_3$ results may have been caused by changes in the response of the ECD to $CHCl_3$ due to co-elution

with water or decomposition of $CHCl_3$ during thermal desorption. Carbotrap is hydrophobic and does not retain water; however, water was not removed in our analysis of samples collected in Tedlar bags and Summa canisters. Smaller amounts of water entered the ECD from the 10-ml sample that was injected from the Tedlar bags than from the 60-ml sample that was injected from the Summa canisters. Consequently, closer agreement was expected between the Tedlar bag and Carbotrap methods than between the Summa canister and Carbotrap methods. It was also possible that thermal decomposition of $CHCl_3$ at the desorption temperature of 300°C contributed to the lower values obtained with the Carbotrap method; however, our laboratory experiments demonstrated only a 10% loss of $CHCl_3$ during thermal desorption at 300°C, which is too small to account for the 15–50% difference between the Carbotrap and Summa canister methods.

The concentrations of CCl_4 in Carbotrap samples were similar to the levels found in the Summa canisters but were higher than those found in the Tedlar bags (Fig. 1B). The VOCs are stable in canisters over long periods if the relative humidity of the sample is at least 10% [4]; however, samples may not be stable in Tedlar bags because of their permeability and the sorption of VOCs to the bag. We monitored the levels of CCl_4 in samples collected in five different bags and stored for a period of 24 h to 57 days at 25°C and found that CCl_4 concentrations remained essentially constant; however, this experiment could not monitor the behavior of CCl_4 in the bag within the first 24 h after collection, during which a 10–30% loss of CCl_4 would have had to occur to make the results comparable to those obtained with the Carbotrap method.

The method detection limit (MDL) and precision of the Carbotrap analysis was determined from the analysis of cartridges that were prepared by injecting gas standards into the cartridges in the laboratory before they were attached to the thermal-desorption probe. We operationally defined the MDL as 3 times the standard deviation of the levels of analytes that were found on sorbent cartridges that were cleaned and analyzed (thermal desorption at 300°C) on the same day without being stored. Method detection limits of 0.01–0.1 ng were obtained for the target analytes and internal standards (Table 1). The ana-
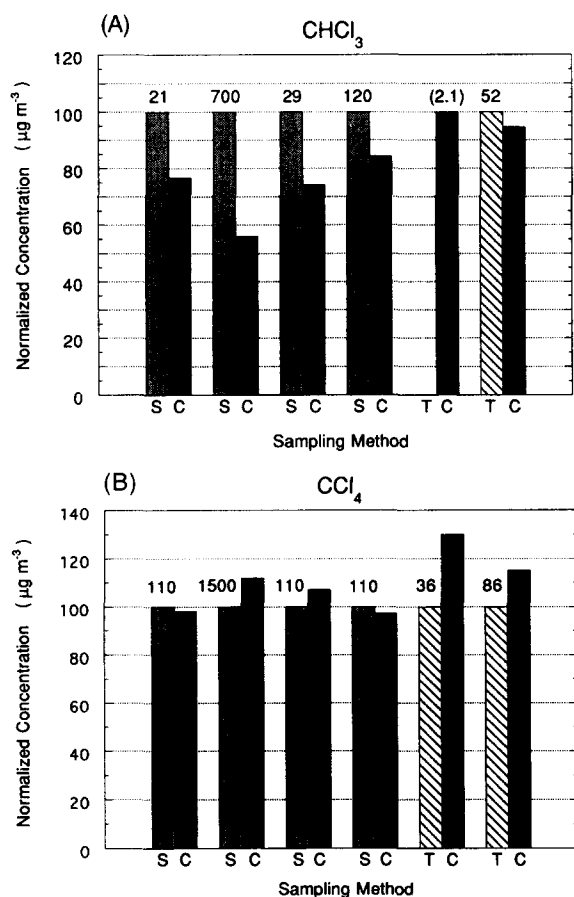

Fig. 1. Normalized analyte concentrations in soil gas samples collected simultaneously by three different methods. (A) Trichloromethane ($CHCl_3$), (B) tetrachloromethane (CCl_4). The numbers within the bar graph are the analyte concentrations ($\mu g\ m^{-3}$) that were measured in the Summa canisters (S) or Tedlar bags (T) with the exception of the value in parentheses which was undetectable in the Tedlar bag. The analyte concentrations that were measured with the Carbotrap cartridges (C) were normalized to the concentrations measured in the Summa canisters and Tedlar bags.

lytical precision, which we define as the standard deviation of the analysis of five cartridges to which standards were added at a level of 5-times the MDL, were all approximately ±5% or less (Table 1).

