

Soil Gas Screening for Chlorinated Solvents at Three Contaminated Karst Sites in Tennessee

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Abstract

Soil gas was sampled using active sampling techniques and passive collectors at three sites in Tennessee to evaluate the effectiveness of these techniques for locating chlorinated solvent sources and flowpaths in karst aquifers. Actively collected soil gas samples were analyzed in the field with a portable gas chromatograph, and the passive soil gas collectors were analyzed in the lab with gas chromatography/mass spectrometry. Results of the sampling indicate that the effectiveness of both techniques is highly dependent on the distribution of the contaminants in the subsurface, the geomorphic and hydrogeologic characteristics of the site, and, in one case, on seasonal conditions. Both active and passive techniques identified areas of elevated subsurface chlorinated solvent concentrations at a landfill site where contamination remains concentrated in the regolith. Neither technique detected chlorinated solvents known to be moving in the bedrock at a manufacturing site characterized by thick regolith and an absence of surficial karst features. Passive soil gas sampling had varied success detecting flowpaths for chloroform in the bedrock at a train derailment site characterized by shallow regolith and abundant surficial karst features. At the train derailment site, delineation of the contaminant flowpath through passive soil gas sampling was stronger and more detailed under winter conditions than summer.

Introduction

Soil gas screening is widely used to evaluate spatial patterns of contamination of soil and water by volatile organic compounds (VOCs) (Kerfoot 1988; Marrin and Kerfoot 1988; Brock 1990; Byrnes et al. 1990; Rivett 1995). Compared with direct sampling of soil or ground water, soil gas screening can offer advantages of cost, timeliness, and better spatial coverage than might otherwise be feasible. Soil gas screening has been used for rapid preliminary assessment of the extent and distribution of ground water contamination across a broad range of environmental settings; however, this technique has not been evaluated specifically for karst aquifers.

Contamination of karst aquifers presents a difficult challenge to environmental scientists, regulators, and managers (Quinlan et al. 1992; Field 1993; Quinlan 1994). The hydraulic characteristics of karst aquifers result in ground water flow patterns that are complex, difficult to predict or model, and commonly counterintuitive (Quinlan 1994). Organic contaminants such as chlorinated solvents, which combine low viscosities with densities greater than that of water, are especially problematic in karst aquifers. Chlorinated solvents can migrate to substantial depths as nonaqueous organic liquids and subsequently act as persistent sources for dissolved-phase contamination (Wolfe et al. 1997).

Spatial patterns of contaminant distribution and movement in karst may diverge radically from those commonly encountered in other settings. A contaminant plume in an unconsol-

idated aquifer may be adequately represented as a contiguous mass, elongated down the hydraulic gradient, with concentrations decreasing and degradation products becoming more advanced with increasing distance from the source (Chapelle 1993). In karst settings, subsurface contaminants commonly discharge at springs far from the contaminant source. More than one spring may discharge contaminants from the same source, even though the springs lie in different, even opposite, directions relative to the source. Or a single spring may discharge contaminants from multiple sources. Contaminant concentrations in karst springs may be relatively stable through time or may vary with seasonal conditions or in response to storms (Farmer and Williams 2001).

Where the source of the contamination is unknown or inaccessible, knowledge of the location of contaminant flowpaths is vital for remediation upgradient from the discharge point. But finding contaminant flowpaths in karst is problematic. Karst conduits are rarely simple, straight pipe-like openings. Rather, they tend to be highly varied in shape, size, and orientation (Field 1993; Quinlan 1994; Wolfe et al. 1997). Whereas dye tracing provides a proven method for establishing connections between sources and discharge points (Quinlan et al. 1992), there is no well-established technique for locating the flowpaths between the connected points.

In 1996, the U.S. Geological Survey (USGS), in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund, initiated a series of

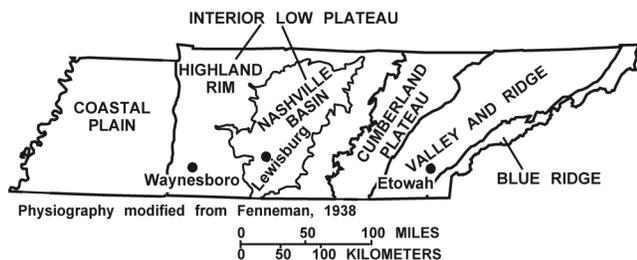


Figure 1. Location of soil gas sampling sites and physiographic provinces in Tennessee.

investigations into the problem of chlorinated solvent contamination in karst (Wolfe et al. 1997; Byl and Williams 2000). One of the investigations focused on the potential of soil gas screening methods for locating flowpaths for chlorinated solvents in karst aquifers. Active and passive soil gas sampling methods were applied at three karst sites in Tennessee where previous investigations had documented chlorinated solvent contamination. The soil gas results were then compared to existing data and conceptual models of contaminant distribution and movement. This paper presents the results of the soil gas investigation.

