

# Mapping Zones of Contaminated Ground-Water Discharge Using Creek-Bottom-Sediment Vapor Samplers, Aberdeen Proving Ground, Maryland

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## Abstract

Forty passive vapor samplers were placed in creek-bottom sediment in an area where ground water contaminated with volatile organic compounds is discharging to surface water. The vapor samplers were composed of activated carbon fused to a ferromagnetic wire in a test tube. The samplers were analyzed in a laboratory using an extranuclear quadrupole mass spectrometer. Data from the samplers reveal distributions of chloroform, tetrachloroethylene, trichloroethylene, and benzene in the bottom sediment that closely correspond to the distribution of those compounds in the adjacent ground water. Moreover, concentrations of tetrachloroethylene in bottom sediment estimated from the samplers are similar to those measured in observation wells near the shoreline. Thus, the passive vapor samplers may be used to locate and map areas where contaminated ground water is being discharged to surface water and to determine the approximate concentrations of specific contaminants in the discharging ground water.

## Introduction

Delineation of the zone through which contaminated ground water discharges to surface water can provide valuable information regarding the lateral extent of the plume of contaminated ground water. Such definition can be important to understanding the chemical processes affecting contaminant migration through the zone. For example, the tendency of organic contaminants to sorb onto organic sediment (Roy and Griffin, 1985) indicates that substantial differences in contaminant migration rates and sorption would be expected between a discharge zone in sandy bottom sediment and one in organic-rich bottom sediment. Moreover, volatile organic compounds may partition into bottom-sediment methane bubbles in areas where the con-

taminated water discharges through organic-rich sediment undergoing methanogenesis (Vroblesky, 1989).

Information regarding the geometry of ground-water discharge zones is, therefore, potentially useful. An increased understanding of discharge-zone geometry provides information on the lateral extent of ground-water contamination near the discharge zone and may lead to more efficient site remediation. The data can potentially also be used to more effectively locate observation well sites and monitor remediation progress.

One problem associated with obtaining such information for volatile organic contaminants is the difficulty involved in collecting a representative sample. Surface-water samples may not provide site-specific information on the chemistry of the discharging ground water because of lateral transport by currents and because of dilution. To obtain site-specific information, it is necessary to collect a sample of the ground water discharging through the bottom sediment. It is often difficult to collect the sample without losing part of the volatile organic compounds in the sample through volatilization. Typical methods used to obtain such samples include collecting a grab sample or a core sample and analyzing the water or the water and sediment together. Other methods involve installing piezometers in bottom sediment to collect water samples (Lee and Cherry, 1978; Welch and Lee, 1989).

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This paper introduces a simple method by which the volatile organic-contaminant content of interstitial water in bottom sediment can be readily measured at discrete points simultaneously over a broad area. The method relies on passive activated-carbon vapor samplers similar to those used in soil-gas surveys (Everett and others, 1984). To test the method, 40 such vapor samplers were installed in the bottom sediment of a creek, which is receiving discharge from a plume of contaminated ground water.

The study site (Figure 1) is in Aberdeen Proving Ground, Maryland. The site contains a landfill that was used periodically for disposal of munitions and chemical-warfare agents from World War II until at least the 1950s. The material was disposed on the ground and in trenches up to 12 ft deep. The subsurface material in the vicinity of the landfill consists of unconsolidated sand and silt, with laterally discontinuous lenses of clay. The depth to the water table ranges from about 8.2 ft near the edge of the landfill to about 1 ft near the shoreline of Watson Creek, based on synoptic measurements and data from automated water-level recorders. Borehole data and chemical analysis of ground-water samplers indicate that contaminants in the ground water are prevented from moving deeper than about 26 ft below land surface by the presence of a laterally continuous layer of clay at that depth. The shallow aquifer is recharged by rainfall infiltration.

