USER'S GUIDE FOR POLYETHYLENE-BASED PASSIVE DIFFUSION BAG SAMPLERS TO OBTAIN VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN WELLS

PART 1: DEPLOYMENT, RECOVERY, DATA INTERPETATION, AND QUALITY CONTROL AND ASSURANCE

Water-Resources Investigations Report 01-4060

Prepared in cooperation with the

U.S. AIR FORCE
U.S. NAVAL FACILITIES ENGINEERING COMMAND
U.S. ENVIRONMENTAL PROTECTION AGENCY
FEDERAL REMEDIATION TECHNOLOGIES ROUNDTABLE
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U.S. ARMY CORPS OF ENGINEERS and
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User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 1: Deployment, Recovery, Data Interpretation, and Quality Control and Assurance

By Don A. Vroblesky

U.S. Geological Survey

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Conversion Factors, Vertical Datum, Acronyms, and Abbreviations

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi^2)	2.590	square kilometer
	Flow	
foot per day (ft/d)	0.3048	meter per day
foot squared per day (ft^2/d)	0.09294	meter squared per day
gallon per minute (gal/min)	0.06308	liter per second
gallon per day (gal/d)	0.003785	cubic meter per day
inch per year (in/yr)	25.4	millimeter per year
	Volume	
gallon (gal)	3.785	liter

Temperature is given in degrees Celsius (°C), which can converted to degrees Fahrenheit (°F) by the following equation: °F = 9/5 (°C) + 32

Sea level refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (µg/L).

Additional Abbreviations	
EDB	1,2-Dibromomethane
AFCEE	Air Force Center for Environmental Excellence
*c*DCE	*cis*-1,2-Dibromoethene
ft^3/d	cubic feet per day
ft^3/mg	cubic feet per milligram
°C	degrees Celsius
g	gram
ITRC	Interstate Technology Regulatory Cooperation
LDPE	low-density polyethylene
L	liter
µg	microgram
µm	micrometer
µL	microliter
mg	milligram
mL	milliliter
mL/min	milliliter per minute
MTBE	Methyl-*tert*-butyl ether
NAVFAC	Naval Facilities Engineering Command
NAPL	non-aqueous phase liquid
PDB	passive diffusion bag
PCE	Tetrachloroethene
TCE	Trichloroethene
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOA	Volatile organic analysis
VOC	Volatile organic compound

User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 1: Deployment, Recovery, Data Interpretation, and Quality Control and Assurance

By Don A. Vroblesky

EXECUTIVE SUMMARY

Water-filled passive diffusion bag (PDB) samplers described in this report are suitable for obtaining concentrations of a variety of volatile organic compounds (VOCs) in ground water at monitoring wells. The suggested application of the method is for long-term monitoring of VOCs in ground-water wells at well-characterized sites.

The effectiveness of the use of a single PDB sampler in a well is dependent on the assumption that there is horizontal flow through the well screen and that the quality of the water is representative of the ground water in the aquifer directly adjacent to the screen. If there are vertical components of intra-bore-hole flow, multiple intervals of the formation contributing to flow, or varying concentrations of VOCs vertically within the screened or open interval, then a multiple deployment of PDB samplers within a well may be more appropriate for sampling the well.

A typical PDB sampler consists of a low-density polyethylene (LDPE) lay-flat tube closed at both ends and containing deionized water. The sampler is positioned at the target horizon of the well by attachment to a weighted line or fixed pipe.

The amount of time that the sampler should be left in the well prior to recovery depends on the time required by the PDB sampler to equilibrate with ambient water and the time required for the environmental disturbance caused by sampler deployment to return to ambient conditions. The rate that the water within the PDB sampler equilibrates with ambient water depends on multiple factors, including the type of compound being sampled and the water temperature. The concentrations of benzene, *cis*-1,2-dichloroethene, tetrachlorethene, trichloroethene, toluene, naphthalene, 1,2-dibromoethane, and total xylenes within the PDB samplers equilibrated with the concentrations in an aqueous mixture of those compounds surrounding the samplers under laboratory conditions within approximately 48 hours at 21 degrees Celsius (°C). A subsequent laboratory study of mixed VOCs at 10 °C showed that tetrachloroethene and trichloroethene were equilibrated by about 52 hours, but other compounds required longer equilabration times. Chloroethane, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, and 1,1-dichloroethene were not equilibrated at 52 hours, but appeared to be equilibrated by the next sampling point at 93 hours. Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane were not equilibrated at 93 hours, but were equilibrated by the next sampling point at 166 hours. Different equilibration times may exist for other compounds. Differences in equilibration times, if any, between single-solute or mixed VOC solutions have not yet been thoroughly examined.

The samplers should be left in place long enough for the well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. Laboratory and field data suggest that 2 weeks of equilibration probably is adequate for many applications; therefore, a minimum equilibration time of 2 weeks is suggested. In less permeable formations, longer equilibration times may be required. When applying PDB samplers in waters colder than previously tested (10 °C) or for compounds without sufficient corroborating data, a side-by-side comparison with conventional methodology is advisable to justify the field equilibration time.

Following the initial equilibration period, the samplers maintain equilibrium concentrations with the ambient water until recovery. Thus, there is no specified time for sampler recovery after initial equilibration. PDB samplers routinely have been left in ground waters having concentrations of greater than 500 parts per million (ppm) of trichloroethene for 3 months at a time with no loss of bag integrity, and at one site, the PDB samplers have been left in place in VOC-contaminated ground water for 1 year with no reported loss of sampler integrity. The effects of long-term (greater than 1 month) PDB-sampler deployment on sampler and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations, however. Moreover, in some environments, development of a biofilm on the polyethylene may be a consequence of long-term deployment. Investigations of semipermeable membrane devices (SPMDs) have shown that the transfer of some compounds across a heavily biofouled polyethylene membrane may be reduced, but not stopped. If a heavy organic coating is observed on a PDB sampler, it is advisable to determine the integrity of the sample by comparison to a conventional sampling method before continuing to use PDB samplers for long-term deployment in that well.