The procedure for sampling soil gas from monitoring wells was also evaluated. A single sorbent cartridge was attached to a well, and 60 ml of soil gas was withdrawn at 15 ml min^{-1}. The sampling manifold was then connected to the well and 3 l of soil gas was removed at 1 l min^{-1}; three 1-l aliquots were collected in Tedlar bags. The manifold was then disconnected and replaced by a single sorbent cartridge. After the withdrawal of a 60-ml volume at 15 ml min^{-1} onto the cartridge, the manifold was reattached, and 4 l of the soil gas was simultaneously collected at 1 l min^{-1} in a Tedlar bag and sampled through another sorbent cartridge at 15 ml min^{-1} while the well was being purged at 1 l min^{-1}. The levels of CCl_4 and $CHCl_3$ increased in both wells during the first purge cycle (Fig. 2). Nearly undetectable levels of CCl_4 and $CHCl_3$ were measured on sorbent cartridges after 90% of the volume of gas within the monitoring wells had been exchanged with fresh soil gas; however, when the manifold was disconnected to make the measurements after the first purge cycle, the wells were briefly exposed to ambient air, and the rate at which gas was withdrawn from the wells was reduced from 1 l min^{-1} to 15 ml min^{-1}. The large reduction in concentrations appeared to indicate that either (1) the entire volume of the well had been evacuated during the purge cycle and replaced by an equal volume of ambient air that entered the well during the time that it took to disconnect the sampling manifold and attach a single sorbent cartridge to the well or (2) the soil gas concentration depended upon the rate at which the gas was withdrawn from the well. After the 1 l min^{-1} flow-rate was restored and 90% of the gas within the wells had again been exchanged, the average concentrations of CCl_4 and $CHCl_3$ increased to levels above those measured when soil gas was withdrawn at 15 ml min^{-1} onto the sorbent cartridge at the end of the first purge cycle, but they were lower than the levels obtained when gas was withdrawn at 1 l min^{-1} near the end of the first purge cycle. The second purge cycle failed to return the system to conditions established during the first purge cycle. The concentrations of CCl_4 and $CHCl_3$
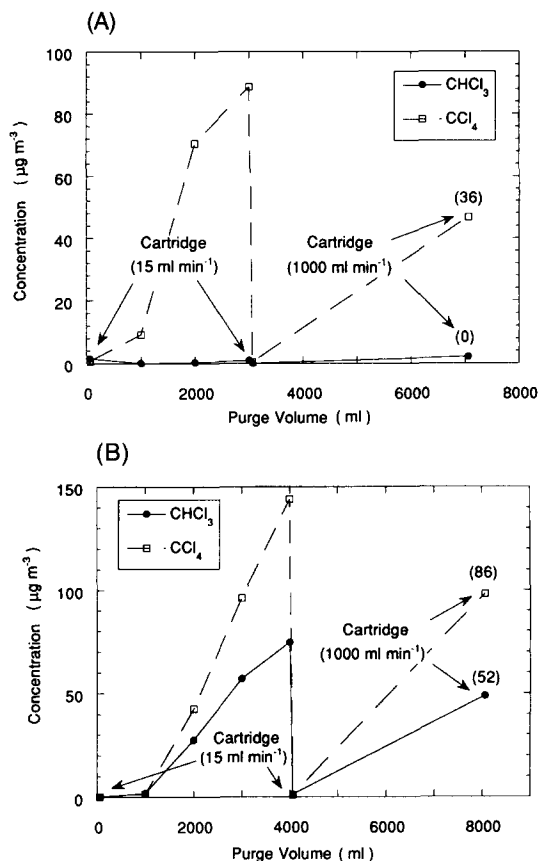

Fig. 2. Concentrations of trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4) in (A) monitoring well 3B (well volume, 1220 ml) and (B) monitoring well 4C (well volume, 1540 ml) as a function of the amount of gas that was withdrawn from the well (purge volume). Numbers in parentheses indicate measurements using Carbotrap cartridges. All other concentrations were measured in Tedlar bags.