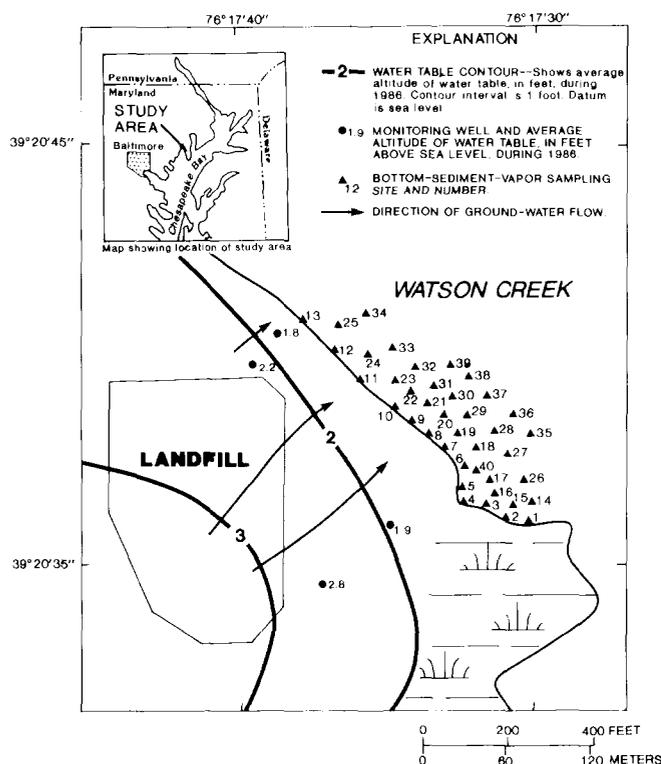
Analysis of several sets of ground-water samples collected from this site during 1986-89 indicate that the shallow ground water within the contaminated zone contains chlo-

roform; 1,1,2,2-tetrachloroethane; 1,2-dichloroethylene; trichloroethylene; tetrachloroethylene; chlorobenzene; dichlorobenzene; benzene; toluene; xylene; 6-methyl-1,3-oxathiane; 1,4-dithiane; and a variety of inorganic constituents. Ground-water movement is from the landfill north-eastward toward Watson Creek (Figure 1). The ground-water flow velocity between the landfill and the creek, based on ground-water flow modeling (Vroblesky and others, 1989) and tree-ring chemistry (Vroblesky and Yanosky, 1990), is between 130 and 330 ft per year. Ground water in the area is not pumped, so the 1986 water levels (Figure 1) and the calculated-flow velocity are representative of ground-water conditions during this investigation. Watson Creek is a pond open to tidal influences through a narrow (about four feet wide) inlet far enough from the study area so that currents within the study area are negligible. The range of tidal amplitude is less than one foot.

## Method

In this investigation, data on the distribution of volatile organic compounds in the ground water within the Watson Creek bottom sediment were obtained by placing passive vapor samplers within the bottom sediment. The samplers are glass test tubes that contain the vapor collectors. The collectors consist of a Curie-point ferromagnetic wire to which activated carbon is chemically fused. Activated carbon has a high affinity for a broad range of hydrocarbon and halogenated hydrocarbon compounds. The samplers were assembled by filling a glass test tube with an inert gas and then placing the collector wire into the tube with the absorbent end away from the opening. The glass tubes were then sealed with airtight screw-on caps that were not removed until the samplers were ready to be installed. Two activated-carbon collector wires were installed in selected containers. After the samplers were retrieved from the bottom sediments, the wires were individually analyzed as a check on the replication of the collection and analysis.

To prevent the movement of water and sediment into the tubes during installation, the tubes were enclosed in 0.001-inch (1.4-mil) thick rescalable waterproof polyethylene bags. Preliminary testing in the laboratory was done to ensure that the bags were permeable to the types of volatile organic compounds known to be present at the site. Twelve open samplers were placed in polyethylene bags, and trapped air was forced out of each bag before sealing. The samplers were adjusted and immobilized within the bags so that only a single layer of polyethylene covered the opening of the tubes. Three samplers were placed in each of four solutions of chlorinated organic compound mixtures for a period of one week, which was the same length of time that the field samplers were exposed. The temperature of the solutions was approximately the same as that in the ground water. The chlorinated organic compounds were chloroform; carbon tetrachloride; 1,1,2,2-tetrachloroethane; and tetrachloroethylene—compounds known to be present in the ground water at the study area. The solutions contained 50  $\mu\text{g}/\text{l}$ , 100  $\mu\text{g}/\text{l}$ , 500  $\mu\text{g}/\text{l}$ , and 1,000  $\mu\text{g}/\text{l}$ , respectively, of each compound. The analytical results showed that the samplers enclosed within the bags absorbed volatile organic



**Fig. 1. Map showing the location of study area, sampling sites, and average water-table contours for 1986. The water-table contours are based, in part, on wells outside of the map area.**