Recovery consists of removing the samplers from the well and immediately transferring the enclosed water to 40-milliliter sampling vials for analysis. The resulting concentrations represent an integration of chemical changes over the most recent portion of the equilibration period (approximately 48 to 166 hours, depending on the water temperature and the type of compound).

The method has both advantages and limitations when compared to other sampling methods. Advantages include the potential for PDB samplers to eliminate or substantially reduce the amount of purge water associated with sampling. The samplers are relatively inexpensive and easy to deploy and recover. Because PDB samplers are disposable, there is no downhole equipment to be decontaminated between wells, and there is a minimum amount of field equipment required. The samplers also have the potential to delineate contaminant stratification in the formation across the open or screened intervals of monitoring wells where vertical hydraulic gradients are not present. In addition, the samplers integrate concentrations over time, which may range between about 48 to 166 hours depending on the compound of interest. Because the pore size of LDPE is only about 10 angstroms or less, sediment does not pass through the membrane into the bag. Thus, PDB samplers are not subject to interferences from turbidity. In addition, none of the data collected suggest that VOCs leach from the LDPE material, or that there is a detrimental effect on the VOC sample from the PDB material.

Water-filled polyethylene PDB samplers are not appropriate for all compounds. The samplers are not suitable for inorganic ions and have a limited applicability for non-VOCs and for some VOCs. For example, although methyl-*tert*-butyl ether and acetone and most semivolatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. A variety of factors influence the ability of compounds to diffuse through the polyethylene. These factors include the molecular size and shape and the hydrophobic nature of the compound. Unpublished laboratory test data of semivolatile compounds in contact with PDB samplers showed a higher concentration of phthalates inside the PDB sampler than outside the PDB sampler, suggesting that the polyethylene may contribute phthalates to the enclosed water. Thus, the samplers should not be used to sample for phthalates.

VOC concentrations in PDB samplers represent concentrations in the vicinity of the sampler within the well screen or open interval. This may be a limitation for PDB samplers and some other types of sampling, such as low-flow sampling, if the ground-water contamination is above or below the screen or not in the sample intervals providing water movement to the PDB samplers. If there is a vertical hydraulic gradient in the well, then the concentrations in the sampler may represent the concentrations in the water flowing vertically past the sampler rather than in the formation directly adjacent to the sampler. Vertically spaced multiple PDB samplers may be needed in chemically stratified wells or where flow patterns through the screen change as a result of ground-water pumping or seasonal water-level fluctuations.

The purposes of this document are to present methods for PDB sampler deployment, and recovery; to discuss approaches to determine the applicability of passive diffusion samplers; and to discuss various factors influencing interpretation of the data. The intended audience for the methodology sections of this report is managers and field personnel involved in using PDB samplers. The discussion of passive diffusion sampler applicability and interpretation of the data is

suited for project managers, technical personnel, and the regulatory community. Part 2 of this report presents case studies of PDB sampler field applications.

INTRODUCTION

The use of PDB samplers for collecting ground-water samples from wells offers a cost-effective approach to long-term monitoring of VOCs at well-characterized sites (Vroblesky and Hyde, 1997; Gefell and others, 1999). The effectiveness of the use of a single PDB sampler in a well is dependent on the assumption that there is horizontal flow through the well screen and that the quality of the water is representative of the ground water in the aquifer directly adjacent to the screen. If there are vertical components of intra-borehole flow, multiple intervals of the formation contributing to flow, or varying concentrations of VOCs vertically within the screened or open interval, then deployment of multiple PDB samplers within a well may be more appropriate for sampling the well.

The samplers consist of deionized water enclosed in a LDPE sleeve (fig. 1) and are deployed adjacent to a target horizon within a screened or open interval of a well. The suggested application is for long-term monitoring of VOCs in ground-water wells. Where the screened interval is greater than 10 feet (ft), the potential for contaminant stratification and/or intra-borehole flow within the screened interval is greater than in screened intervals shorter than 10 ft. It is important that the vertical distribution of contaminants be determined in wells having 10-ft-long well screens, and that both the vertical distribution of contaminants and the potential for intra-borehole flow be determined in wells having screens longer than 10 ft. For many VOCs of environmental interest (table 1), the VOC concentration in water within the sampler approaches the VOC concentration in water outside of the PDB sampler over an equilibration period. The resulting concentrations represent an integration of chemical changes over the most recent part of the equilibration period (approximately 48 to 166 hours, depending on the water temperature and the type of compound being sampled). The approach is inexpensive and has the potential to eliminate or substantially reduce the amount of purge water removed from the well.

A variety of PDB samplers have been utilized in well applications (fig. 1). Although the samplers vary in specific construction details, a typical PDB sampler consists of a 1- to 2-ft-long LDPE tube closed at both ends and containing laboratory-grade deionized water (fig. 1). The typical diameter for PDB samplers used in a 2-inch-diameter well is approximately 1.2 inches; however, other dimensions may be used to match the well diameter. Equilibration times may be longer for larger diameter PDB samplers. On the outside of the PDB sampler, a low-density polyethylene-mesh sometimes is used for protection against abrasion in open boreholes and as a means of attachment at the prescribed depth. The PDB sampler can be positioned at the target horizon by attachment to a weighted line or by attachment to a fixed pipe.

