

# Guidance on the Use of Passive-Vapor-Diffusion Samplers to Detect Volatile Organic Compounds in Ground-Water-Discharge Areas, and Example Applications in New England

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## Abstract

Polyethylene-membrane passive-vapor-diffusion samplers, or PVD samplers, have been shown to be an effective and economical reconnaissance tool for detecting and identifying volatile organic compounds (VOCs) in bottom sediments of surface-water bodies in areas of ground-water discharge. The PVD samplers consist of an empty glass vial enclosed in two layers of polyethylene membrane tubing. When samplers are placed in contaminated sediments, the air in the vial equilibrates with VOCs in pore water. Analysis of the vapor indicates the presence or absence of VOCs and the likely magnitude of concentrations in pore water.

Examples of applications at nine hazardous-waste sites in New England demonstrate the utility of PVD samplers in a variety of hydrologic settings, including rivers, streams, ponds, wetlands, and coastal shorelines. Results of PVD sampling at these sites have confirmed the presence and refined the extent of VOC-contaminated ground-water-discharge areas where contaminated ground water is known, and identified areas of VOC-contaminated ground-water discharge where ground-water contamination was previously unknown. The principal VOCs detected were chlorinated and petroleum hydrocarbons. Vapor

concentrations in samplers range from not detected to more than 1,000,000 parts per billion by volume. These results provided insights about contaminant distributions and ground-water-flow patterns in discharge areas, and have guided the design of focused characterization activities.

## INTRODUCTION

Passive-vapor-diffusion (PVD) samplers are designed and primarily used as a reconnaissance tool to detect and identify volatile organic compound (VOC) contaminated ground water discharging into surface-waters bodies at and near hazardous-waste sites (Vroblesky and others, 1996; Vroblesky and Robertson, 1996; Vroblesky and Hyde, 1997). Determining the location of discharging contaminated ground water is important for plume mapping, evaluating risk potential to human health and the environment, and designing focused site-characterization and monitoring activities. Applications of PVD samplers at and near nine hazardous-waste sites in New England demonstrated the samplers' effectiveness in detecting and delineating VOCs in a variety of hydrologic settings including rivers, streams, ponds, wetlands, and coastal shorelines. The PVD samplers also have been used successfully as passive-soil-gas samplers in unsaturated zones to map ground-water contamination (Vroblesky and others, 1992).

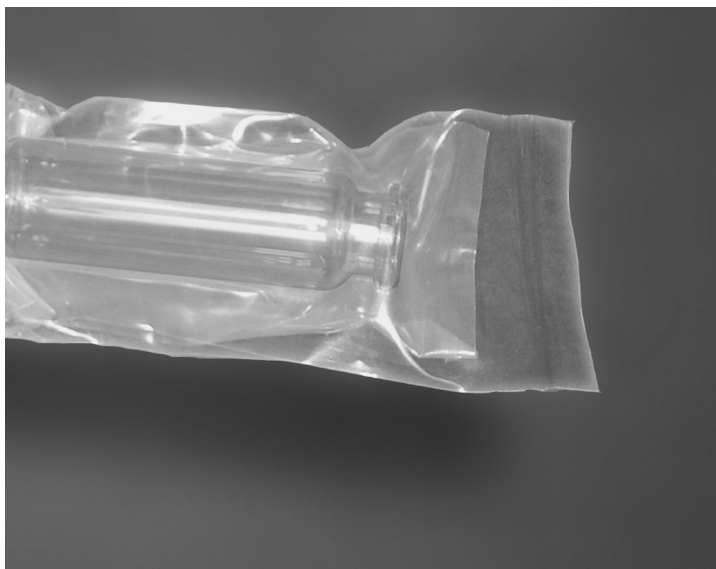
The PVD samplers, developed by the U.S. Geological Survey (USGS) (Vroblesky and others, 1996) consist of an empty, uncapped, glass vial enclosed in two layers of low-density polyethylene membrane tubing (fig. 1) that are permeable to many VOCs of environmental interest, such as petroleum and chlorinated compounds (table 1), but not permeable to water (Vroblesky and others, 1991). When samplers are buried in VOC-contaminated pore water in the bottom sediment of surface-water bodies, an equilibrium begins to develop between VOC concentrations in water and the air in the vial. Equilibrium times, which are dependent on many factors such as hydraulic conductivity of the sediment and temperature of the pore water, generally range from 1 to 3 weeks. During sampler recovery the outer tubing, which is used to prevent sediment, which may be contaminated, from coming into contact with the inner tubing and the opened vial, is removed. A cap is then screwed on to the vial, thereby securing the inner tubing tight against the vial opening to prevent loss of VOCs vapor in equilibrium with water concentrations at the sampler deployment point.

Concentrations of VOCs detected in air in a sampler indicate vapor-phase concentrations in sediment-pore water. The relative concentration partitioning into the air and water varies among VOCs and is described by Henry's law constant for the particular VOC. A compound with a relatively high vapor pressure and

low solubility will tend to become more concentrated in the vapor phase than in the water phase. Several of VOCs with lower vapor pressure tend to be more concentrated in the water phase, but still maintain a vapor-phase signature. Because the low-density polyethylene membrane tubing is not a major barrier to VOC diffusion over time, PVD samplers provide a vapor phase into which VOCs can diffuse from the aqueous phase. The VOCs in water near PVD samplers diffuse through the tubing into the air within the glass vial. Vapor-phase concentrations in the vial are typically reported in parts per billion by volume (ppb v).

In theory, these vapor concentrations can be converted to concentrations in water through Henry's Law and Henry's Law constants for specific chemicals. In practice, however, uncertainties about Henry's Law constants, pore-water temperatures, equilibration times for various types of sediments, and analytical precision, limit this application. If concentrations in water are needed, however, a modification of this approach, which is a single layer, water-filled membrane tubing sampler, will provide aqueous-phase VOC concentrations in a ground-water-discharge area (Vroblesky and others, 1999).

