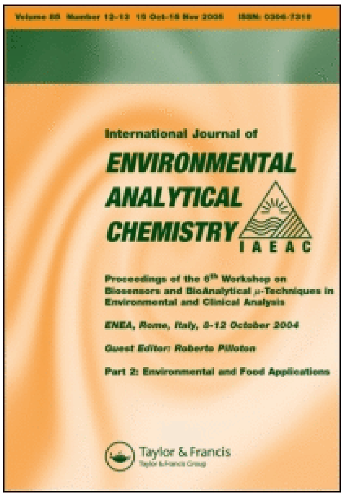

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Shallow-Probe Soil-Gas Sampling for Indication of Ground-Water Contamination by Chloroform

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Soil-gas sampling and analysis for indication of ground-water contamination by chloroform was field tested. The field testing included evaluation of: The repeatability of results, the correlation of results of soil-gas analyses with ground-water concentrations, the differences in results among closely spaced samples and the depth profile of chloroform concentrations in soil-gas samples. The sampling probe gave good repeatability, although leakage of sample from syringes between sampling and analysis is postulated as a reason for variability in results. Soil-gas concentrations correlated with ground-water data at a level above 95% significance. Short-range variability of results ranged from 12% to 43% over 2 meters with leakage of sample from syringes postulated as a reason for the higher variability. A depth-dependence of the chloroform concentration consistent with a vertical transport mechanism of gas-phase diffusion was observed.

KEY WORDS: Soil-gas sampling, groundwater contamination, chloroform, volatile organic compounds (VOCs).

INTRODUCTION

Sampling and analysis of soil gases for the location of volatile organic compounds (VOCs) below the ground surface was originally used for oil exploration[1] and has recently been used for location of ground-water contamination by VOCs.[2] Because of the comparative low cost of a soil-gas survey relative to drilling exploratory wells and analyzing ground water for determination of the areal extent of subsurface contamination by VOCs, the technology is attractive for preliminary site-characterization efforts.

Vertical transport of VOCs from contaminated ground water has been described by a model which uses three mechanisms for transport through the three subsurface zones.[3] In the saturated zone or water table, vertical transport of dissolved VOCs is postulated to occur through transverse dispersion and in the intermediate zone, or capillary fringe, vertical transport is by a combination of dispersion and liquid/vapor partitioning. In the upper or unsaturated zone, gas-phase diffusion is the flux-controlling process and is described using Fick's Law.[4]

$$\mathrm{VOC\ Flux} = D^*(n - W_0)\frac{dCa}{dz} \tag{1}$$

where D^* is the diffusion coefficient of the VOC in soil gas, n is the porosity of the soil, W_0 is the irreducible water content of the soil, Ca is the concentration of the VOC in soil-gas, and z is depth below the surface. Equation 1 predicts a linear VOC concentration profile in the unsaturated zone. In addition, since Ca must approach zero at the ground surface, Eq. (1) predicts that both the VOC vertical flux and concentration at a fixed depth will be directly proportional to the dissolved VOC concentration in the ground-water below, given a constant air-filled porosity, depth to ground water, and soil-gas diffusion coefficient.

In this paper, we describe a shallow-probe design, we report method-performance data, and we discuss an evaluation of the theory of diffusion-controlled VOC flux through the unsaturated zone. The method-performance study assessed: the quality of the sampler as indicated by repeatability of results, the value of the results of soil-gas analyses for indication of ground-water contamination as shown by their correlation with ground-water analytical results, and the magnitude of short-range variability of soil-gas results. In addition, the vertical concentration profile was evaluated as a test of the theory of diffusion-controlled vertical transport of VOCs in the vadose zone. The probe design and the soil-gas and ground-water sampling and analyses were performed under contract to the U.S. Environmental Protection Agency.[5]