PDB samplers for use in wells are available commercially. Authorized distributors as of March 2001 are Columbia Analytical Services (800-695-7222; www@caslab.com) and Eon Products (800-474-2490; www.eonpro.com). A current list of vendors and PDB-sampler construction details can be obtained from the U.S. Geological Survey Technology Transfer Enterprise Office, Mail Stop 211, National Center, 12201 Sunrise Valley Drive, Reston, Virginia 20192 (telephone 703-648-4344; fax 703-648-4408). PDB samplers employ patented technology (U.S. patent number 5,804,743), and therefore, require that the user purchase commercially produced samplers from a licensed manufacturer or purchase a nonexclusive license for sampler construction from the U.S. Geological Survey Technology Enterprise Office at the above address.

The purposes of this document are to present methods for PDB sampler deployment, and recovery; to discuss approaches for determining the applicability of passive diffusion samplers; and to discuss various factors influencing interpretation of the data. The intended audience for the methodology sections of this report is managers and field personnel involved in using PDB samplers. The discussion of PDB sampler applicability and interpretation of the data is suited for project managers, technical personnel, and the regulatory community. Part 2 of this report presents case studies of PDB-sampler field applications.

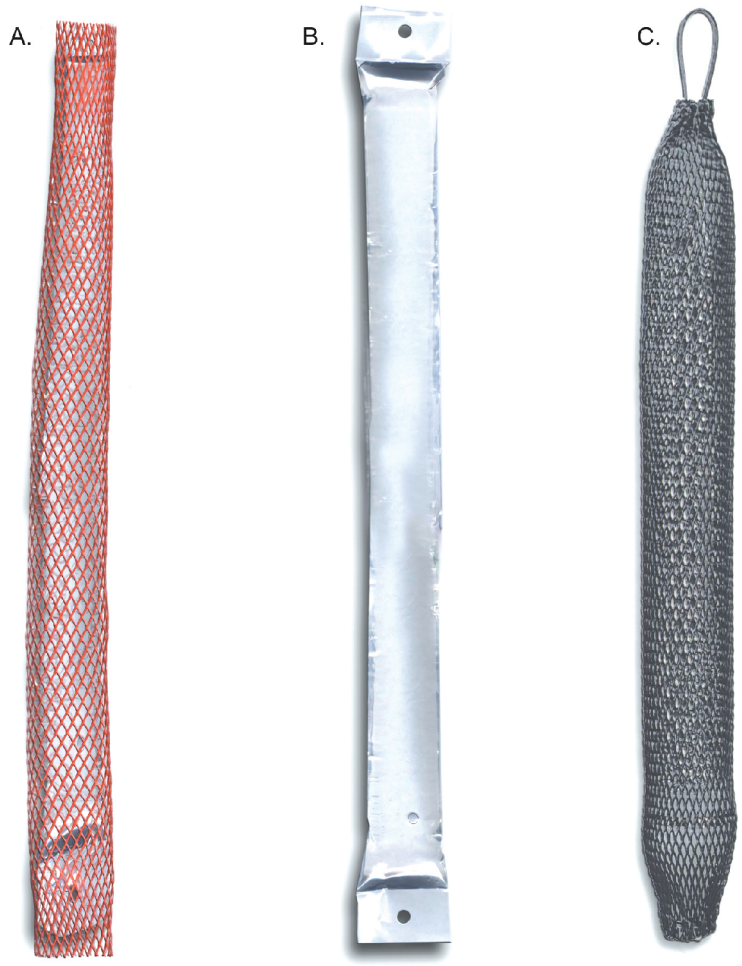

Figure 1. Typical water-filled passive diffusion bag samplers used in wells, including (A) diffusion bag with polyethylene mesh, (B) diffusion bag without mesh, and (C) bag and mesh attached to bailer bottom.

Table 1. Compounds tested under laboratory conditions for use with passive diffusion bag samplers
[From Vroblesky and Campbell, 2001]

Tested compounds showing good correlation (average differences in concentration of 11 percent or less between diffusion-sampler water and test-vessel water) in laboratory tests			
Benzene	2 Chlorovinyl ether	*cis*-1,2-Dichloroethene	1,1,1-Trichloroethane
Bromodichloromethane	Dibromochloromethane	*trans*-1,2-Dichloroethene	1,1,2-Trichloroethane
Bromoform	Dibromomethane	1,2-Dichloropropane	Trichloroethene
Chlorobenzene	1,2-Dichlorobenzene	*cis*-Dichloropropene	Trichlorofluoromethane
Carbon tetrachloride	1,3-Dichlorobenzene	1,2-Dibromoethane	1,2,3-Trichloropropane
Chloroethane	1,4-Dichlorobenzene	*trans*-1,3-Dichloropropene	1,1,2,2-Tetrachloroethane
Chloroform	Dichlorodifluoromethane	Ethyl benzene	Tetrachloroethene
Chloromethane	1,2-Dichloroethane	Naphthalene	Vinyl chloride
	1,1-Dichloroethene	Toluene	Total xylenes
Tested compounds showing poor correlation (average differences in concentration greater than 20 percent between diffusion-sampler water and test-vessel water) in laboratory tests			
Acetone*	Methyl-*tert*-butyl ether	Styrene	

*T.M Sivavec and S.S. Baghel, General Electric Company, written commun., 2000

Summary of Passive Diffusion Bag Sampler Advantages and Limitations

Advantages

1. PDB samplers have the potential to eliminate or substantially reduce the amount of purge water associated with sampling.

2. PDB samplers are inexpensive.

3. The samplers are easy to deploy and recover.

4. Because PDB samplers are disposable, there is no downhole equipment to be decontaminated between wells.

5. A minimal amount of field equipment is required.

6. Sampler recovery is rapid. Because of the small amount of time and equipment required for the sampling event, the method is practical for use where access is a problem or where discretion is desirable (that is, residential communities, business districts, or busy streets where vehicle traffic control is a concern).