The ease of constructing, deploying, and retrieving PVD samplers renders this method well-suited for reconnaissance of VOC plumes discharging to surface waters. A large amount of spatial data can be collected in a short period with PVD samplers. For example,



**Figure 1.** Glass vial in two layers of polyethylene tubing.

**Table 1.** Volatile organic compounds detected under field conditions with passive-vapor-diffusion samplers at contaminated ground-water-discharge areas in New England and South Carolina and the range of minimum reporting limits for these compounds at the nine New England sites

Volatile organic compound	Range of minimum reporting limits, in parts per billion by volume
Benzene .....	6 to 25
Ethylbenzene .....	40 to 90
<i>meta/para</i> -xylene.....	40 to 90
<i>ortho</i> -xylene .....	60 to 100
Toluene .....	20 to 40
Tetrachloroethene .....	5 to 25
Trichloroethene.....	5 to 25
Chlorobenzene.....	40 to 70
<i>cis</i> -1,2-Dichloroethene .....	25 (a target compound at only one site)
1,1,1-Trichloroethane .....	8 (a target compound at only one site)
methyl <i>tert</i> butyl ether .....	Not a target compound at the New England sites

from experience with PVD samplers in New England, construction of samplers, deployment of samplers in streambed sediments at 50 ft intervals along a 2,000 ft reach, retrieval of samplers after equilibration is reached (about two weeks), and on-site chemical analysis, may be accomplished in a total of three days. Results from this sampling may guide the placement of well points in shallow waters and monitoring wells or the selection of sediment-sampling locations where VOCs in water and sediments are detected. Once vapor concentrations of VOCs are detected with the PVD samplers, then water samples can be collected with other methods.

This report describes advantages and limitations of PVD samplers, offers guidance on the use of PVD samplers, and summarizes results from nine sites in New England where PVD samplers have provided useful information about VOC plumes in ground water. The report is designed mainly for personnel who are designing characterization studies that may include the use of PVD samplers and for personnel who will be constructing and installing the samplers. This report was prepared by the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency (USEPA) Technical Innovation Office (TIO), and USEPA's Region I.

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## ADVANTAGES AND LIMITATIONS OF PASSIVE-VAPOR-DIFFUSION SAMPLERS

Advantages and limitations are presented here, before the details of PVD-sampler assembly, deployment, and recovery are described, to ensure that project design personnel who may be considering or are planning to use PVD samplers understand capabilities of this method. These advantages and limitations may also be useful for technicians who assemble, deploy, and recover these samplers.

### Advantages

1. The PVD method takes advantage of converging ground-water-flow lines and upward hydraulic gradients at ground-water-discharge areas to bring the target contaminants into contact with the samplers.
2. The method has been effective in delineating VOC-contamination-discharge areas beneath surface-water bodies.
3. PVD samplers can be areally and vertically distributed to gain information on contaminant-discharge heterogeneity.

4. The samplers are inexpensive. A low-cost sampler can be made from grocery-store sandwich bags and empty glass vials.
5. In many situations, the samplers are easy to deploy and recover.
6. Sampler recovery is rapid. The data can be analyzed on site with field gas chromatography, or the capped samples can be stored for later analysis. A stability test with 40-mL volatile organic analysis (VOA) vials showed that VOC concentrations in unpunctured, sealed vials did not substantially decrease in over 121 hours (Vroblesky and others, 1996).
7. Because the pore size of low density polyethylene tubing is about 10 angstroms or less, sediment does not pass through the membrane into the bag. The outer bag, therefore, effectively prevents contaminated soil from contacting the inner bag.
8. A variation of a PVD sampler can be used as a soil-gas sampler in unsaturated sediment to delineate shallow VOC plumes (Vroblesky and others, 1992). Vapor-filled polyethylene samplers also can be used with a sorbent to allow the samplers to accumulate VOC concentrations over the deployment period (Vroblesky and others, 1991). Still another variation consists of water-filled, low-density polyethylene tubing sampler deployed in bottom sediments at ground-water-discharge areas to yield aqueous concentrations of VOCs (Vroblesky and others, 1999).

## Limitations

1. Because the change in VOC concentrations within PVD samplers in response to changes in ambient concentrations typically takes 24 hours or longer, VOC concentrations within the samplers represent an integration of concentrations from the most recent part of the deployment period until the samplers attain equilibrium. The equilibration time depends on several factors, including the temperature and the rate of water movement past the sampler. Under laboratory conditions, equilibration times in static water ranged from about 24 hours at 21°C to about 102 hours at 10°C. Under field conditions, equilibration times can range from as little as 12 hours in a rapidly discharging unconsolidated sand, to three weeks or more in colder, less permeable sediment. Suggested PVD deployment periods are typically two weeks, but may vary depending on site-specific temperature and hydraulic conditions. The required equilibration time is a disadvantage over some types of real-time sampling methods, such as extracting water from a core or pumping water from a small-diameter probe. Unlike these methods, however, the PVD samplers can provide an undisturbed sample, which minimizes the risk of short-term concentration changes from sediment disturbance and reduces the uncertainty associated with the source of water from a sample obtained from pumping.
2. The PVD samplers are appropriate only for volatile compounds.
3. Analysis of the samples requires a gas chromatograph.
4. Deployment of the samplers in shallow waters typically is a simple task; however, deployment in deep waters may require the services of SCUBA divers or other installation methods.
5. In some streams, the source of detected VOCs may not be readily determined without further work because of complexities in hydraulics and sediment heterogeneity that lead to unusual contaminant-discharge distributions. For example, in some streams of the Rocky Mountains region, where ground-water-flow direction is approximately parallel to streamflow, locations of ground-water-discharge areas can change with time. Furthermore, if the samplers are deployed in an area of VOC-contaminated bottom sediment derived from sediment transport along the stream, then the VOC concentrations in the PVD samplers may reflect contaminant concentrations in the sediment rather than in discharging ground water. Consequently, an effort should be made to ensure that the sampling location is a gaining reach.
6. The samplers must be deployed in an area where ground water is discharging to surface water to adequately reflect ground-water concentrations. In areas where the water in contact with the PVD samplers is largely infiltrated surface water, the concentrations detected by the PVD



samplers probably will represent surface-water or sediment-contaminant concentrations rather than ground-water concentrations.

7. Transient flow of ground water, such as bank storage after a flood wave or tidal cycle, may cause temporary or cyclic changes in concentrations of VOCs that could affect interpretations about the extent and concentration level of VOCs in ground water.
8. Follow-up studies that use other sampling methods are needed to determine actual concentrations of VOCs in water, if that is a goal of the study. The PVD samplers provide VOC concentrations as a gas. Because the partition between aqueous and vapor phases depends on several factors, such as temperature and pressure, which may vary from site to site and are not always known, calculations of aqueous-phase concentrations from PVD samplers should be considered estimates. An alternative approach to obtaining aqueous-phase VOC concentrations in a ground-water-discharge area is to use a water-filled, low-density polyethylene sampler as described elsewhere (Vroblesky and others, 1999).
9. Caution should be used when deploying PVD samplers in streambeds subject to rapid erosion, because the samplers may be washed away. Samplers also may be difficult to find when the surveyor flags are submerged in high flows in streams or buried beneath sediment as flows recede.