EXPERIMENTAL SECTION

Apparatus

The soil-gas probe used was a 2.3-meter, 19-mm O.D. pipe of high-strength steel with a conical tip with horizontal 3-mm sampling ports. The ports lead to a central plenum connected to a 3-mm stainless steel tube inside the pipe. Figures 1 and 2 show the probe head, tip, and body. The stainless steel tubing is connected to a septum-equipped stainless steel sampling manifold. Figure 3 shows the manifold. Soil-gas was drawn from the subsurface into the manifold by use of an MSA Samplair hand air-sampling pump. Subsamples were taken from the manifold with Hamilton Gastight syringes. Soil-gas analyses were performed on-site using an Analytical Instruments Development Model 511 gas chromatograph (GC) with a ^{3}H electron-capture detector (ECD) and a 183-cm × 3-mm stainless steel column packed with 10 percent DC-200 on Chromosorb W HP (80/100). The GC was operated at 43°C (oven), 37°C (injector), and 37°C (detector). A Shimadzu C-R3A integrator and Hewlett Packard 7155A recorder were used to record the chromatograms. Analytical instruments were in a modified van, and electrical power was provided by a gasoline-powered generator operated approximately 6.4 meters (20 feet) down wind. Water samples were taken in 45-mL septum-capped vials (Pierce Chemical Company) and were analyzed by U.S. Environmental Protection Agency procedures using a Finnegan GC/MS.[6]

Procedure

Sampling probes were hammered 1.3 meters (4 feet) into the ground with a sledge hammer, and the sampling manifold was attached. Seventy-five (75) cm^3 of gas was drawn through the sampling assembly and subsamples were withdrawn from the manifold in Hamilton Gastight syringes for analysis. The subsamples were transported in an opaque plastic box to an on-site van equipped with the analytical equipment for soil-gas analyses. The ground-water ana-

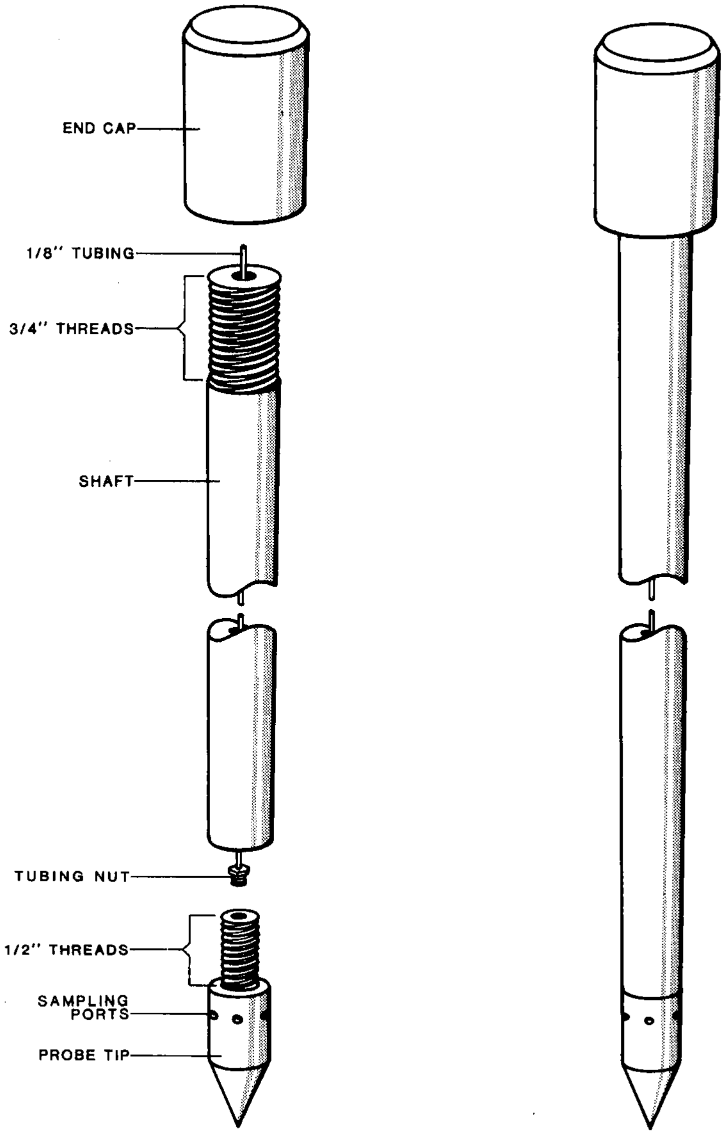

Figure 1 Schematic of the sampling probe.