Site Selection and Sampling Strategy

The two major criteria used in selecting sites for this study were documentation of chlorinated solvent contamination and karst geology and geomorphology. The selected sites are in Waynesboro, Etowah, and Lewisburg, Tennessee (Figure 1). All three sites are listed with the Tennessee Superfund Program and have been the subjects of environmental investigations (unpublished reports available for examination at the Tennessee Division of Superfund). Soil or water chemistry data at each of the sites had been combined with hydrogeologic information to produce conceptual models of contaminant distribution and movement. These conceptual models had been refined through subsequent investigations and seemed to provide reasonably accurate representations of contaminant hydrology at the sites.

The karst geology and geomorphology of the three sites represent a cross section of karst settings in Tennessee and elsewhere in the unglaciated south-central United States. Bedrock lithologies include thin-bedded shaley limestone, consolidated chert, and massive, cavernous, nearly pure limestone and dolomite. Regolith thickness ranges from <1 m to >30 m. Structure varies from nearly horizontal or gently (<5°) dipping beds to steep folds with dips >40°. Surficial karst development ranges from ubiquitous and active to virtually absent. The following summaries are based on site files available for public inspection at the Tennessee Department of Environment and Conservation, Division of Superfund, in Nashville, Tennessee. Tennessee Division of Superfund (TDSF) site identification numbers are provided in the following:

The site at Waynesboro, Tennessee (TDSF site number 91-502), is an inactive municipal landfill that operated between 1970 and 1972 and received ~40,000 L of chlorinated solvents, polychlorinated biphenyls (PCBs), and other organic and inorganic waste. The landfill is situated in the western Highland Rim subsection of the Interior Low Plateau Physiographic