## **PART 1. GUIDANCE ON THE USE OF PASSIVE-VAPOR-DIFFUSION SAMPLERS**

*By Don A. Vroblesky*

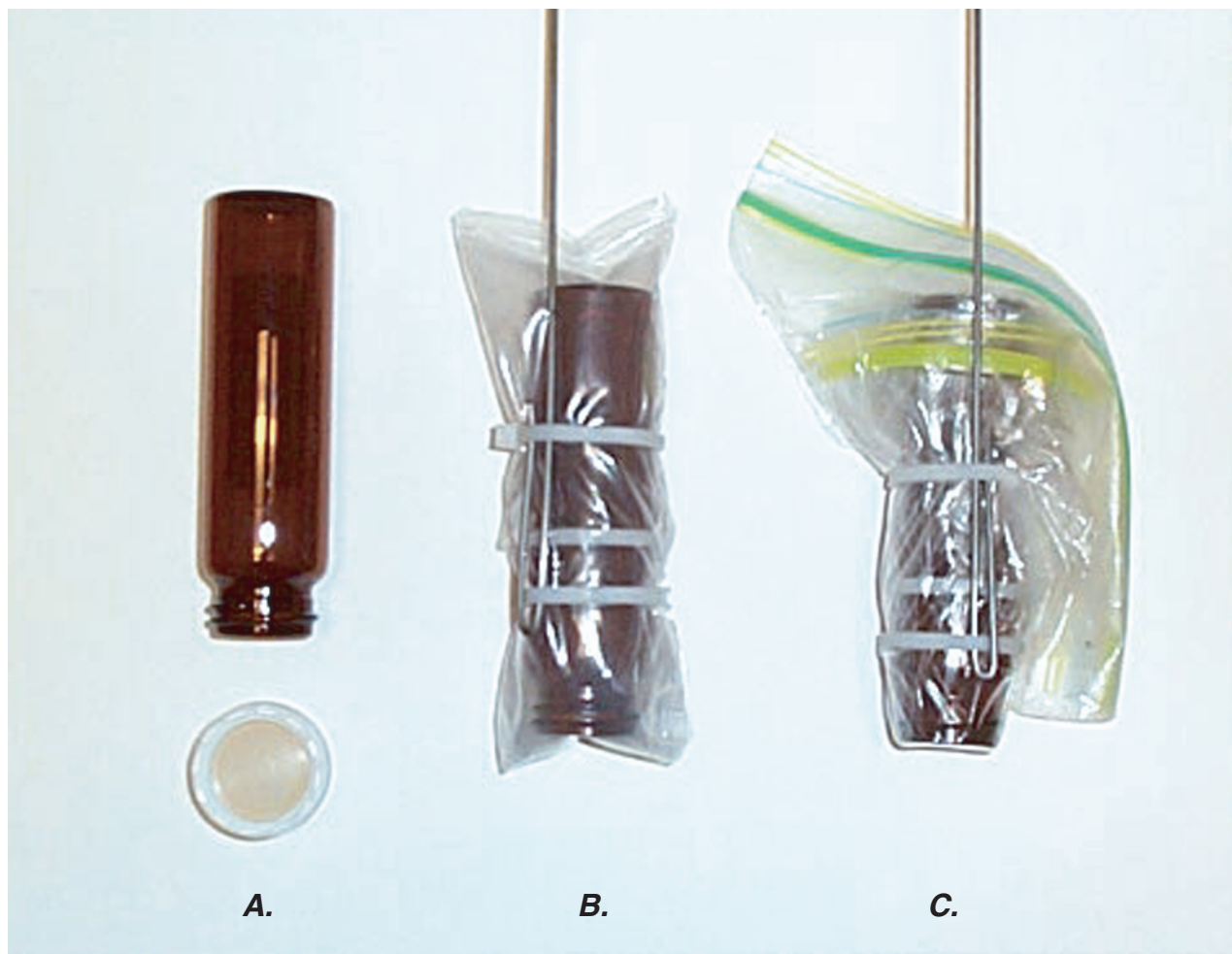
This section of the report provides guidance on PVD-sampler assembly, deployment, and recovery to detect volatile organic compounds in ground-water-discharge areas. As an aid to ensure proper use of this method and interpretation of the data collected, factors affecting PVD-sampler deployment, data interpretation, and quality control and assurance, are also discussed.

## **ASSEMBLY OF SAMPLERS**

Several approaches may be used to construct a PVD sampler. A vial may be enclosed in "lay-flat," low-density polyethylene (LDPE) tubing, flexible tubing that is laid flat and wound-up in a roll, and then heat-sealed at both ends, or the vial may be enclosed in zipper-type sealable sandwich bags (fig. 2). The vials should be glass and sealable with a septated cap. Typical vials used include 20-mL crimp-top glass vials and 40-ml volatile organic analysis (VOA) glass screw-top vials. Vials used in the studies summarized in this report are 40-mL VOA screw-top vials. When the 20-mL crimp-top glass vials are used, 2-, 3-, or 4-mil LDPE may be used for the bag material. When 40-mL VOA vials are used, 2- or 3-mil LDPE for the inner material is advised, because the cap is difficult to screw onto 4-mil LDPE. The septum for the cap should be Teflon or Teflon coated. The effort for constructing PVD samplers is approximately equivalent for the two methods. Also, the material costs differ little between methods, except for the initial purchase of a heat sealer if constructing samplers with tubing. The LDPE tubing, however, is more resilient to punctures and abrasion during placement and retrieval, and is therefore preferred to construction with sandwich bags, particularly for placement in coarse gravels.

To construct a PVD sampler from lay-flat LDPE tubing and a heat sealer, the following supplies are needed: 2-in. wide (approximately 1.5-in. diameter), 2-, 3-, or 4-mil lay-flat LDPE tubing; a glass vial, a wire surveyor flag, self-locking nylon ties, and a heat sealer. The following approach describes a typical PVD-construction sequence.

1. Cut an 8-in. length of 2-in. wide lay-flat LDPE tubing. The inner layer of tubing should be 2- or 3-mil thick when VOA vials are used and 2-, 3-, or 4-mil when crimp-top serum vials are used. For the studies summarized in this report, 40-mL VOA screw-top vials were used.
2. Heat-seal one end. The heat sealer should be adjusted to provide a uniform seal without melting through the LDPE. Multiple seals may be required with some heat sealers with less than 400 watts of impulse power.
3. Insert an uncapped empty 40-mL glass VOA vial or a 20-mL crimp-top serum vial into the tube. Store the cap in a clean environment away from the PVD samplers until the sample is recovered.



**Figure 2.** Passive-vapor-diffusion samplers with (A) vial and screw cap, (B) uncapped glass vial sealed in polyethylene tubing and secured to wire surveyor flag, and (C) glass vial sealed in polyethylene sandwich bags and secured to wire surveyor flag.