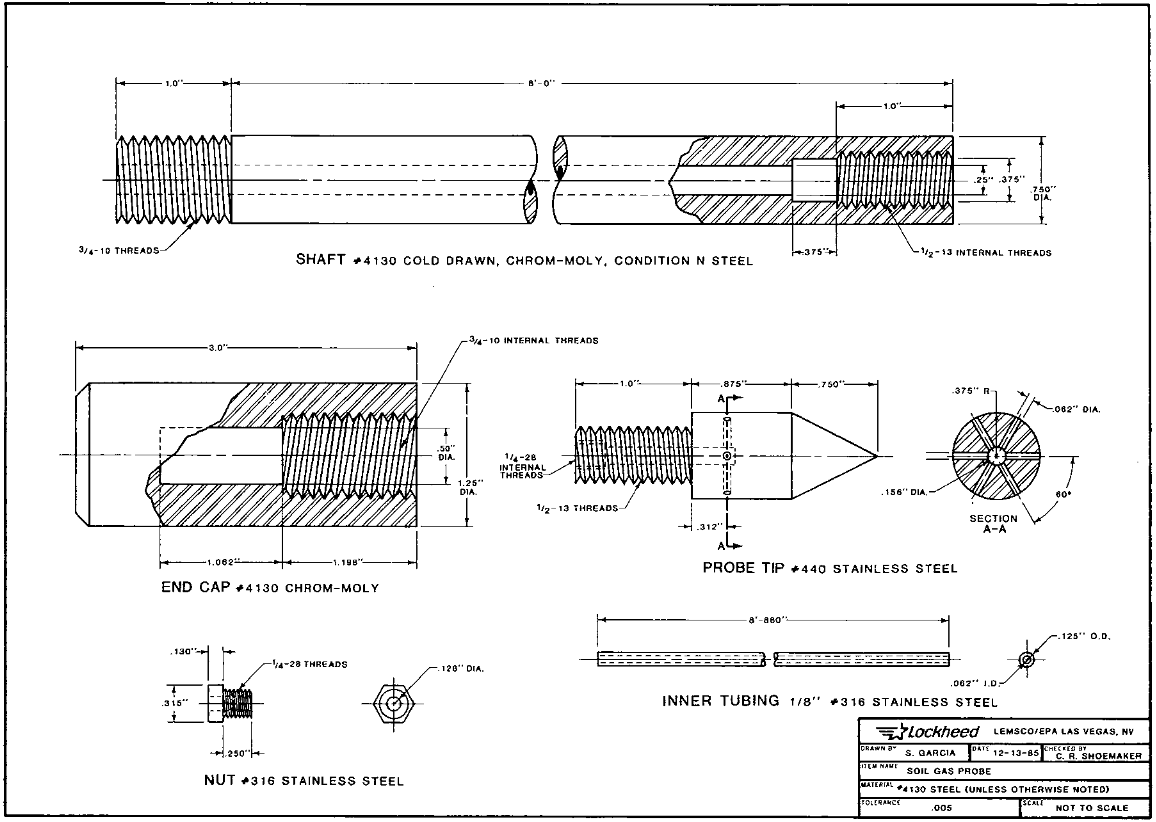

Figure 2 Design specification of sampling probe components.

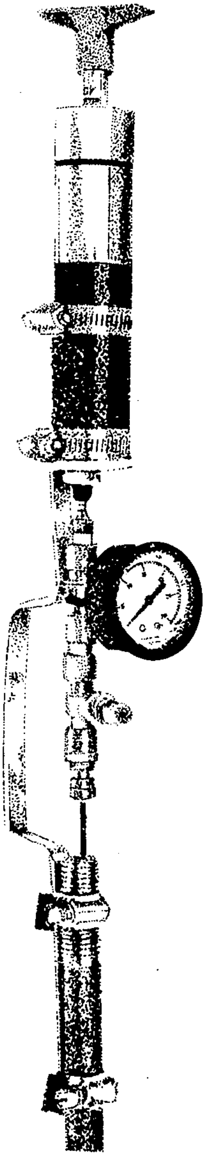

Figure 3 Sampling manifold.