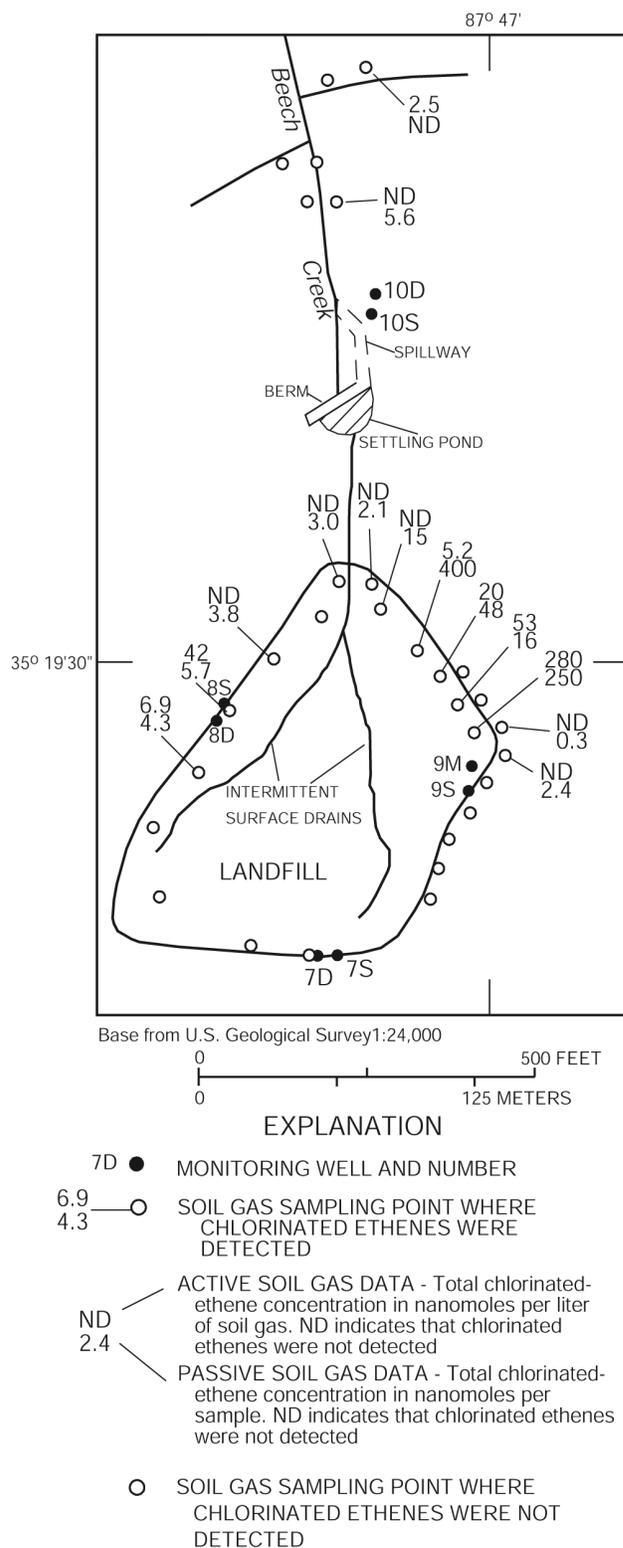


Figure 2. Location of sampling points and soil gas sampling results at the Waynesboro, Tennessee, landfill site, June 1998.

Province (Fenneman 1938). Geology and geomorphology at the site are fairly typical of the western Highland Rim. Regolith consists of residual clay, silt, and chert gravel >30 m in thickness, which overlies gently dipping to nearly horizontal impure limestone interbedded with shale and chert. Surface evidence for karst development is minimal, with fluvial dissection being a much more active process. Topographic relief at the site is ~30 m.

Table 1
Analytical Results for Selected Organic Contaminants in Well Water Samples Collected at the Waynesboro, Tennessee, Landfill Site, September 1997

Number	Screened Interval	PCE	TCE	DCE	cDCE	TCA	Aroclor 1242
7S	15.5 – 18.5	—	—	—	—	—	—
7D	47 – 53	<2	55.4	<2	<2	<2	<2
8S	5.5 – 8.5	<2	<2	<2	<2	<2	<2
8D	22.9 – 28.9	—	—	—	—	—	—
9S ^a	6.1 – 9.1	<2	284 × 10 ⁶	<2	<2	<2	182.2 × 10 ⁶
9M	11 – 14	198.1	9707	7.4	98.3	41.9	28.4
10S	13.7 – 16.7	<2	8.5	<2	<2	<2	<2
10D	34.8 – 37.8	<2	15.1	<2	<2	<2	<2

Screened interval in meters below land surface; concentrations in µg per liter
PCE = tetrachloroethene; TCE = trichloroethene; DCE = 1,1-dichloroethene
cDCE = *cis*-1,2-dichloroethene; TCA = 1,1,1-trichloroethane
<2 = below detection limit of 2 µg per liter
^a Well 9S sampled in July 1997

Table 2
Analytical Results for Selected Chlorinated Solvents in Water Samples from Blair Spring Near Etowah, Tennessee

Constituent	Month Sampled	
	7/86	12/97
Chloroethane	22	<2
1,1-Dichloroethane	62	<2
1,1-Dichloroethene	21	13
1,1,1-Trichloroethane	91	<2
Trichloroethene	13	<2

Concentrations in micrograms per liter
7/86 = July 1986; 12/97 = December 1997
<2 = below detection limit of 2 µg/L

A network of monitoring wells established in 1997 (Figure 2) revealed the presence in ground water of tetrachloroethene (PCE), trichloroethene (TCE) and several of its degradation products, and the PCB Aroclor 1242. The highest concentrations and greatest number of contaminants were noted near the eastern boundary of the landfill. Columns of free-product TCE and the PCB Aroclor 1242 were found in well 9S, and elevated concentrations of these and other contaminants were noted in well 9M (Table 1). Monitoring results from well 9M indicate some contaminant movement into the bedrock. However, the much higher contaminant concentrations in well 9S and subsequent site investigations suggest that the regolith thickness and numerous clay-rich or cherty confining layers have kept the bulk of the contaminant mass in the regolith.

Because there is no indication of a discrete conduit flow-path routing contaminants away from the site, we adopted a conventional soil gas sampling strategy for this study. Thirty points were sampled for soil gas along the periphery of the site and along the head of a nearby stream that drains the site (Figure 2). The distance between adjacent points was 30.5 m along most of the site periphery and 15.2 m along the eastern boundary of the landfill. A double line of points was established

in the vicinity of wells 9S and 9M (Figure 2). We expected the soil gas results to reflect the results of water-quality monitoring and indicate highest contaminant levels near the eastern landfill boundary.