4. Remove the excess air space from the LDPE tubing. This can be accomplished by squeezing the LDPE tubing tightly against the vial or by twisting the tubing to tighten it against the vial.
- 5a. Position the unsealed end of the bag across the sealing element of the heat sealer, so that the sealing element is as close as practical to the mouth of the enclosed vial without stretching the LDPE across the opening (fig. 3). The LDPE should not be folded or wrinkled where it crosses the heating element of the heat sealer. Seal the bag. Once the bag is sealed, trim off the excess LDPE tubing. In this method, the LDPE is not necessarily tight across the vial opening.
- 5b. An optional method to arranging the heat-sealed end of the inner LDPE tubing across the vial opening is to, after both ends of the tubing are sealed, pull the tubing over the vial opening and fold the heat-sealed end of the tubing against the glass vial. After folding, secure the folded tubing to the vial with a self-locking nylon tie in a place where it will not interfere with attaching a vial cap during sampler recovery. In this method, the LDPE should be tight against the vial opening. This method improves sampler integrity over the first method because it reduces the probability of accidentally cutting the inner LDPE while removing the outer LDPE during sampler recovery.



**Figure 3.** Heat sealing of glass vial in polyethylene tubing.

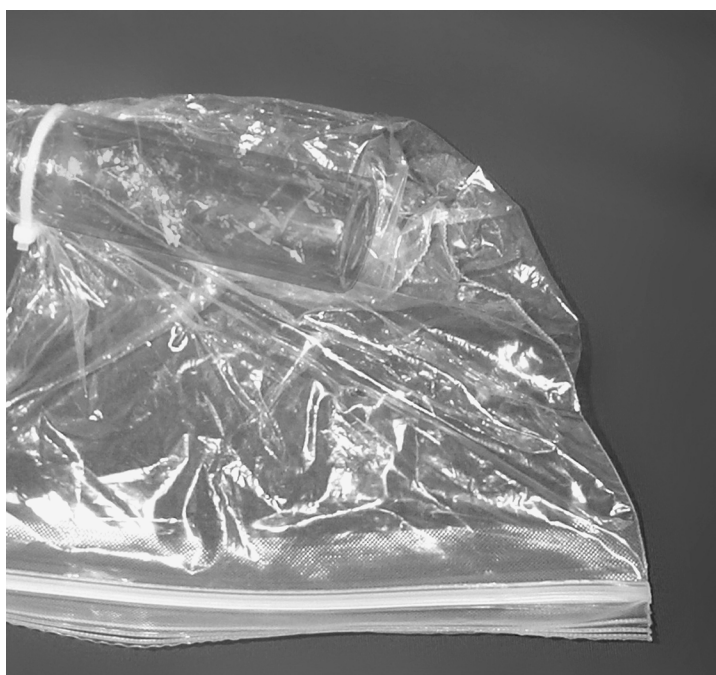
6. Once the inner LDPE tubing is secure, cut another 8-in. length of 2-in. wide lay-flat LDPE tubing. This tubing will constitute the outer layer, which will be removed during sampler recovery to prevent sediment from interfering with capping the vials.
7. Heat-seal one end. The heat sealer should be adjusted to provide a uniform seal without melting through the LDPE. Multiple seals may be required with some heat sealers with less than 400 watts of impulse power.
8. Place the glass vial enclosed in the inner layer of LDPE into the new LDPE tube.
9. Press the LDPE against the vial to remove the excess air space from the outer LDPE tubing. The lack of air space will reduce buoyancy and maintain a consistent vapor volume.
10. Position the unsealed end of the bag across the sealing element of the heat sealer so that the sealing element is as close as practical to the mouth of the enclosed vial. No folds or wrinkles should be present where the LDPE tubing crosses the heating element of the heat sealer. Seal the bag. Once the bag is sealed, trim off the excess LDPE tubing.
11. Attach a wire surveyor flag to the PVD sampler to aid in sampler recovery. A practical method of attachment is to use self-locking nylon ties. The ties are attached tightly enough so that the surveyor flag does not pull free from the sampler during sampler recovery. The vial is attached so that the vial opening is in the opposite direction of the surveyor flag (fig. 2). One approach is to allow approximately 2 in. of wire extending beyond the nylon tie. The 2 in. of wire is then bent back 180 degrees over the nylon tie and laid adjacent to the wire above the tie. Add another nylon tie to secure the bent part of the wire tight against the vial (fig. 2). By this method, the surveyor flag does not pull free from the sampler during retrieval. The widest practical spacing between nylon ties will reduce a tendency for samplers to rotate on the wire and become wedged in sediment during retrieval.

The following method details how to construct a sampler with sandwich bags instead of lay-flat tubing.

1. Place an uncapped empty glass vial in a zipper-type polyethylene sandwich bag. Store the cap in a clean environment away from the PVD samplers until sampler recovery.

2. Remove the excess air space from the bag to reduce buoyancy of the sampler when deployed. This can be accomplished by squeezing or rolling the bag around the vial. Seal the bag with the zipper.
3. Secure the bag around the vial opening by tightening a self-locking nylon tie below the vial opening so that the tie and the excess bag will not interfere with capping the vial. A single layer of LDPE should now be tight across the vial opening (fig. 4).
4. Place the glass vial enclosed in the LDPE bag into another sandwich bag. Remove excess air from the outer bag and seal it with the zipper.
5. Attach a wire surveyor flag to the PVD sampler to aid in sampler recovery. A practical method of attachment is to use self-locking nylon ties. The

ties are attached tightly enough so that the surveyor flag does not pull free from the sampler during sampler recovery. The vial is attached so that the vial opening is in the opposite direction of the surveyor flag (fig. 2). One approach is to allow approximately 2 in. of wire extending beyond the nylon tie. The 2 in. of wire is then bent back 180 degrees over the nylon tie and laid adjacent to the wire above the tie. Add another nylon tie to secure the bent part of the wire tight against the vial (fig. 2). By this method, the surveyor flag does not pull free from the sampler during retrieval. The widest practical spacing between nylon ties will reduce a tendency for samplers to rotate on the wire and become wedged in sediment during retrieval.



**Figure 4.** Glass vial positioned in sandwich bag so that a single layer of low-density polyethylene is tight across the opening and the self-locking nylon tie does not interfere with capping.