lyses were performed at a remote laboratory. The GC/ECD detection limit for chloroform in soil gas was 5 ppbv while the GC/MS detection limit for chloroform in ground water was 5 μg/L. Testing of the GC/MS method by 15 laboratories yielded a mean recovery of 78 percent and a coefficient of variation (CV) of 12 percent.[6] Standards of chloroform were prepared in 45-mL septum-capped vials (Pierce Chemical Company) by serial dilution of headspace vapors from pure chloroform (Omegakit, Alltech Assoc., Deerfield, Ill). Blanks of ambient air were drawn through the probes and analyzed before use, and syringes were purged with ultrapure nitrogen between uses to eliminate false results from probe leakage or carryover from previous samples.

SURVEY SITE

A site of known chloroform ground-water contamination in Pittman, Nevada, was chosen for the study. Chloroform is a typical VOC and has similar Henry's Law constants and gas-phase diffusion coefficients to other VOCs. A set of ground-water monitoring wells have been drilled at the site 64 meters apart in a line perpendicular to the northward direction of ground-water flow. Figure 4 shows the subsurface geohydrology at the site.

The geohydrology of the site is relatively simple. Unconfined ground water occurs at a depth of 2 to 4 meters in calcified unconsolidated alluvium overlying a clay aquiclude. The soil type is a Caliza very gravelly sandy loam with a 2 to 8 percent clay content that decreases with depth, and a low shrink-swell potential.[7] The permeability of the soils is moderately rapid, at 5 to 150 cm per hour. The ground surface, water table, and aquiclude all slope downward approximately 1 degree to the north. The ground water moves northward at approximately 0.5 meters per day. Two distinct VOC ground water plumes exist at the site; one is chiefly chloroform while the other is mainly benzene and chlorobenzene. This study deals with the cloroform plume.

EXPERIMENTAL DESIGN

As a check on the repeatability of sampling, duplicate or triplicate

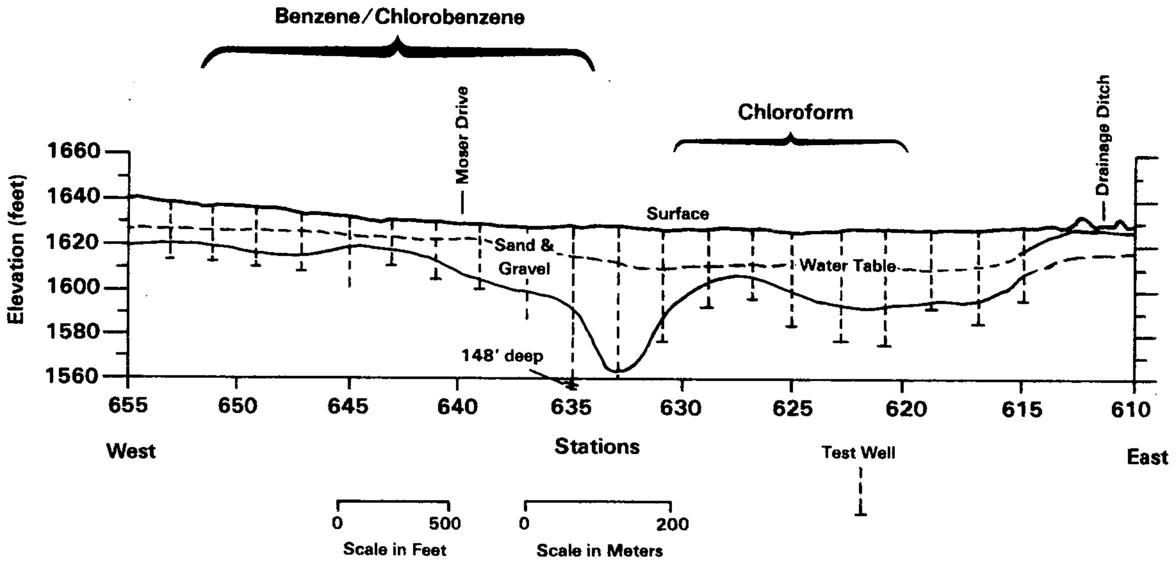

Figure 4 Hydrogeologic cross section along the Pittman Lateral.

samples were analyzed from each subsurface location sampled. A low variability among these results would indicate valid sampling equipment and procedures.