7. Multiple PDB samplers, distributed vertically along the screened or open interval, may be used in conjunction with borehole flow meter testing to gain insight on the movement of contaminants into and out of the well screen or open interval or to locate the zone of highest concentration in the well. Analytical costs when using multiple PDB samplers sometimes can be reduced by selecting a limited number of the samplers for laboratory analysis based on screening by using field gas chromatography at the time of sample collection.

8. Because the pore size of LDPE is only about 10 angstroms or less, sediment does not pass through the membrane into the bag. Thus, PDB samplers are not subject to interferences from turbidity. In addition, none of the data collected suggest that VOCs leach from the LDPE material or that there is a detrimental effect from the PDB material on the VOC sample.

Limitations

1. PDB samplers integrate concentrations over time. This may be a limitation if the goal of sampling is to collect a representative sample at a point in time in an aquifer where VOC-concentrations substantially change more rapidly than the samplers equilibrate. Laboratory results obtained indicate that a variety of compounds equilibrated within 48 hours at 21 °C (Vroblesky and Campbell, 2001). Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane may require between 93 and 166 hours to equilibrate at 10 °C (T.M. Sivavec and S.S. Baghel, General Electric Company, written commun., 2000). The initial equilibration under field conditions may be longer to allow well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment.

2. Water-filled polyethylene PDB samplers are not appropriate for all compounds. For example, although methyl-*tert*-butyl ether and acetone (Vroblesky, 2000; Paul Hare, General Electric Company, oral commun., 2000) and most semivolatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. A variety of factors influence the ability of compounds to diffuse through the polyethylene membrane. These factors include the molecular size and shape and the hydrophobic nature of the compound. Compounds having a cross-sectional diameter of about 10 angstroms or larger (such as humic acids) do not pass through the polyethylene because the largest (transient) pores in polyethylene do not exceed about 10 angstroms in diameter (Flynn and Yalkowsky, 1972; Hwang and Kammermeyer, 1975; Comyn, 1985). The samplers are not appropriate for hydrophilic polar molecules, such as inorganic ions. A detailed discussion of the relation between hydrophobicity and compound transport through polyethylene can be found in Gale (1998). Unpublished laboratory test data (D.A. Vroblesky, U.S. Geological Survey, written commun., 1998) of semivolatile compounds in contact with PDB samplers showed a higher concentration of phthalates inside the PDB sampler than outside the PDB sampler, suggesting that the polyethylene may contribute phthalates to the enclosed water. Thus, the samplers should not be used to sample for phthalates.

3. PDB samplers rely on the free movement of water through the well screen. In situations where ground water flows horizontally through the well screen, the VOC concentrations in the open interval of the well probably are representative of the aquifer water in the adjacent formation (Gillham and others, 1985; Robin and Gillham, 1987; Kearl and others, 1992; Powell and Puls, 1993; Vroblesky and Hyde, 1997). In these situations, the VOC concentration of the water in contact with the PDB samplers, and therefore, the water within the diffusion samplers, probably represents local conditions in the adjacent aquifer. However, if the well screen is less permeable than the aquifer or the sandpack, then under ambient conditions, flowlines may be diverted around the screen. Such a situation may arise from inadequate well development or from iron bacterial fouling of the well screen. In this case, the VOC concentrations in the PDB samplers may not represent concentrations in

the formation water because of inadequate exchange across the well screen. PDB samplers have not yet been adequately tested to determine their response under such conditions.

4. VOC concentrations in PDB samplers represent ground-water concentrations in the vicinity of the screened or open well interval that move to the sampler under ambient flow conditions. This is a limitation if the ground-water contamination lies above or below the well screen or open interval, and requires the operation of a pump to conduct contaminants into the well for sampling.

5. In cases where the well screen or open interval transects zones of differing hydraulic head and variable contaminant concentrations, VOC concentrations obtained using a PDB sampler may not reflect the concentrations in the aquifer directly adjacent to the sampler because of vertical transport in the well. However, a vertical array of PDB samplers, used in conjunction with borehole flow meter testing, can provide insight on the movement of contaminants into or out of the well. This information then can be used to help determine if the use of PDB samplers is appropriate for the well, and to select the optimal vertical location(s) for the sampler deployment.

6. In wells with screens or open intervals with stratified chemical concentrations, the use of a single PDB sampler set at an arbitrary (by convention) depth may not provide accurate concentration values for the most contaminated zone. However, multiple PDB samplers distributed vertically along the screened or open interval, in conjunction with pump sampling (as appropriate), can be used to locate zone(s) of highest concentration in the well. Multiple PDB samplers also may be needed to track the zone of maximum concentration in wells where flow patterns through the screened interval change as a result of ground-water pumping or seasonal water-table fluctuations.

PASSIVE DIFFUSION BAG SAMPLER DEPLOYMENT

A variety of approaches can be used to deploy the PDB samplers in wells. A typical deployment approach, described in this section, is to attach the PDB samplers to a weighted line. It also is acceptable to attach the weights directly to the PDB sampler if the attachment point is of sufficient strength to support the weight. The weights attached to the bottom of the line are stainless steel and can be reused, but must be thoroughly decontaminated with a detergent before the first use or before using in a different well. Rope, such as 90 pound, 3/16 inch braided polyester, can be used as the line for single-use applications if it is of sufficient strength to support the weight and sampler, is nonbuoyant, and is subject to minimal stretch; however, the rope should not be reused because of the high potential for cross contamination. Stainless-steel or Teflon-coated stainless-steel wire is preferable. The weighted lines should not be reused in different wells to prevent carryover of contaminants. A possible exception is coated stainless-steel wire, which can be reused after sufficient decontamination. An alternative deployment approach, not discussed in this section, is to attach the PDB samplers to a fixed pipe in the well (Vroblesky and Peters, 2000, p. 3; also included in Part 2 of this publication). The PDB samplers should not contact non-aqueous phase liquid (NAPL) during deployment or retrieval to prevent cross contamination. An approach that can be utilized to deploy diffusion samplers through a layer of floating NAPL is described in the field test at Naval Station North Island, California (Vroblesky and Peters, 2000, p. 3-4; also included in Part 2 of this publication).