## DEPLOYMENT OF SAMPLERS

Effective use of the samplers to delineate discharging contaminated ground water requires that samplers be deployed in ground-water-discharge areas. Many approaches have been used to identify gaining reaches of streams (zones where ground water discharges to surface water). To verify that the target section of the surface water is a gaining reach, install a streambed piezometer. In its simplest form, a streambed piezometer can be a pipe driven a few feet into the bed sediment. A bolt loosely fitted into the bottom of the pipe before installation can prevent sediment from moving into the pipe. After deployment a narrow rod then can be used to drive out the bolt to allow water to enter the pipe. After stabilization, comparison of ground-water-head measurements within the piezometer to surface-water stage outside the piezometer can indicate whether the head gradient is upward (gaining reach) or downward (losing reach). With this method, care should be taken to avoid a clogged pipe or a pipe with a leaky connection to surface water along the annular space between pipe and streambed sediments.

Many other methods have been used to identify areas of upwelling ground water beneath surface water. Near-shore discharge through a lakebed has been estimated with seepage devices (Lee, 1977) and hydraulic potentiometers (Winter and others, 1988). In areas where temperature differences between ground water and surface water are greater than normally expected, surface-water-temperature measurements and aerial infrared photography have been used to identify areas of ground-water discharge to streams (Silliman and Booth, 1993), lakes, and wetlands (Olafsson, 1979; Lee, 1985; Lee and Tracey, 1984; Baskin, 1998). Discharge areas of ground water to lakes sometimes can be located by towing temperature and specific-conductance probes from a boat (Lee, 1985). Researchers also have used the distribution of aquatic plant species as indicators of ground-water discharge to fens (Glaser and others, 1981; 1990; Verhoeven and others, 1988; Wassen and others, 1989), to saline wetlands (Swanson and others, 1984), and to a lake (Rosenberry and others, 2000).

Even within gaining reaches of a stream, the distribution of contaminant discharge can be complex. After storms, ground-water discharge may

be dominated by release of bank storage. This transient flow may temporarily mask contaminated ground-water discharge.

Deployment of PVD samplers involves burying of samplers in the bottom sediment of a surface-water body. Ideally, the samplers should be buried at the bottom of the transition zone from surface water to ground water to ensure that the sample collected represents VOCs in ground water. Delineating the transition zone, however, often is difficult, and holes dug beneath the water tend to rapidly refill with sediment. Samplers placed at shallow depths (for example, 0 to 0.5 ft) may be within this transition zone and samples may be affected by surface water. Samplers placed at shallow depths may also become dislodged. Samplers placed at greater depths (for example, greater than 1.5 ft) may be below the transition zone, but also may be difficult to retrieve. The most effective depths of sampler deployment may vary spatially and with time, and are dependent on many factors, including hydraulic conductivities of the sediments and hydrologic conditions. With the deployment method described, a practical target depth is between 0.5 and 1.5 ft. Deployment depths are described in detail more in the section "Factors Affecting Deployment of Samplers and Data Interpretation."

In shallow waters, waters up to 2 ft deep, where the samplers can be installed with hand augers or shovels (fig. 5), one approach to digging the hole is to shovel the sediment until the likelihood of hole collapse makes further digging impractical. At that point, insert the shovel into the sediment and push forward to create an opening between the back of the shovel and the sediment. In more cohesive sediment, the hole can be excavated with a hand auger. Exercise care during insertion of the PVD sampler into the hole to prevent rupturing of the polyethylene membrane covering the vial opening. Backfill the hole with the inserted PVD sampler with the sediment removed from the hole. Ensure that the hole has been adequately backfilled above the sampler to minimize entrainment of the top-most sediment layer above the PVD sampler to the bottom of the hole. To reduce the potential for contamination from sample-labeling pens, label the surveyor flag either several days before PVD-sampler construction (to allow vapors from water-proof markers to dissipate) or after the sampler is buried.





**A.**



**B.**

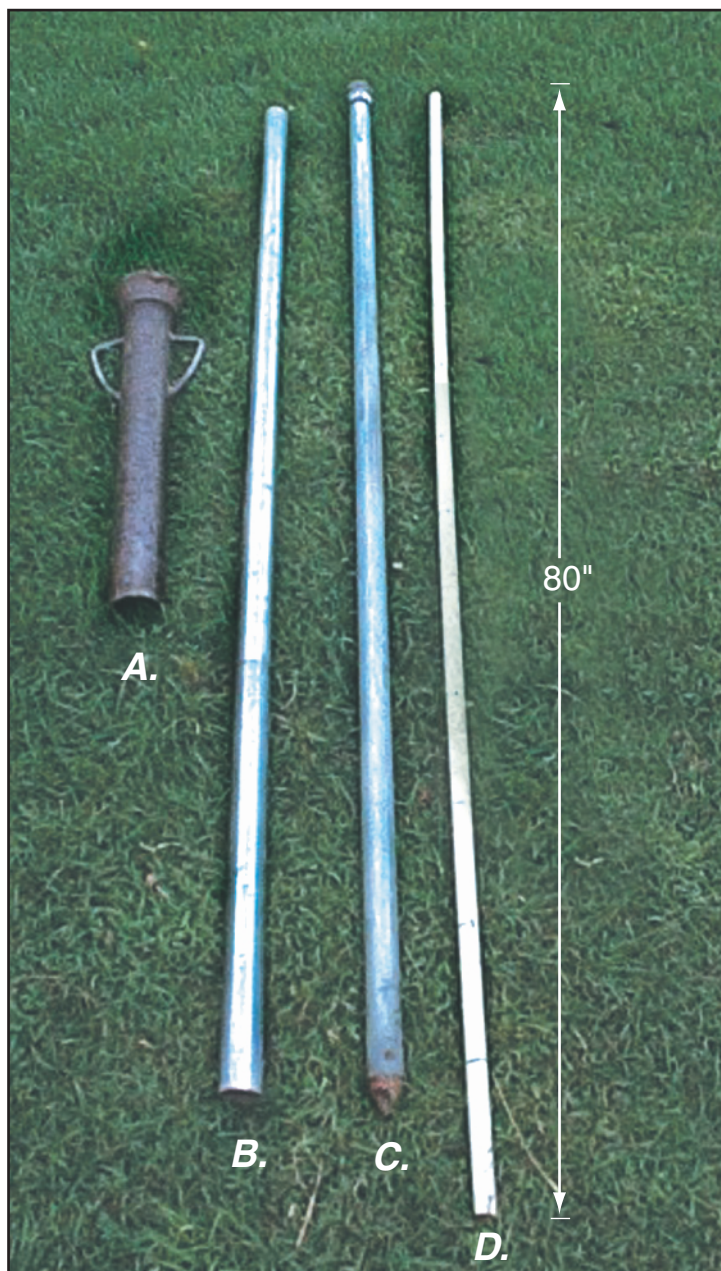


**C.**

**Figure 5.** Installation method for passive-vapor-diffusion samplers in water 0 to 2 feet deep. (A) passive-vapor-diffusion sampler secured to wire surveyor flag and tools used for installation, (B) insertion of sampler in space behind flattened surface of steel bar driven into cobble bottom sediments, and (C) passive-vapor-diffusion sampler installed.