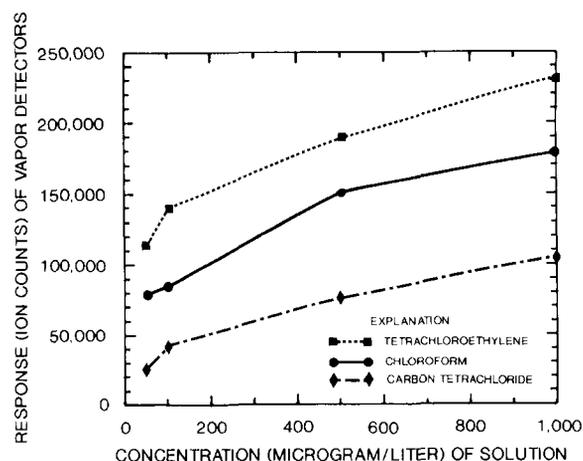
compounds at all of the test-solution concentrations of 50  $\mu\text{g}/\text{l}$  (Figure 2).

Field preparation of the sampler involved removing the cap from the tube, enclosing the tube in a polyethylene bag, and taping the bagged tube to a wooden rod with the open end of the tube facing down. The influence of the polyethylene bags was tested in the field at eight sites. The test consisted of pairing one tube in a bag with a tube not enclosed in a bag. The openings of both sampling tubes were adjacent to each other to minimize environmental variability.

Forty samplers were installed in saturated creek-bottom sediment (Figure 1) during March 1989 in an area where ground water contaminated with volatile organic constituents was thought to be discharging to surface water. In soft sediment, the rod was used to push the sampler into the sediment to a depth of about 6 to 14 in. In hard sediment, a hole was excavated using a shovel, and the sampler was buried to a depth of about 6 in. The samplers were installed in a grid pattern at 50-ft intervals in the central part of the area and at 100-ft intervals near the northwestern and southeastern edges of the grid. Samplers were installed at more closely spaced, irregular intervals in the area of suspected maximum contaminant discharge. The grid extended approximately 810 ft parallel to the shoreline and approximately 200 ft offshore. The samplers were allowed to remain undisturbed for one week before they were retrieved. The caps were installed on the tubes immediately after each sampler was retrieved. The samplers were taken to the PETREX laboratory of Northeast Research Institute, a commercial supplier of the samplers, where the sorbed constituents were removed from the activated carbon and analyzed using a mass spectrometer equipped with a Curie-point pyrolysis/thermal desorption inlet. (Use of the firm name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.)

The original intent of this investigation was to determine whether passive vapor samplers could be used to determine the presence or absence of specific organic compounds discharging from ground water into surface water. Therefore, the concentrations of the compounds detected by the vapor collectors are reported in terms of relative concentrations (flux values). However, as a test of whether quantification is possible, a concentration-response curve (Figure 2) was used to convert the flux values of tetrachloroethylene detected by the vapor collectors in Watson Creek at sites 5, 7, 8, 9, 10, 11, and 12 to concentrations of tetrachloroethylene in water. The resulting concentrations were compared to concentration of tetrachloroethylene found in the ground water of nearby monitoring wells located onshore.

The response curve (Figure 2) was derived using data from the preliminary test of the samplers in the laboratory. The samplers used to derive the response curve were analyzed at a higher electron multiplier gain than were the field samplers, resulting in a doubling of the sensitivity. Thus, the concentrations for tetrachloroethylene determined from the field-sampler flux values were divided by two to correct for the difference in multiplier gain.



**Fig. 2. Graph showing response of samplers enclosed in polyethylene bags to various concentrations of tetrachloroethylene, chloroform, and carbon tetrachloride in standard solutions.**

Ground-water samples were collected from existing onsite wells within a three-hour period during the week that the bottom-sediment vapor collectors were in place. Samples were obtained using teflon bailers after removing three casing volumes of water from the wells. A field check of the purging technique showed that the quantity of water removed was adequate to provide a representative sample of the ground water (Oliveros and others, 1988). A water sample from Watson Creek was obtained within the network of vapor samplers at the same time the wells were being sampled. The ground- and surface-water samples were chilled and delivered to a commercial laboratory for analysis of volatile organic compounds the same day they were collected.