If the PDB sampler is to be compared with a conventional pumping approach to sampling, then it is suggested that both the pump and the PDB sampler be deployed at the same time, with the sampler attached near (such as directly below) the pump inlet. This approach eliminates potential concentration differences between the two methods that may result from well disturbance during equipment removal and deployment at the time of sampling. An alternative method is to deploy the PDB samplers independently of the pumps and recover the samplers immediately prior to placing the pump down the well.

PDB samplers are available either prefilled (field ready) with laboratory-grade deionized water or unfilled. The unfilled samplers are equipped with a plug and funnel to allow for field filling and sample recovery. To fill these samplers, remove the plug from the sampler bottom, insert the short funnel into the sampler, and pour laboratory-grade deionized water into the sampler. The sampler should be filled until water rises and stands at least half way into the funnel. Remove excess bubbles from the sampler. Remove the funnel and reattach the plug. A small air bubble from the plug is of no concern.

The following steps should be used for deploying PDB samplers in wells:

1. Measure the well depth and compare the measured depth with the reported depth to the bottom of the well screen from well-construction records. This is to check on whether sediment has accumulated in the bottom of the well, whether there is a nonscreened section of pipe (sediment sump) below the well screen, and on the accuracy of well-construction records. If there is an uncertainty regarding length or placement of the well screen, then an independent method, such as video imaging of the well bore, is strongly suggested.

2. Attach a stainless-steel weight to the end of the line. Sufficient weight should be added to counterbalance the buoyancy of the PDB samplers. This is particularly important when multiple PDB samplers are deployed. One approach, discussed in the following paragraphs, is to have the weight resting on the bottom of the well, with the line taut above the weight. Alternatively, the PDB sampler and weight may be suspended above the bottom, but caution should be exercised to ensure that the sampler does not shift location. Such shifting can result from stretching or slipping of the line or, if multiple samplers are attached end-to-end rather than to a weighted line, stretching of the samplers.

3. Calculate the distance from the bottom of the well, or top of the sediment in the well, up to the point where the PDB sampler is to be placed. A variety of approaches can be used to attach the PDB sampler to the weight or weighted line at the target horizon. The field-fillable type of PDB sampler is equipped with a hanger assembly and weight that can be slid over the sampler body until it rests securely near the bottom of the sampler. When this approach is used with multiple PDB samplers down the same borehole, the weight should only be attached to the lowermost sampler. An additional option is to use coated stainless-steel wire as a weighted line, making loops at appropriate points to attach the upper and lower ends of PDB samplers. Where the PDB sampler position varies between sampling events, movable clamps with rings can be used. When using rope as a weighted line, a simple approach is to tie knots or attach clasps at the appropriate depths. Nylon cable ties or stainless-steel clips inserted through the knots can be used to attach the PDB samplers. An approach using rope as a weighted line with knots tied at the appropriate sampler-attachment points is discussed below.

(a) For 5-ft-long or shorter well screens, the center point of the PDB sampler should be the vertical midpoint of the saturated well-screen length. For example, if the well screen is at a depth of 55 to 60 ft below the top of casing, and the measured depth of the well is 59 ft, then the bottom of the well probably has filled with sediment. In this case, the midpoint of the sampler between the attachment points on the line will be midway between 55 and 59 ft, or at 57 ft. Thus, for a 1.5-ft-long sampler, the attachment points on a weighted line should be tied at distances of 1.25 ft (2 ft – 0.75 ft) and 2.75 ft (2 ft + 0.75 ft) from the top of the sediment in the well, or the bottom of the well, making adjustments for the length of the attached weight. When the PDB sampler is attached to the line and installed in the well, the center of the sampler will be at 57-ft depth. If, however, independent evidence is available showing that the highest concentration of contaminants enters the well from a specific zone within the screened interval, then the PDB sampler should be positioned at that interval.

(b) For 5- to 10-ft-long well screens, it is advisable to utilize multiple PDB samplers vertically along the length of the well screen for at least the initial sampling (fig. 2). The purposes of the multiple PDB samplers are to determine whether contaminant stratification is present and to locate the zone of highest concentration. The midpoint of each sampler should be positioned at the midpoint of the interval to be sampled. For 1.5-ft-long samplers, at each sampling depth in the screened interval, make two attachment points on the weighted line at a distance of about 1.5 ft apart. The attachment points should be positioned along the weighted line at a distance from the bottom end of the weight such that the midpoint between the knots will be at the desired sampling depth along the well screen. Sampler intervals are variable, but a simple approach is to use the top knot/loop of one sampler interval as the bottom knot/loop for the overlying sampler interval.

Figure 2. Example of multiple PDB samplers prepared for deployment.

(c) PDB samplers should not be used in wells having screened or open intervals longer than 10 ft unless used in conjunction with borehole flow meters or other techniques to characterize vertical variability in hydraulic conductivity and contaminant distribution or used strictly for qualitative reconnaissance purposes. This is because of the increased potential for cross contamination of water-bearing zones and hydraulically driven mixing effects that may cause the contaminant stratification in the well to differ from the contaminant stratification in the adjacent aquifer material. If it is necessary to sample such wells, then multiple PDB samplers should be installed vertically across the screened or open interval to determine the zone of highest concentration and whether contaminant stratification is present.