The results of the soil-gas analyses were compared to those of ground-water analyses to determine their correlation with ground-water contamination. A high degree of correlation would show that the results are meaningful in indication of ground-water contamination. The soil-gas results were from a 1.3-meter (4-foot) depth at four locations symmetrically placed at 6.4-meters (20 feet) from each of four ground-water monitoring wells. The mean of these four results was used in calculations. At each ground-water monitoring well at each side of the plume, one additional location (6.4 metres toward the plume) was sampled. Figure 5 shows the surface locations of the 1.3-meter (4-foot) deep sampling points and of the ground-water monitoring wells.

At one location a trapezoidal pattern of closely spaced 1.3-meter (4-foot) depth sampling points was used and at another three points separated by 1 meter (3 feet) along a north–south line were sampled at five depths between 0.3 meters (1 foot) and 1.7 metres (5 feet) in 0.3-meter increments. The results of analyses of these samples were

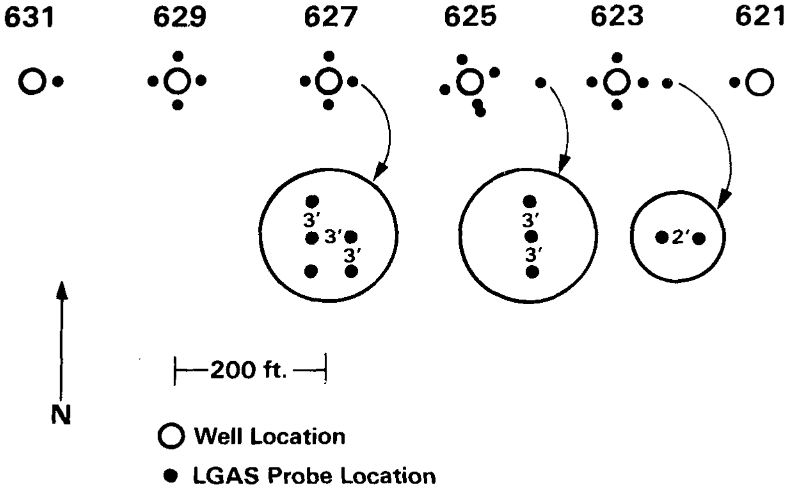

Figure 5 Sampling locations in the area of the chloroform plume.

used to estimate the magnitude of short-range variability of the results of the technique. Such information can help define the spatial resolution of the method and is important for design of sampling networks. The data from the five depths was used to assess the depth profile of VOC concentrations as a test of gas-phase diffusion as the VOC vertical-transport mechanism. A linear depth profile would agree with this theory.

RESULTS AND DISCUSSION

The validity of sampling can be assessed by the precision of the soil-gas analysis data in Tables I and II. The analytical precision, as indicated by analyses of standards over the course of a day, was characterized by a coefficient of variation (CV; 100 × standard deviation ÷ mean) of 2 percent while the CVs from analyses of triplicate and duplicate samples are higher. No statistical correlation exists between the CV and the sampling depth or the soil-gas chloroform concentration. Although only measured at one location (625) at just above the detection limit of 5 μg/L in ground-water

Table I Chloroform ground water (μg/L) and soil-gas (ppbv)[a] concentrations

Well (no.)	Ground-water concentration	Soil-gas concentration[b]				
		6.4 m west	6.4 m north	6.4 m east	6.4 m south	Mean
631	N.D.[c]	—	—	5(0)	—	5
629	11	10(2)	25(2)	27(5)	31(1)	23
627	175	28(5) (WSW)	72.9(0.1) (NNW)	125(53)[d] (ENE)	45.6(0.2)[e] (8 m SEE)	67
625	866	266(6)	326(10)	376(6)	511(17)	370
623 (32 m W)	—	—	—	—	150	
623	555	115(6)	12(5)	6(3)	27(2)	40
621	28	10.5(0.3)	—	—	—	10.5

[a] ppbv—parts per billion by volume; these units are independent of pressure and temperature.
[b] Triplicate analyses; standard deviation in parenthesis.
[c] Not detected; value of 5 used in regression.
[d] Mean of 4 closely-spaced points (see text).
[e] Duplicate determinations.