In water deeper than about 2 ft, manual insertion of a sampler in a hand-augered hole or behind a shovel blade is not practical in conventional wading gear (hip or chest waders). A drive-point assembly has been effective in water 2 to 4 ft deep where chest waders are needed. The drive-point assembly has also been used from a row boat (Campbell and others, 2002) and through an ice cover (Lyford and others, 2000; Church and others, 2002) to install samplers in soft bottom sediment at depths to about 7 ft. Greater depths of installation may be possible from a boat, barge, or through ice, but has not been attempted. The drive-point assembly and its application are illustrated in figures 6 and 7.

Drive-point assemblies can be constructed at various lengths to suit different needs. The drive-point assembly most commonly used in New England studies consists of a 72-in. long, 1 3/4-in. outside diameter (OD), 1 5/8-in. inside diameter (ID) electrical conduit outer pipe; a 74-in. long, 1 1/2-in. OD, 1 3/8-in. ID electrical conduit inner pipe; and an 80-in. long, 7/8-in. OD, 3/4-in. ID polyvinylchloride (PVC) pipe. A 2-in. OD pipe cap is attached to the top of the 1 1/2-in. inner pipe, and a 2-in. long steel point is flush-mounted to the bottom. The outer and inner pipes are driven into the bottom sediments by striking the pipe cap on the inner pipe with a sledge or slide hammer. At the desired depth of installation, the inner pipe is removed, leaving a hole in the sediment extending about 2-in. deeper than the bottom of the outer pipe. The surveyor flag end of the PVD sampler is then pushed into the PVC pipe to where it is stopped by the tubing of the sampler. The PVC pipe and attached sampler are then inserted and pushed through the outer pipe into the sediment. The sampler is held in place by the PVC pipe as the outer pipe is removed. Sediments then collapse around the sampler, and the PVC pipe is removed from the sediment.



**Figure 6.** Drive-point assembly for installation of passive-vapor-diffusion sampler in water 2 to 4 feet deep in clayey silt to coarse sand and gravel sediments. (A) slide hammer, (B) 1 5/8-inch inside diameter steel electrical conduit, (C) 1 3/8-inch inside diameter steel electrical conduit with machined point, (D) polyvinylchloride sampler-insertion pipe.





**A.**



**B.**



**C.**



**D.**



**E.**



**F.**

**Figure 7.** Drive-point method for installation of passive-vapor-diffusion sampler in water 2 to 4 feet deep in clayey silt to coarse sand and gravel sediments. (A) 1 5/8-inch inside diameter (ID) steel electrical conduit with 1 3/8-inch ID steel insert conduit with 2-inch point driven into pond-bottom sediment with slide hammer, (B) insert pipe removed after driven to desired depth, (C) insertion of passive- vapor-diffusion sampler to polyvinylchloride (PVC) pipe (surveyor flag and wire inserted into pipe with sampler exposed), (D) insertion of PVC pipe with sampler into sediment through 1 5/8-inch ID steel conduit, (E) removal of 1 5/8-inch ID steel conduit, and (F) removal of PVC pipe leaving sampler installed in sediment.



At depths greater than 4 ft, divers may be needed to install PVD samplers. Divers have been used to install samplers in pond-bottom sediment to pond depths of 30 ft (Savoie and others, 2000). Divers inserted PVD samplers in soft sediment by hand and used a trowel in gravelly sediments.

For studies in New England, the samplers were found to be resistant to removal by high flows if buried to depths of 8 in. or greater into the sediment. Less than five percent of the approximate 1,250 samplers installed in the New England sites were lost. In a few instances, firmly planted samplers were not found when the surveyor wire flag broke free from the self-locking nylon ties upon retrieval, or when stream-channel sediment buried the flag.

## RECOVERY OF SAMPLERS

The amount of time PVD samplers must remain deployed in the sediment before recovery is, in part, based on the data-quality objective of the study. If the objective is to identify the presence or absence of VOC(s), samplers could be recovered within a few days. Field studies suggest that this can be accomplished after a deployment period of 8 days or less, and as little as 24 hours in some environments. If the objective is to estimate the concentration(s) of VOC(s), samplers cannot be recovered until enough time for equilibrium has elapsed. As discussed earlier, several factors, such as hydraulic conductivity of streambed sediments, hydraulic gradients, and water temperatures, affect the amount of equilibration time needed. Field evidence, discussed in Appendix I, suggests that an equilibrium period of approximately 2 weeks is adequate for most investigations in sandy formations. Longer or shorter periods may be appropriate depending on water temperatures and hydraulic conditions. It is important to remember, however, that PVD samplers typically are deployed in sediments as a reconnaissance tool to locate areas where ground water contaminated with VOCs is discharging. For this use, determining the presence or absence of target VOCs may be sufficient to meet the data-quality objectives of the sampling. A recent study showed that within 24 hours in four separate streams, the recovered PVD samplers contained chlorinated aliphatic compounds from discharging ground water at concentrations well above detection

limits, although the samplers had not yet equilibrated with the ground water concentrations at three of the sites (Vroblesky and Campbell, 2001).

Recovery of PVD samplers can be accomplished relatively rapidly. A 2-member team is needed; one person with “dirty hands” who retrieves samplers and touches the outer tubing only; the other person with “clean hands” who caps and stores samplers and touches the inner tubing only. A second clean hands person may be needed in situations where sets of samplers (10 or 20 samplers) are delivered to an on-site portable laboratory several times a day, and to assist in labeling and note taking. The specific recovery steps are listed below:

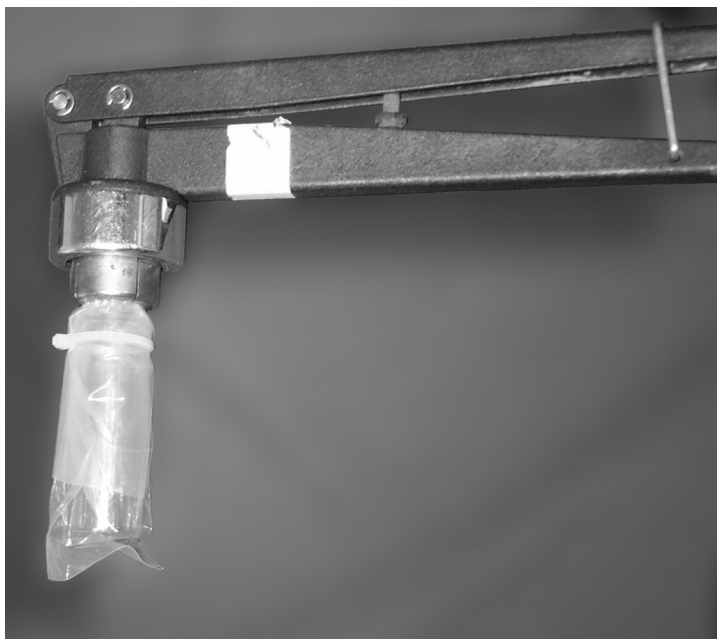
1. Pull the surveyor flag or excavate the sediment to remove the PVD sampler. Pull with a steady tension rather than a sudden forceful extraction that can cause nylon ties to break. Examine the sampler for integrity. Record unusual features, such as discoloring or water inside the outer bag. Discard or quickly cap and record a sampler with a ruptured inner seal.
2. Cut and remove the outer tubing or bag from around the vial opening. Do not pierce or cut the inner tubing or bag, because this can allow trapped vapors within the vial to escape or allow ambient air to enter, resulting in incorrectly low VOC concentrations within the vial. An alternative approach to removing the outer tubing that reduces the chance of puncturing the inner bag is to cut the outer nylon ties. After cutting the ties, use scissors to cut the end of the outer tubing adjacent the vial opening, and then push on the opposite end of the outer tubing to slide the sampler into the hands of the clean-hands person. Diagonal cutters (electrician’s pliers) are effective for cutting nylon ties that attach samplers to surveyor flags. Inspect the sampler and record any unusual features, such as discoloring or water inside the inner bag. Discard or quickly cap and record a sampler with a ruptured inner seal.
3. Cap the vial by screwing (fig. 8) or crimping (fig. 9) a cap onto the vial to seal the inner tubing or bag over the vial opening. Use caps that have a Teflon or Teflon-lined septum to allow sampling by syringe.

4. Label the vial after capping if the vial is removed from the labeled surveyor flag. The inner tubing or bag may be cut around the bottom of the cap and removed to facilitate labeling.
5. Store the PVD samplers away from any potential VOC-contaminant sources and in a chilled environment (4°C; ice or refrigerator), to reduce VOC leakage. If the vapor in the sampler is to be analyzed immediately, chilled storage is not needed.

The vapor sample obtained from the recovered PVD sampler can be analyzed on site with a gas chromatograph. Guidance on the use of a gas chromatograph is described in Appendix 2.



**Figure 8.** Screwing a septated cap onto a glass vial encased in the inner low-density polyethylene tubing.



**Figure 9.** (A) Attaching and (B) crimping a septated cap onto a glass vial encased in the inner low-density polyethylene tubing.

## FACTORS AFFECTING DEPLOYMENT OF SAMPLERS AND DATA INTERPRETATION

The effectiveness of PVD samplers as a reconnaissance tool to detect discharge areas of VOC-contaminated ground water depends on a variety of factors affecting contaminated ground-water discharge. Understanding these factors will help in selecting optimal sampler-deployment locations and will aid in data interpretation.

Aquifer and streambed lithologic heterogeneity affects discharge complexity and the optimal sampler-deployment locations. Using PVD samplers, Lyford and others (1999a) found that an irregular pattern of trichloroethene discharge to the Royal River, Maine, was related to the lithologic heterogeneity of the aquifer and riverbed sediments, and that significantly higher concentrations of contaminants discharged at sand boils. Conant (2000) found that contaminant discharge to a river in Ontario was predominantly associated with local gaps in the semi-confining unit beneath the river. Discharge of ground water beneath lakebeds can be particularly difficult to investigate because the water can discharge at low rates over a large area, and both rate and area can change with time. Winter (1976, 1978) has shown that the discharge is controlled predominantly by the spatial distribution of heads and hydraulic conductivity in the aquifer, as well as the bathymetry and sediment type of the lake bottom.

Another factor affecting contaminant discharge to rivers is the orientation of the river relative to the flow direction of the ground-water contamination. An investigation in Greenville, South Carolina, showed that reaches of a stream that were at a sharp angle to the axis of contamination-plume migration received greater contaminant discharge than reaches oriented approximately parallel to the direction of contaminant transport (Vroblesky, 2000). In a channel meandering through a tidally flooded wetland, the highest concentrations of discharging contaminants were found where the meander approached the shoreline that contained the ground-water contamination (Vroblesky and Lorah, 1991). This area was the most probable contaminant-discharge area because of its proximity to the ground-water contamination, and because the stream reach was oriented approximately perpendicular to the ground-water-flow path. Particular effort, therefore, should

be exercised during sampler deployment in sediment beneath a meandering stream to ensure adequate density of sampling locations in reaches where the stream is oriented at sharp angles to the contaminant transport direction. Similarly, care should be exercised in wetlands to adequately target zones where channel meanders approach the shoreline that contains the ground-water contamination.

When deploying samplers in lakes or large streams, consideration should be given to the depth of the contaminant plume as it approaches the surface-water body. Knowing this depth will help estimate the probable distance of contaminant discharge from the shoreline. In thick aquifers, there is often a deeper flow system beneath shallow stream subsystems (Toth, 1963). Thus, contaminant discharge from a distant source, which travels in the deep aquifer system, will discharge into the surface-water body at a greater distance from the shoreline than nearby contaminants that travel in a shallower flow system. Savoie and others (2000) found that contaminants emanating from a source approximately 1.5 miles upgradient from the shoreline of a kettle pond discharged into the pond 100 to 350 ft offshore. A second previously unknown plume was detected discharging into the pond at a distance of 25 to 200 ft offshore (Savoie and others, 2000). Samplers deployed near the shore would not have detected these plumes.

Similar considerations for placement of PVD samplers should be given to deployment in streams. In an ideal gaining stream with homogeneous bottom sediment and similar ground-water hydraulic gradients on both sides of the channel, ground water moving beneath a particular shoreline typically discharges to the stream closer to that shoreline than to the opposite shoreline. In this case, VOCs detected near a particular shoreline probably came from ground water derived in the upgradient direction of that shoreline. The lithologic and hydrologic complexities of streams, however, can create complex discharge pathways, sometimes making it difficult to select optimum-sampler placement sites and to identify contaminant-source directions.

Temporal changes in the locations of discharge areas also can affect concentrations of VOCs in discharge and affect interpretation of data from PVD samplers. A study of a small Coastal Plain stream in South Carolina to which petroleum hydrocarbons were

discharging showed that the stream contained an upstream gaining reach and a downstream losing reach. The boundary between the two reaches migrated upstream during periods of low ground-water levels and streamflow and downstream during periods of high ground-water levels and streamflow (Vroblesky and others, 1997). Thus, PVD samplers placed near the gaining/losing boundary in this stream can be expected to intercept upward moving ground water during part of the year and downward moving surface water during a different part of the year. Additional temporal variations in contaminant discharge through a streambed have been observed following nearby well construction (Vroblesky and Robertson, 1996).