4. The samplers should be attached to the weights or weighted line at the time of deployment. For samplers utilizing the hanger and weight assembly, the line can be attached directly to the top of the sampler. PDB samplers utilizing an outer protective mesh can be attached to a weighted line by using the following procedure:

(a) Insert cable ties through the attachment points in the weighted line.

(b) At each end of the PDB sampler, weave the ends of the cable ties or clamp through the LPDE mesh surrounding the sampler and tighten the cable ties. Thus, each end of the PDB sampler will be attached to a knot/loop in the weighted line by means of a cable tie or clamp. The cable ties or clamps should be positioned through the polyethylene mesh in a way that prevents the PDB sampler from sliding out of the mesh.

(c) Trim the excess from the cable tie before placing the sampler down the well. Caution should be exercised to prevent sharp edges on the trimmed cable ties that may puncture the LDPE.

5. When using PDB samplers without the protective outer mesh, the holes punched at the ends of the bag, outside the sealed portion, can be used to attach the samplers to the weighted line. Stainless-steel spring clips have been found to be more reliable than cable ties in this instance, but cable ties also work well.

6. Lower the weight and weighted line down the well until the weight rests on the bottom of the well and the line above the weight is taut. The PDB samplers should now be positioned at the expected depth. A check on the depth can be done by placing a knot or mark on the line at the correct distance from the top knot/loop of the PDB sampler to the top of the well casing and checking to make sure that the mark aligns with the lip of the casing after deployment.

7. Secure the assembly in this position. A suggested method is to attach the weighted line to a hook on the inside of the well cap. Reattach the well cap. The well should be sealed in such a way as to prevent surface-water invasion. This is particularly important in flush-mounted well vaults that are prone to flooding.

8. Allow the system to remain undisturbed as the PDB samplers equilibrate.

PASSIVE DIFFUSION BAG SAMPLER AND SAMPLE RECOVERY

The amount of time that the samplers should be left in the well prior to recovery depends on the time required by the PDB sampler to equilibrate with ambient water and the time required for environmental disturbances caused by sampler deployment to return to ambient conditions. The rate that the water within the PDB sampler equilibrates with ambient water depends on multiple factors, including the type of compound being sampled and the water temperature. The concentrations of benzene, *cis*-1,2-dichloroethene (*c*DCE), tetrachlorethene (PCE), trichloroethene (TCE), toluene, naphthalene, 1,2-dibromoethane (EDB), and total xylenes within the PDB samplers equilibrated with the concentrations in an aqueous mixture of those compounds surrounding the samplers under laboratory conditions within approximately 48 hours at 21 °C (Vroblesky and Campbell, 2001). A subsequent laboratory study of mixed VOCs at 10 °C showed that PCE and TCE were equilibrated by about 52 hours, but other compounds required longer equilibration times (T.M. Sivavec and S.S. Baghel, General Electric Company, written commun., 2000). Chloroethane, *c*DCE, *trans*-1,2-dichloroethene, and 1,1-dichloroethene were not equilibrated at 52 hours, but appeared to be equilibrated by the next sampling point at 93 hours. Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane were not equilibrated at 93 hours, but were equilibrated by the next sampling point at 166 hours. Different equilibration times may exist for other compounds. Differences in equilibration times, if any, between single-solute or mixed-VOC solutions have not yet been thoroughly examined.

Under field conditions, the samplers should be left in place long enough for the well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. The results of borehole dilution studies show that wells can recover to 90 percent of the predisturbance conditions within minutes to several hours for permeable to highly permeable geologic formations, but may require 100 to 1,000 hours (4 to 40 days) in muds, very fine-grained loamy sands, and fractured rock, and may take even longer in fractured shales, recent loams, clays, and slightly fractured solid igneous rocks (Halevy and others, 1967).

In general, where the rate of ground-water movement past a diffusion sampler is high, equilibration times through various membranes commonly range from a few hours to a few days (Mayer, 1976; Harrington and others, 2000). One field investigation showed adequate equilibration of PDB samplers to aquifer trichloroethene (TCE) and carbon tetrachloride (CT) concentrations within 2 days in a highly permeable aquifer (Vroblesky and others, 1999). In other investigations, PDB samplers recovered after 14 days were found to be adequately equilibrated to chlorinated VOCs (Obrien & Gere Engineers, Inc., 1997a, 1997b; Hare, 2000); therefore, the equilibration period was less than or equal to 14 days for those field conditions. Because it appears that 2 weeks of equilibration probably is adequate for many applications, a minimum equilibration time of 2 weeks is suggested. When applying PDB samplers in waters colder than previously tested (10 °C) or for compounds without sufficient corroborating field data, a side-by-side comparison with conventional sampling methodology is advisable to justify the field equilibration time.

In less permeable formations, longer equilibration times may be required. It is probable that water in the well bore eventually will equilibrate with the pore-water chemistry; however, if the rate of chemical change or volatilization loss in the well bore exceeds the rate of exchange between the pore water and the well-bore water, then the PDB samplers may under-

estimate pore-water concentrations. Guidelines for equilibration times and applicability of PDB samplers in low-permeability formations have not yet been established. Therefore, in such situations, a side-by-side comparison of PDB samplers and conventional sampling methodology is advisable to ensure that the PDB samplers do not underestimate concentrations obtained by the conventional method. A detailed discussion of diffusion rates relevant to diffusion sampler equilibrium in slow-moving ground-water systems can be found in Harrington and others (2000).