## Results

The bottom-sediment vapor samplers detected the presence of a broad range of volatile organic constituents also present in the ground water collected from nearby onshore observation wells. The amount of compound extracted from the activated carbon ranged from undetectable to greater than 200,000 ion counts for most compounds. The distributions of selected organic compounds in ground water and bottom sediment are shown in Figures 3 to 6. The concentrations of tetrachloroethylene in the Watson Creek bottom sediment and interstitial water in the ground-water discharge zone at the shoreline, determined from the ion-count response of the vapor collectors, were 350  $\mu\text{g}/\text{l}$  (site 5), 550  $\mu\text{g}/\text{l}$  (site 7), 475  $\mu\text{g}/\text{l}$  (site 8), 510  $\mu\text{g}/\text{l}$  (site 9), 500  $\mu\text{g}/\text{l}$  (site 10), 440  $\mu\text{g}/\text{l}$  (site 11), and 310  $\mu\text{g}/\text{l}$  (site 12).

Analysis of the samplers from field sites where two samplers were taped together (one bagged and one unbagged) indicated variations in the relative response. For most compounds, the samplers enclosed in the bags usually collected greater concentrations of the compound than the ones not enclosed in a bag (Table 1). Chlorobenzene was consistently more concentrated in the samplers enclosed in the polyethylene bags.

**Table 1. Ratios of Flux Values of Volatile Organic Compounds Detected in Samplers Inside Bags to Flux Values Detected in Samplers Not Enclosed in Bags**

Sampler number	Ratios of ion counts detected in bagged versus unbagged samplers							
	BNZ	CF	TOLN	DCE	XYL	CBNZ	TCE	PCE
6	3.6	ND	>1	3.5	ND	12.0	1.4	4.1
7	1.3	0.9	1.0	0.8	1.0	1.0	0.4	1.6
8	2.3	7.2	ND	1.9	ND	5.5	1.4	2.5
9	1.9	0.6	1.0	1.0	3.7	1.1	1.0	1.1
10	2.6	1.0	3.2	2.9	>1	12.4	1.4	6.2
11	0.9	1.6	1.0	2.0	3.2	1.8	0.9	1.6
12	ND	1.0	ND	1.1	1.7	>1	1.1	1.0
16	0.9	ND	3.5	<1	ND	ND	0.2	<1

[For analyses in which the sampler within the bag detected flux values of a particular compound and the corresponding sampler without a bag did not, the symbol >1 is used. In the reverse situation, the symbol <1 is used. ND means not detected in either sampler.]

[BNZ = benzene; CF = chloroform; TOLN = toluene; DCE = dichloroethylene; XYL = xylene; CBNZ = chlorobenzene; TCE = trichloroethylene; and PCE = tetrachloroethylene.]

Comparison of duplicate samples (two collectors in a single tube) indicated that replication was substantially better at higher flux values. At flux values of less than 4,000 ion counts, the difference ranged from 23 to 55 percent. At flux values greater than 4,000 ion counts, the difference ranged from 3.8 percent to 17.9 percent. An exception to this trend occurred for toluene, which had 37.8 percent difference at flux values of about 34,000 ion counts and 18.9 percent difference at 53,000 ion counts. The flux values used to define areas of probable contaminated ground-water discharge for chloroform, tetrachloroethylene, trichloroethylene, and benzene were greater than 100,000 ion counts; thus, the replication is considered adequate for order-of-magnitude contouring.

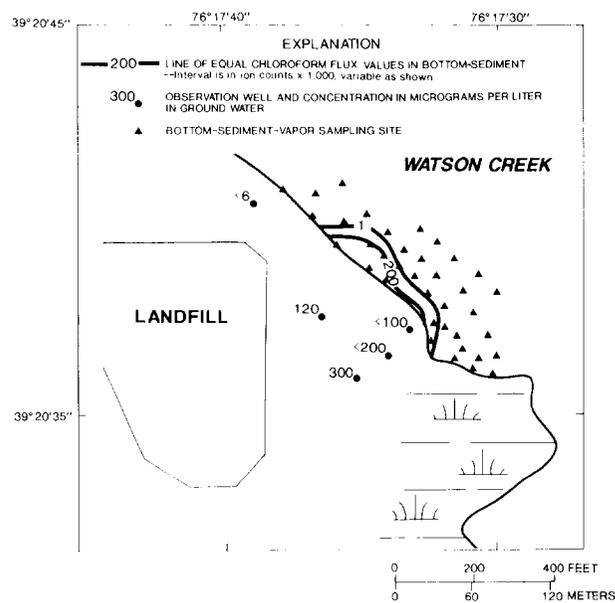
The water sample from Watson Creek, collected from within the network of vapor samplers, showed the presence of organic compounds detected by the vapor samplers. Specific constituents included chloroform (7.6 µg/l), tetrachloroethylene (4.2 µg/l), benzene (3.9 µg/l), and trichloroethylene (6.5 µg/l).