Table II Chloroform concentrations for the three-probe depth study

Location (base at 32 m W of no. 623)	Depth (m)	Chloroform concentration (ppbv)			
		Syringe			Mean (SD)
		No. 1	No. 2	No. 3	
base	0.3	22.9	23.0	—	23.0 (0.1)
3 ft north	0.3	23.5	22.3	—	22.9 (0.8)
6 ft north	0.3	18.2	18.3	20.1	19 (1)
base	0.6	76.9	75.3	—	76 (1)
3 ft north	0.6	72.8	69.2	68.3	70 (2)
6 ft north	0.6	55.4	60.2	—	58 (3)
base	1.0	109	110	—	109 (1)
3 ft north	1.0	111	110	—	111 (1)
6 ft north	1.0	83.4	111	102	99 (14)
base	1.3	160	146	—	153 (9)
3 ft north	1.3	150	148	—	149 (1)
6 ft north	1.3	122	142	—	132 (14)
base	1.6	188	177	—	183 (8)
3 ft north	1.6	150	183	—	167 (23)
6 ft north	1.6	206	206	202	205 (2)
base	1.8	256	216	—	236 (29)

samples, carbon tetrachloride was measured in soil gas at all sampling locations. This is probably due to the fact that the Henry's Law constant for carbon tetrachloride is 10 times that of chloroform (in μg/L in soil-gas $\div$ μg/L in ground-water). There is a linear correlation between the soil-gas chloroform CV and the CV of carbon tetrachloride; this implicates factors that affect the whole soil-gas sample in determination of the precision of results. Such factors would include leakage of sample from syringes during transport between sampling and analysis. It can also be noted that the results in Table II are substantially more precise than those listed in Table I. One consistent difference between these two data sets is that samples were transported 300 to 700 meters between sampling and analysis for the data in Table I, while the van containing the analytical equipment was less than 10 meters from the sampling locations when the data in Table II was taken. This difference in distances caused a consistently shorter time between sampling and analysis of samples for the data in Table II. This relationship between variability of results and sample holding time is also consistent with leakage of soil gas from syringes as the factor that determined the precision of results in this study.

In order to assess how well results indicated ground-water contamination, the mean values of the chloroform soil-gas concentrations in parts per billion by volume (ppbv) measured in the four samples around each borehole were compared to the ground-water chloroform concentrations in μg per liter. Table I lists both data sets. A correlation coefficient indicating a linear correlation of greater than 95 percent significance ($r = 0.85$; $n = 6$) was obtained. This shows that the results of soil-gas measurements of chloroform are a good indicator of ground-water contamination at this site. Figure 6 shows the spatial distribution of the soil-gas and ground-water chloroform concentrations measured.

Because the 6.5 meter (20-foot) and 13 meter (40-foot) lateral separations between sampling points could cause variations in soil-gas analytical results due to real variations in ground-water chloroform concentrations, the coefficients of variation (CVs) of the results from the four samples around each well were calculated. The values obtained were much higher than those from samples separated by one to three meters, indicating that these variations are due to larger factors than those affecting the closely spaced samples. These factors could include changes in the ground-water chloroform concentrations or subsurface inhomogeneities. Figure 6 shows the ground-water chloroform concentrations and the soil-gas analysis results as a function of the east–west coordinate. It can be seen that the east and west samples at each well correctly reflect the east-west soil-gas and ground-water gradients. This indicates that much of the variability among these samples separated by 13 meters is due to changes in the ground-water chloroform concentrations.