Following the initial equilibration period, the samplers maintain equilibrium concentrations with the ambient water until recovery. Thus, there is no specified maximum time for sampler recovery. PDB samplers have routinely been left in ground waters having concentrations of greater than 500 ppm of TCE for 3 months at a time with no loss of bag integrity, and at one site, the PDB samplers have been left in place in VOC-contaminated ground water for 1 year with no reported loss of sampler integrity (Paul Hare, General Electric Company, oral commun., 2000). The effects of long-term (greater than 1 month) PDB-sampler deployment on sampler and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations. Moreover, in some environments, development of a biofilm on the polyethylene may be a consequence of long-term deployment. Investigations of semipermeable membrane devices (SPMDs) have shown that the transfer of some compounds may be reduced, but not stopped, across a heavily biofouled polyethylene membrane (Ellis and others, 1995; Huckins and others, 1996; Huckins and others, in press). If a heavy organic coating is observed on a PDB sampler, it is advisable to determine the integrity of the sample by comparing contaminant concentrations from the PDB sampler to concentrations from a conventional sampling method before continuing to use PDB samplers for long-term deployment in that well.

Recovery of PDB samplers is accomplished by using the following approach:

1. Remove the PDB samplers from the well by using the attached line. The PDB samplers should not be exposed to heat or agitated.

2. Examine the surface of the PDB sampler for evidence of algae, iron or other coatings, and for tears in the membrane. Note the observations in a sampling field book. If there are tears in the membrane, the sample should be rejected. If there is evidence that the PDB sampler exhibits a coating, then this should be noted the validated concentration data.

3. Detach and remove the PDB sampler from the weighted line. Remove the excess liquid from the exterior of the bag to minimize the potential for cross contamination.

4. A variety of approaches may be used to transfer the water from the PDB samplers to 40-mL volatile organic analysis (VOA) vials. One type of commercially available PDB sampler provides a discharge device that can be inserted into the sampler. If discharge devices are used, the diameter of the opening should be kept to less than about 0.15 inches to reduce volatilization loss. Two options are presently available to recover water from the sample using discharge devices. One option involves removing the hanger and weight assembly from the sampler, inverting the sampler so that the fill plug is pointed upward, and removing the plug. The water can be recovered by directly pouring in a manner that minimizes agitation or by pouring through a VOC-discharge accessory inserted in place of the plug. The second approach involves piercing the sampler near the bottom with a small-diameter discharge tube and allowing water to flow through the tube into the VOA vials. In each case, flow rates can be controlled by tilting or manipulating the sampler. Alternatively, the PDB sampler can be cut open at one end using scissors or other cutting devices which have been decontaminated between use for different wells. Water can then be transferred to 40-ml VOA vials by gently pouring in a manner that minimizes water agitation. Acceptable duplication has been obtained using each method. Preserve the samples according to the analytical method. The sampling vials should be stored at approximately 4 °C in accordance with standard sampling protocol. Laboratory testing suggests that there is no substantial change in the VOC concentrations in PDB samplers over the first several minutes after recovery; however, the water should be transferred from the water-filled samplers to the sample bottles immediately upon recovery.

5. A cost-effective alternative when using multiple PDB samplers in a single well is to field screen water from each sampler using gas chromatography. These results can be used to decide which of the multiple PDB samplers should be sent to an EPA-approved laboratory for standard analysis. Typically, at least the sample containing the highest concentration should be analyzed by a laboratory.

6. If a comparison is being made between concentrations obtained using PDB samplers and concentrations obtained using a conventional sampling approach, then the well should be sampled by the conventional approach soon after (preferably on the same day) recovery of the PDB sampler. The water samples obtained using PDB samplers should be sent in the same shipment, as the samples collected by the conventional approach for the respective wells. Utilizing the same laboratory may reduce analytical variability.

7. Any unused water from the PDB sampler and water used to decontaminate cutting devices should be disposed in accordance with local, state, and Federal regulations.

DETERMINING APPLICABILITY OF PASSIVE DIFFUSION BAG SAMPLERS AND INTERPRETATION OF DATA

When attempting to determine whether the use of PDB samplers is appropriate at a particular well, a common approach is to do a side-by-side comparison with a conventional sampling method during the same sampling event. This approach is strongly suggested in wells having temporal concentration variability. In a well having relatively low temporal concentration variability, comparison of the PDB-sampler results to historical concentrations may provide enough information to determine whether the PDB samplers are appropriate for the well. In general, if both PDB and conventional sampling produce concentrations that agree within a range deemed acceptable by local, state, and Federal regulatory agencies and meet the site-specific data-quality objectives, then a PDB sampler may be approved for use in that well to monitor ambient VOC concentrations. If concentrations from the PDB sampler are higher than concentrations from the conventional method, it is probable that concentrations from the PDB sampler adequately represent ambient conditions because there usually is a greater potential for dilution from mixing during sampling using conventional methods than during sampling using PDB samplers.

If, however, the conventional method produces concentrations that are significantly higher than those obtained using the PDB sampler, then it is uncertain whether the PDB-sampler concentrations represent local ambient conditions. In this case, further testing can be done to determine whether contaminant stratification and/or intra-borehole flow is present. Multiple sampling devices can be used to determine the presence of contaminant stratification, and borehole flowmeters can be used to determine whether intra-borehole flow is present. When using flowmeters to measure vertical flow in screened boreholes, however, the data should be considered qualitative because of the potential for water movement through the sand pack. Borehole dilution tests (Halevy and others, 1967; Drost and others, 1968; Grisak and others, 1977; Palmer, 1993) can be used to determine whether water is freely exchanged between the aquifer and the well screen.