Because the VOC concentration within a PVD sampler represents an equilibrium between the vapor phase in the sampler and the adjacent aqueous solution, changing aqueous-contaminant concentrations produce a corresponding change in the vapor-phase concentrations. If PVD samplers in a local area are removed sequentially over time following an equilibration period, they can be used to track temporal changes in the contaminant concentrations of discharging ground water (Vroblesky and Robertson, 1996). Because PVD samplers are sensitive to temporal fluctuations, samplers for a particular sampling event should all be collected sequentially within a few hours of each other to obtain a "snapshot" of the contaminant-discharge distribution.

The depth to which the samplers are installed also may affect the results. The samplers should be installed at or below the ground-water/surface-water interface; however, the location of the interface typically is difficult to delineate. It may be at the sediment/water interface or at some depth below the sediment. In some areas, the interface may shift as a result of daily or seasonal fluctuations in river stage and ground-water flow. Surface water may enter the sediment at the head of riffles and dropoffs and re-enter the river at the upstream edge and base of pools (Vaux, 1968; Boulton, 1993). The surface water also can leave the channel laterally and travel through the streambanks before eventually re-entering the channel downstream (Harvey and Bencala, 1993). The movement of surface water into bed sediments is more pronounced in high permeability sediment than in low permeability sediment; therefore, PVD samplers buried in shallow sandy horizons in these zones may intercept local

surface water rather than discharging ground water. Contaminated ground water upwelling beneath these zones may be diverted and discharge farther downstream (Conant, 2000). For practical reasons, PVD samplers often are buried at a uniform depth of approximately 0.5 to 1.5 ft, which may or may not be below the ground-water/surface-water interface. It is important, therefore, to consider the implications of subsurface streamflow when interpreting the PVD-sampler data.

Furthermore, if the samplers are deployed in an area of VOC-contaminated bottom sediment derived from sediment transported in the stream, then the VOC concentration in the PVD samplers may reflect contaminant concentrations in the sediment rather than in discharging ground water. It is important, therefore, to consider the possibility of stream transport of contaminated sediment when interpreting PVD data. In some cases, this situation probably can be resolved by deploying the samplers beneath such sediment.

An additional factor affecting data interpretation and sampler deployment is the potential for removal of the target compounds by micro-organisms in the sediment. The large diversity of micro-organisms and oxidation reduction conditions commonly found in wetland sediments may lower contaminant concentrations locally. Consequently, PVD samplers buried beneath the organic-rich bed sediments may detect a substantially higher concentration of VOCs than samplers placed in the upper part of the organic-rich sediment. In this situation PVD samplers can help evaluate VOC loss over a particular interval.

## **QUALITY CONTROL AND ASSURANCE**

The primary purpose of most studies that use PVD samplers is to determine or verify the presence of VOCs. Relative concentrations of VOCs detected at the site are also of interest. Variability and bias introduced during sample collection, however, affects the interpretation of the results. Confidence in the detections and the relative concentrations of VOCs in samples collected with PVD samplers can be evaluated by collecting a series of quality-control (QC) samples, such as duplicate, trip, and equipment-blank samples.

Duplicate or co-located samples provide information needed to estimate the precision of concentration values affected by the combination of uncertainties associated with field variability, sample processing, and the analytical method. A duplicate PVD sampler consists of two separate samplers deployed adjacent to each other in the same hole. These samplers are typically held together side-by-side to the same surveyor flag with nylon ties to ensure that the open end of the vials are at the same depth. To account for sampler variability, at least 10 percent of the samplers should be duplicates. Examples from studies in New England show that a VOC was detected in 1 of the duplicate samples but not in the other in only about 2.5 percent of the 437 duplicate samples. The relative percent difference (RPD) between VOC concentrations in the 83 duplicate samples where a VOC was detected in both samples ranged from 0 to nearly 200 percent. About 75 percent of these RPDs, however, were less than 30 percent, which is a reasonable range for a reconnaissance tool. Duplicate samplers also can provide a backup in case one of the samplers is compromised.

Trip blanks are PVD samplers that are prepared offsite, typically with construction of all the samplers expected to be used at the site. They are stored and transported to the sampling location with the other PVD samplers and capped at the sampling location when the PVD samplers are deployed. The trip blanks are then stored with other samples as they are recovered, and analyzed with the recovered samples. A positive detection in the trip blank means that the PVD samplers were exposed to specific contaminant(s) sometime before deployment. To some extent, this detection imparts a degree of uncertainty to the detections of that specific compound in the recovered PVD samples. It should be noted, however, that the samplers re-equilibrate to their surroundings. If background samples do not contain the specific contaminant, then it is highly probable that sufficient deployment time elapsed to allow concentrations of the specific contaminant to re-equilibrate to ambient conditions in all of the deployed samplers.

Some of the PVD samplers should be deployed in an area of the surface-water body considered to be away from potential VOC contamination, such as upstream in rivers. If contaminants are found in

samplers from a target area, but not in the background samplers, then this provides increased confidence that the contaminants are not an artifact of the methodology.

## PART 2. EXAMPLE APPLICATIONS IN NEW ENGLAND

During 1996 through 2000, PVD samplers were used at nine Superfund sites in New England to identify likely discharge areas for VOCs in ground water (fig. 10). These sites were selected for study because contamination of ground water by VOCs was known or suspected. The sites represent a variety of hydrologic settings including rivers, streams, ponds, wetlands, and coastal shorelines (table 2). Samplers, all constructed by methods described in Vroblesky and others (1996), were placed in sediments ranging from clayey silt to cobbles. Vapor concentrations in samplers ranged from not detected to more than 1,000,000 parts per billion by volume (ppb v). The principal VOCs detected include the chlorinated compounds tetrachloroethene (PCE), trichloroethene (TCE), and chlorobenzene, and the petroleum compounds benzene, ethylbenzene, *meta-para-xylene*, *ortho-xylene*, and toluene. At all nine Superfund sites, discharge areas of known ground-water plumes contaminated with VOCs were confirmed and refined with PVD samplers. At four of these sites, results of PVD sampling has led to the identification of previously unknown plumes of contaminated ground water and has helped guide further characterization of ground water at these sites. The following sections briefly describe each of the nine study areas, state the purpose and design of PVD sampling, present sampling results on maps, and summarize findings. Also included is a summary of the quality control and assurance results for the nine studies. These summaries were extracted from published reports. Additional detail about any of these studies can be found in the cited reports.