The short-range variability of results from the technique can be estimated by evaluation of the precision among results from the closely spaced samples. The coefficient of variation (CV) among the trapezoidal pattern of samples was 42 percent; this result was calculated omitting one data point where the sampling manifold leaked. Table I lists the actual data. However, the CV among results from the three locations 1 meter apart along a north–south line was only 12 percent (Table III). These data may be a more reasonable

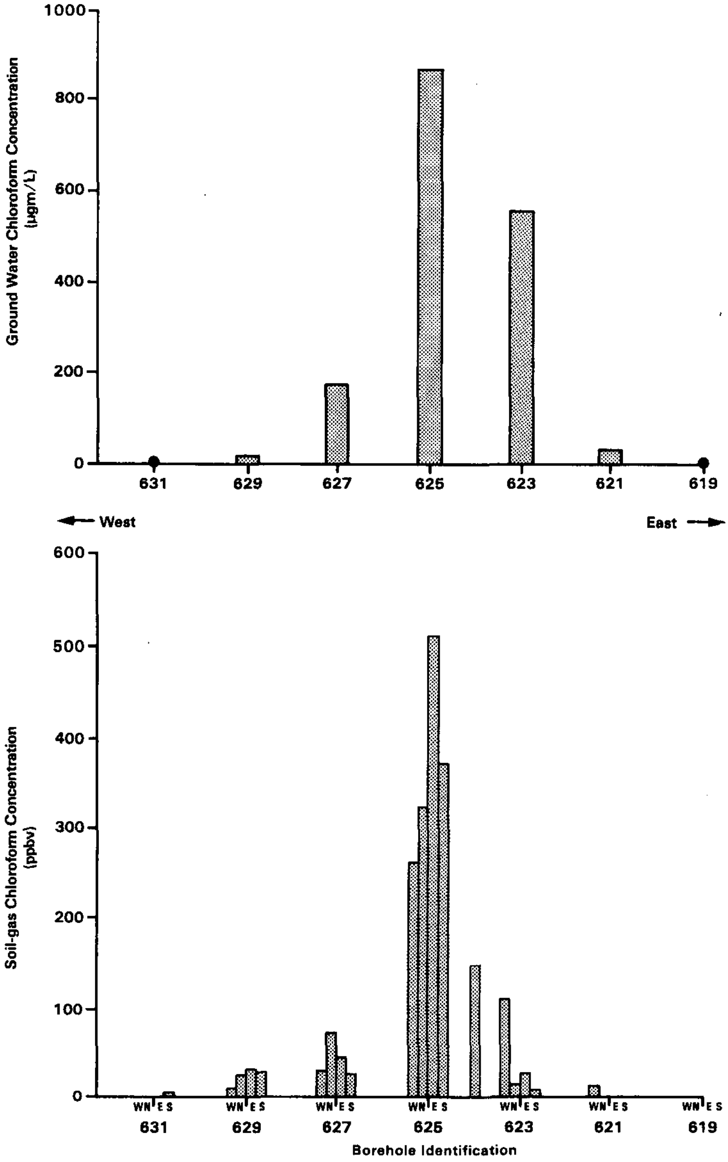

Figure 6 Soil-gas and ground-water chloroform plumes.

Table III Results of closely spaced samples at a 1.3-meter depth

Location (no.)	Chloroform concentration (ppbv)			
	Syringe 1	Syringe 2	Syringe 3	Mean (SD)
627, 20′E, 3′S	54	54	57	55 (2)
627, 23′E, 3′S	166	161	155	161 (6)
627, 23′E	119	119	99	112 (12)
627, 20′E	—	—	—	bad sample
627, 20′E, 3′N	171	171	—	171 (0)

picture of the actual variability in the soil gas because of the leakage that affected the data in Table I.

The vertical profile of the soil-gas chloroform concentration was assessed using the data in Table II. The correlation coefficients between the chloroform concentration and depth show that a linear correlation of greater than 99 percent significance exists. This finding agrees with the prediction of vertical flux of VOCs through the unsaturated zone by diffusion. The diffusion coefficient used in Eq. (1) is not the gas-phase diffusion coefficient, but must be modified for tortuosity and solubility and sorption effects in the unsaturated zone. Without knowledge of the tortuosity, porosity, irreducible water content, and other soil characteristics through the vadose zone at the site, calculation of the vertical chloroform flux from this data is not possible. Work to directly measure vertical fluxes and to passively sample VOCs is currently underway.

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