The site near Etowah, Tennessee (TDSF site number 54-505), is a manufacturing plant in the Valley and Ridge Physiographic Province (Fenneman 1938). Some 15 to 30 m of residual clay, sand, and gravel overlie steeply folded (dips of 40° and greater), massive, cavernous dolomite. Between 1965 and 1972, waste finishing oils and solvents were burned in an open pit. Burning ceased in 1972, but disposal of organic wastes in the pit continued until 1977. The pit was subsequently excavated and the contaminated soil treated. The total volume of organic wastes disposed of at the site is poorly documented, with estimates ranging from 4000 to 400,000 L (Wolfe et al. 1997); a similar degree of uncertainty exists in estimates of the volume of excavated and treated soil.

Excavation appears to have removed most of the contaminants, which were concentrated in the thick, clay-rich regolith; however, an undetermined volume of contaminants remains in the cavernous bedrock. Water-quality sampling in 1986 revealed dissolved chlorinated solvents in the discharge of Blair Spring, ~400 m southwest of the excavated trench (Table 2; Figure 3). Chlorinated solvent concentrations in samples from monitoring wells north, northeast, and southeast of the trench were below detection limits or notably lower than concentrations found in Blair Spring. Water samples from monitoring well G5, drilled between the trench and Blair Spring (Figure 3) in 1988, contained 1,1-dichloroethane at a concentration 0.040 mg/L, similar to concentrations found in Blair Spring (Roberson 2000).

Available water-quality data suggest a flowpath of dissolved chlorinated solvents from the excavated area to Blair Spring that passes through the vicinity of monitoring well G5 (Figure 3). We designed the soil gas sampling strategy at this site to maximize the likelihood of detecting chlorinated solvent vapors along the probable contaminant flowpath. Twenty-one soil gas sampling points were established, arrayed in a staggered double line between monitoring well G5 and Blair Spring (Figure 3).