in samples collected in the Tedlar bags and sorbent cartridges during the second purge cycle were similar; however, unlike the sorbent cartridge sample that was collected at the conclusion of the first purge cycle by withdrawing soil gas at 15 ml min^{-1} from the well, the sorbent cartridge collected during the second purge cycle was collected while the well was being purged at 1 l min^{-1}. These results indicate that the measured concentration is sensitive to both the volume of soil gas that is withdrawn from the well and the rate at which the soil gas is withdrawn. The experiment demonstrated that several volumes of soil

gas must be withdrawn from the monitoring well to exchange the air that has accumulated in the well prior to sample collection, and additional purging may produce lower measured concentrations of the contaminants in the soil gas. Thus, the measured concentrations may depend upon the porosity and water content of the soil, characteristics that control the ability of the soil to supply air at a rate comparable to the rate at which air is being withdrawn during sampling.

4. Conclusions

The VHOCs were efficiently desorbed from Carbotrap at 200°C; however, a temperature of 300°C was necessary for complete desorption of analytes that penetrated to the rear of the sorbent bed during sampling. At a thermal desorption temperature of 300°C, decomposition losses for $CHCl_3$, C_7F_8 and C_2Cl_4, were 10, 15 and 5%, respectively. Breakthrough volumes for $CHCl_3$ and CCl_4 in the soil gas matrix were at least 1000 ml. The sorbent cartridges are stable for at least 30 days at 20°C, however, low-level samples may become contaminated during storage if precautions are not taken to completely eliminate ambient air from the storage containers. The Carbotrap method compared favorably with whole air methods in which samples were collected in Summa passivated stainless-steel canisters and Tedlar bags. The MDL of the Carbotrap method for VHOCs in soil gas is about 1 μg m^{-3} (for a 60-ml sample volume), with a precision of about ±5%. The measured concentration of VHOCs in soil-gas monitoring wells was sensitive to the volume of gas that was withdrawn from the well. Several volumes of the well had to be removed to replace the gas in the well with fresh soil gas. A comparison of two successive purge cycles of a monitoring well indicated that the measured concentration was determined by the ability of the soil to supply air at a rate comparable to the rate at which air is being withdrawn from the well.

Acknowledgments

References

[1] P.K. Aggarwal, M.C. Hansen and W.T. Kickels, Proceedings of the 1994 Federal Environmental Restoration III and Waste Minimization II Conference and Exhibition, Vol. I, April 1994, New Orleans, LA, 1994, p. 28.
[2] R.K.M. Jayanty, Atmos. Environ., 23 (1989) 777.
[3] H. Westberg and P. Zimmerman, in L. Newman (Editor), Measurement Challenges in Atmospheric Chemistry, American Chemical Society, Washington, DC, 1993, p. 275.
[4] K.D. Oliver, J.D. Pleil and W.A. McClenny, Atmos. Environ., 20 (1986) 1403.
[5] A. Fabbri, G. Crescentini, F. Mangani, A.R. Mastrogiacomo and F. Bruner, Chromatographia, 23 (1987) 856.
[6] D. Helmig and J.P. Greenberg, J. Chromatogr. A, 677 (1994) 123.
[7] P.V. Doskey and J.S. Gaffney, Geophys. Res. Lett., 19 (1992) 381.
[8] P.V. Doskey, J. High Resolut. Chromatogr., 14 (1991) 724.
[9] C. Morris, R. Berkley and J. Bumgarner, Anal. Lett. 16 (1983) 1585.
[10] F. Mangani, A.R. Mastrogiacomo and O. Marras, Chromatographia, 15 (1982) 712.
[11] R.H. Brown and C.J. Purnell, J. Chromatogr., 178 (1979) 79.
[12] G. Bertoni, F. Bruner, A. Liberti and C. Perrino, J. Chromatogr., 203 (1981) 263.
[13] S.A. Hazard and J.L. Brown, Abstracts of the 1993 Pittsburgh Conference, March 1993, Atlanta, GA, 1993, Paper 581.
[14] D.L. Heavner, M.W. Ogden and P.R. Nelson, Environ. Sci. Technol., 26 (1992) 1737.