## Discussion and Conclusions

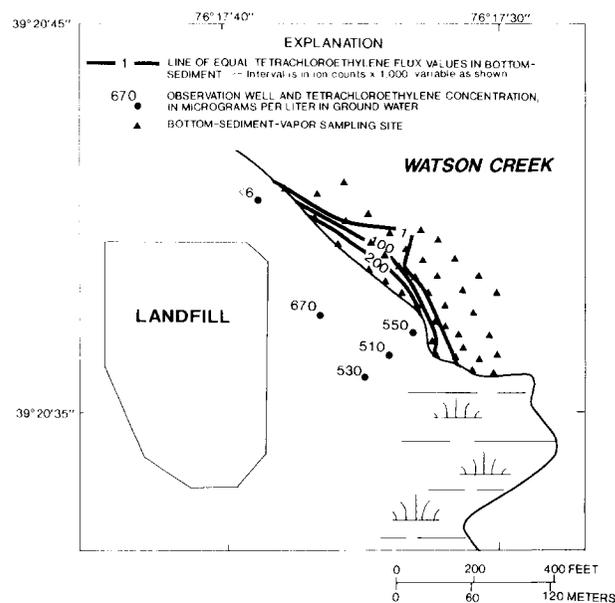
The bottom-sediment vapor samplers were capable of detecting a variety of volatile compounds present at the site. The distribution of organic constituents detected by the samplers in Watson Creek bottom sediment agrees with the distribution of the compounds in ground water. The areas where chloroform (Figure 3) and tetrachloroethylene (Figure 4) are found in the bottom sediment are hydraulically downgradient from the area where the compounds are found in the ground water. Benzene (Figure 5) also is concentrated in the bottom sediment near an area of known benzene contamination in the ground water.

The distance northwestward along the shoreline where contaminants were detected in the bottom sediment appears to be related to the distribution of the contaminants in the

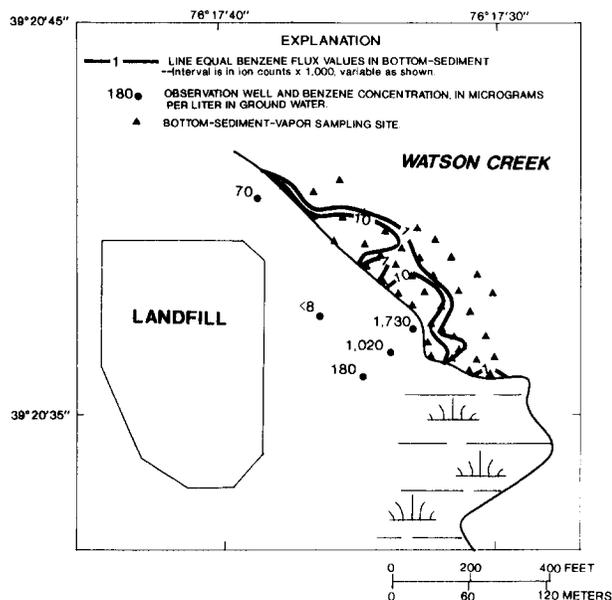
ground water. Chloroform, tetrachloroethylene, and trichloroethylene were not detectable in the ground water north of the landfill. Correspondingly, chloroform and trichloroethylene were not detected in the adjacent bottom sediment at site 13; and tetrachloroethylene was present at 2,000 ion counts, which was negligible compared to the maximum detected flux value of 245,000 ion counts. In contrast, benzene was present in the ground water north of the landfill (Figure 5) and in the adjacent bottom sediment at site 13 at flux values within 96 percent of the maximum observed value.