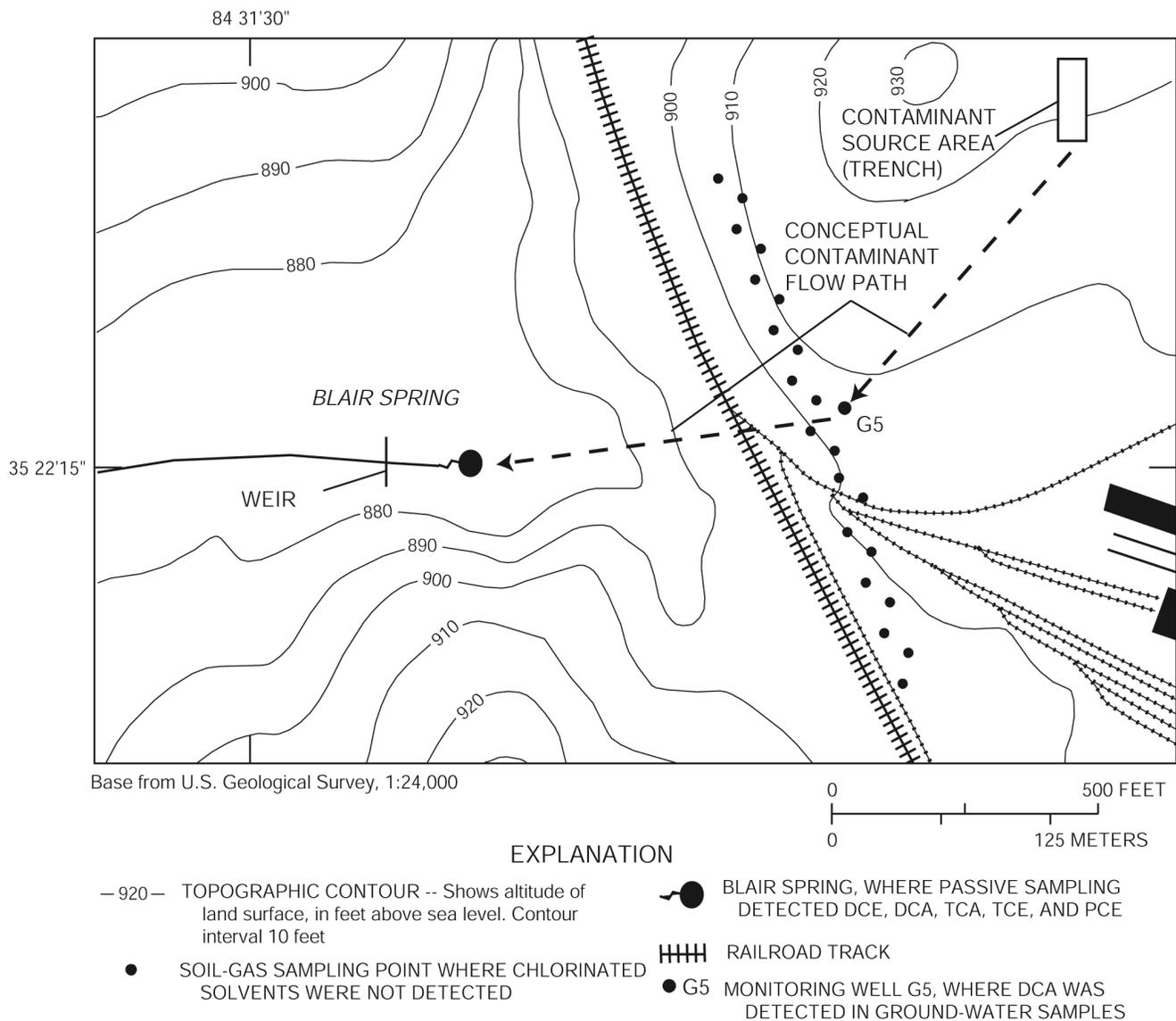


Figure 3. Locations of sampling points and soil gas sampling results at the Etowah, Tennessee, manufacturing site, June and July 1998.

The site at Lewisburg, Tennessee (TDSF site 59-502), is the location of a train derailment in 1990 where ~57,000 L of chloroform and 15,000 L of styrene were spilled into a sink-hole plain. The site is located in the Nashville Basin subsection of the Interior Low Plateau Physiographic Province (Fenneman 1938). Major geologic and geomorphic characteristics include shallow (<1 m) regolith, gently dipping strata, and an abundance of karst features—notably sinkholes, cave streams, and regolith-filled, vertical, solution-enlarged joints (cutters). Ground water flow is concentrated in cave streams developed at contacts between units of pure, massive limestone and thin-bedded, shaley confining units (Crawford and Ulmer 1994; Farmer and Hollyday 1999).

Within a few days after the spill, contaminant discharge was noted at Wilson Spring, ~650 m from the derailment (Figure 4). The hydraulic connection between the spill area and Wilson Spring was confirmed by a dye trace (Crawford and Ulmer 1994). Much of the styrene volatilized or flushed through the karst system during the first few months after the spill, and by 1994, >15,000 L of chloroform had been recovered through 16 recovery wells and excavation of a collapsed

cave (Crawford and Ulmer 1994). A substantial volume of chloroform, however, migrated downward into inaccessible parts of the karst bedrock and continues to provide a source for dissolved contamination discharging at Wilson Spring. In the summer of 1999, chloroform concentrations in Wilson Spring were ~1 mg/L (Blair 2000).

We designed a sampling strategy at the Lewisburg site similar to that at Etowah, with two lines of sampling points aligned across the most probable flowpath between the contaminant source area and the discharge point (Figure 4). One of the lines consisted of 11 points spaced 30 m apart. A second line of nine points was established along a series of sinkholes located ~50 m to the southeast of and nearly parallel to the first line of sample points (Figure 4). Eleven additional points were sampled at this site around the derailment site (source area), at Wilson Spring (main discharge point), and various sinkholes.

Materials and Methods

Active and passive soil gas sampling methods were employed in this study. Active soil gas sampling followed procedures described by Brock (1990). At each sampling point, a hole with a diameter of 1.27 cm was driven to a depth of 0.8 to 1 m. A stainless-steel probe with a diameter of 0.63 cm was inserted into the hole and sealed at land surface with modeling clay. Soil gas was withdrawn using a peristaltic or hand pump at a rate of ~80 mL/min for three minutes to purge the hole of approximately two volumes of ambient air and to establish equilibrium between the probe interior and the soil atmosphere. Using a glass syringe, soil gas samples were withdrawn from the latex tubing that connected the probe to the pump. The samples were injected into a field gas chromatograph equipped with an isothermal capillary column and a photoionization detector.