**Fig. 3. Map showing distribution of chloroform in bottom sediment and in ground water, March 1989.**

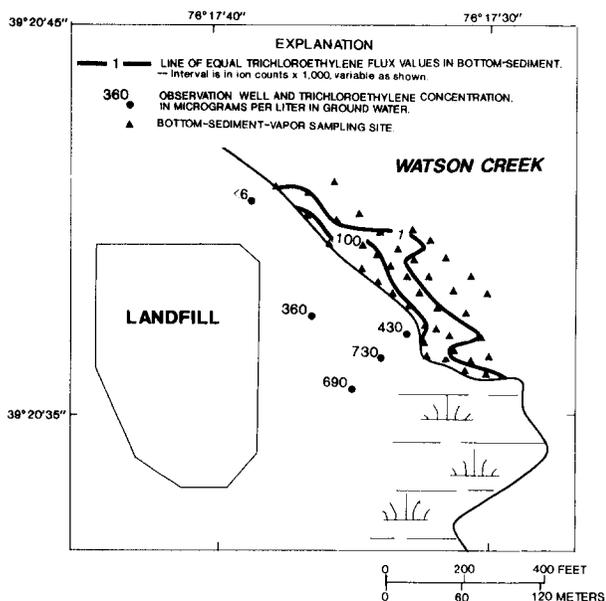


**Fig. 4. Map showing distribution of tetrachloroethylene in bottom sediment and in ground water, March 1989.**



**Fig. 5. Map showing distribution of benzene in bottom sediment and in ground water, March 1989.**

Similar conclusions can be drawn concerning the distance southeastward along the shoreline where contaminants were detected in the bottom sediment. The main body of trichloroethylene (Figure 6) in the ground water appears to be offset slightly farther southeastward than for chloroform (Figure 3) or tetrachloroethylene (Figure 4). In a like manner, the area where trichloroethylene was detected in the bottom sediment also extends farther southeastward along the shoreline (Figure 6) than for chloroform (Figure 3) or tetrachloroethylene (Figure 4).



**Fig. 6. Map showing distribution of trichloroethylene in bottom sediment and in ground water, March 1989.**

The close correlation of volatile organic contaminants in Watson Creek bottom sediment and interstitial water with the same contaminants in the upgradient ground water strongly suggests that the contaminants detected by the samplers in the bottom sediment are derived from ground-water discharge. The presence of the same contaminants in the surface water of Watson Creek further substantiates the hypothesis. Thus, it appears that the distribution of the bottom-sediment volatile contaminants can be used to delineate the areal extent of the main body of contaminated ground water being discharged.

With such knowledge, several generalizations can be made regarding the distribution of subsurface contamination. The discharge areas of tetrachloroethylene, trichloroethylene, and benzene are somewhat broader than that for chloroform, perhaps reflecting a difference in transport characteristics or a difference in distribution within the landfill. The main body of ground-water contamination appears to be about 650 ft wide near the discharge area. The chloroform plume appears to be centrally located within the main body of ground-water contamination and to be approximately 400 ft wide near the discharge area. The discharge area of contaminated ground water extends about 60 to 120 ft from the shoreline into Watson Creek.

The concentrations of tetrachloroethylene in ground water determined from the response of the samplers along the shoreline were similar to concentrations of tetrachloroethylene found in the ground water from observation wells. The nearest monitoring well to the shoreline contained 550  $\mu\text{g}/\text{l}$  of tetrachloroethylene (Figure 4), which was the same concentration estimated for sampler 7, only 60 ft from the well. Similar concentrations (440 to 510  $\mu\text{g}/\text{l}$ ) were estimated for the remaining samplers along the shoreline within the main area of contamination. Lower concentrations were found in the samplers at the southeastern (site 5, 350  $\mu\text{g}/\text{l}$ ) and northwestern (site 12, 310  $\mu\text{g}/\text{l}$ ) edges of the contaminated area. Quantification of the vapor-sampler data for tetrachloroethylene demonstrates that the response of the detectors can be used to estimate the approximate concentrations of specific compounds in the discharging ground water at the sampling site.

Comparison of the results from samplers enclosed in polyethylene bags and those not enclosed in bags showed that, in most cases, higher concentrations of the organic compounds were found in the bagged samplers than in the unbagged samplers (Table 1). In no case did all of the compounds perform similarly for a particular pair of samplers; therefore, significant variability due to difference in the collection wires is unlikely. The results imply that the differences between the response of samplers inside bags and those not inside bags are at least partly related to the bag. Thus, in general, enclosing the samplers in the bags appears to enhance the detection potential of the samplers for the compounds examined during this study.

The method presented here provides a rapid and easy means of locating areas where contaminated ground water is being discharged to surface water. Moreover, it provides information on the areal extent and concentrations of ground-water contaminants in the immediate vicinity of the

discharge zone. Additional potential uses for such data would be to aid in optimal siting of observation wells and in monitoring the progress of site remediation.

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