The gas chromatograph was calibrated using samples collected from the headspace in 40 mL vials containing 20 mL of VOC-free water spiked with known concentrations of seven target compounds. Spike solutions were added to the VOC-free water in capped VOC vials using gas-tight syringes. The vials were shaken for ~30 seconds and then allowed to stand for several minutes before 0.200 mL of headspace was removed with a gas-tight syringe and injected into the gas chromatograph. Headspace concentrations in vials were estimated using the known aqueous concentrations in the vials and nondimensional Henry's law constants, assuming equilibrium between aqueous and headspace concentrations and a sample temperature of 77°F (25°C). Standards were analyzed at the beginning and end of each day and after every 10 samples. An additional instrument blank was analyzed at the start of each day, and equipment blanks were run throughout the field sampling. The blanks indicated no contamination of the equipment.

Passive soil gas sampling in this study used GORE-SORBER® modules (W.L. Gore and Associates). The modules consist of a small mass of hydrophobic sorbent enclosed in a vapor-permeable membrane that is impermeable to liquid water. We placed the modules at the bottoms of the 1.27 cm diameter holes used for the active soil gas sampling and sealed the hole with an appropriately sized cork. Recommended deployment time is two weeks but longer if heavy rains occur that might dilute aqueous concentrations or interfere with the movement of contaminant vapors.

Exposure times in this study were 19 to 22 days for the initial deployment at all three sites in June and July 1998, and 30 days for a second deployment at the Lewisburg site in January and February 1999. Upon removal from the ground, the modules were sealed in glass vials and shipped to the vendor, where the sorbed contaminants were thermally desorbed and analyzed for selected VOCs (Table 3) with a gas chromatograph and mass spectrophotometer.

Seven trip blanks, each consisting of a passive soil gas collector in a standard vial, were used in this study. The trip blanks accompanied the deployed collectors to the field and were returned to the lab in the same shipment as the collectors recovered in the field. None of the seven trip blanks indicated accidental contamination.

Results and Discussion

Active and passive soil gas sampling yielded similar results at the Waynesboro landfill site. The overall spatial pattern of chlorinated ethene detection can be shown by converting analytical results from the two methods to the molar equivalents of their respective units, summing the results for each method at each point, and plotting the summed values on a site map (Figure 2).

In general, the soil gas results are consistent with results of water-quality monitoring at the site. Most of the sampling points where both techniques detected chlorinated ethenes are along the northeast boundary of the landfill (Figure 2), where the highest concentrations of ground water contaminants have been detected. Both active and passive soil gas sampling detected the highest chlorinated ethene concentrations (280 nmol/L soil gas and 250 nmol sorbed, respectively) at a sampling point directly downgradient (north) of wells 9S and 9M (Figure 2), where free product or high concentrations of chlorinated ethenes were previously detected in ground water samples (Table 1). Concentrations of chlorinated ethenes in soil gas decreased with distance downgradient from wells 9S and 9M (Figure 2). Chlorinated ethenes also were detected in both passive and active soil gas samples at two sampling points along the western side of the landfill site near well 8S (Figure 2), where previous ground water sampling had not detected these compounds (Table 1).

Passive soil gas sampling detected chlorinated ethenes at seven points where active sampling detected none (Figure 2). One factor that may be responsible for this difference is the sensitivity of the sampling methods to subsurface contaminants. The passive sampler results reflect the cumulative exposure of the samplers to VOCs in the subsurface during a two-week period, compared with the instantaneous concentration detected with active sampling. Technical evaluation of passive soil gas sampling (Tetra Tech EM 1998) indicates that passive samplers may detect lower concentrations of VOCs than active soil gas sampling because target compounds accumulate in the samplers even when concentrations are below active sampling detection limits.

The timing of sample collection may have affected the detection of chlorinated ethenes by the two methods. Active soil gas sampling was conducted on June 3, 1998, for sampling points along the periphery of the landfill and on June 8, 1998, for sampling points near the head of the small stream north of the landfill. Passive soil gas collectors were deployed at the sampling points from June 17 to July 9, 1998. Changing environmental conditions, notably rainfall and variations in atmospheric pressure, may have affected contaminant soil gas concentrations during the study period, resulting in the differences in detection by the two sampling methods.

Both active and passive soil gas sampling provided information on contaminant distribution and movement in the regolith that was consistent with ground water sampling results at the Waynesboro landfill site. Both techniques identified the area associated with the highest chlorinated ethene concentrations previously detected in ground water samples. Both techniques also were able to identify the general direction of ground water and contaminant movement in the regolith. These results indicate that soil gas screening may pro-