Once the source of the difference between the two methods is determined, a decision can be made regarding the well-specific utility of the PDB samplers. Tests may show that VOC concentrations from the PDB samplers adequately represent local ambient conditions within the screened interval despite the higher VOC concentration obtained from the conventional method. This may be because the pumped samples incorporated water containing higher concentrations either from other water-bearing zones induced along inadequate well seals or through fractured clay (Vroblesky and others, 2000), from other water-bearing zones not directly adjacent to the well screen as a result of well purging prior to sampling (Vroblesky and Petkewich; 2000), or from mixing of chemically stratified zones in the vicinity of the screened interval (Vroblesky and Peters, 2000).

The mixing of waters from chemically stratified zones adjacent to the screened interval during pumping probably is one of the more important sources of apparent differences between the results obtained from PDB sampling and conventional sampling because such stratification probably is common. Vertical stratification of VOCs over distances of a few feet has been observed in aquifer sediments by using multilevel sampling devices (Dean and others, 1999; Pitkin and others, 1999), and considerable variation in hydraulic conductivity and water chemistry has been observed in an aquifer in Cape Cod, Massachusetts, on the scale of centimeters (Wolf and others, 1991; Smith and others 1991; Hess and others, 1992). Multiple PDB samplers have been used to show a change in TCE concentration of 1,130 (µg/L over a 6-ft vertical screened interval in Minnesota (Vroblesky and Petkewich, 2000). Tests using PDB samplers in screened intervals containing VOC stratification showed that the PDB-sampler data appeared to be point-specific, whereas the pumped sample integrated water over a larger interval (Vroblesky and Peters, 2000).

The decision on whether to use PDB samplers in such situations depends on the data-quality objectives for the particular site. If the goal is to determine and monitor higher concentrations or to examine contaminant stratification within the screened interval, then the PDB samplers may meet this objective. If the goal is to determine the average concentrations for the entire screened interval, then a pumped sample or an average from multiple diffusion samplers may be appropriate.

As an aid in the decision-making process, the following section examines the influences that hydraulic and chemical heterogeneity of an aquifer can have on sample quality in long-screened wells. Because VOC concentrations from PDB samplers commonly are compared to VOC concentrations from other sampling methodologies, the second section examines the differences in sample quality between these methodologies in situations of hydraulic and chemical heterogeneity.

Influences of Hydraulic and Chemical Heterogeneity on Sample Quality in Long-Screened Wells

Sampling biases and chemical variability in long-screened wells, which can be loosely defined as wells having significant physical and chemical heterogeneity within the screened interval and in the adjacent aquifer (Reilly and Leblanc, 1998), have been the subject of numerous investigations. Sources of chemical variability in such wells include non-uniform flow into wells (Robbins and Martin-Hayden, 1991; Reilly and Gibs, 1993; Chiang and others, 1995; Church and Granato, 1996; Reilly and LeBlanc, 1998), lithologic heterogeneity (Reilly and others, 1989; Robbins, 1989; Martin-Hayden and others, 1991; Gibs and others, 1993; Reilly and Gibs, 1993), and in-well mixing. In a well open across a chemically or hydraulically heterogeneous section of the aquifer, differences in the sampling methodology can produce significant differences in the sampling results.

Long-screened wells have the potential to redistribute chemical constituents in the aquifer where there are vertical hydraulic gradients within the screened interval. Water can move into the well from one horizon and exit the well at a different horizon (Church and Granato, 1996; Reilly and LeBlanc 1998). If there is vertical flow in the screened or open interval, and the zone of low hydraulic head (outflow from the well) is within the contaminated horizon, then the PDB samplers (or any standard sampling methodology) can underestimate or not detect the contamination. The reason is that, in this case, the contaminated horizon does not contribute water to the well under static conditions. Instead, water from other horizons with higher hydraulic head will invade the contaminated horizon by way of the well screen. Under pumped conditions, the majority of the extracted water will be from the most permeable interval, which may not be the contaminated zone. Even when pumping induces inflow from the contaminated interval, much of that inflow will be a reflection of the residual invaded water from other horizons. In this situation, a substantial amount of purging would be required before water representative of the aquifer could be obtained (Jones and Lerner, 1995). Such sampling is not likely to reflect a significant contribution from the contaminated zone, and concentrations in the contaminated zone probably will be underestimated.

Similarly, if VOC-contaminated water is flowing into the well and is exiting the well at a different horizon, then VOCs will be present along the screened interval between the two horizons. In this case, VOC concentrations in the screened interval may be representative of aquifer concentrations at the inflow horizon, but may not be representative of aquifer concentrations near the outflow horizon.

In areas where vertical stratification of VOC concentrations is anticipated, using multiple PDB samplers may more fully characterize the contaminated horizon than using a single PDB sampler. This is particularly true in wells having screens 10 ft or longer; however, significant VOC stratification has been observed over intervals of less than 5 ft (Vroblesky and Peters, 2000). Because of the increased probability of vertical concentration or hydraulic gradients within the open interval of long-screened (greater than 10 ft) wells, it is advisable to determine the zones of inflow and outflow within the screened or open interval of these wells using borehole flowmeter analysis (Hess, 1982; 1984; 1986; 1990; Young and others, 1998).

Comparison of Passive Diffusion Bag Sampling Methodology to Conventional Methodologies

Traditional sampling methodologies, such as the purge-and-sample (or conventional purging method), low-flow or low-volume sampling, and using straddle packers and multilevel samplers, produce VOC

concentrations that may differ from VOC concentrations obtained from PDB samplers because the methodologies sometimes are influenced in different ways by aquifer hydraulic and chemical heterogeneity. This section examines potential sources of concentration differences between traditional methodologies and the PDB methodology.

The purge-and-sample approach to ground-water monitoring differs from the diffusion-sampler approach primarily because the area of the screened or open interval that contributes water to the purged sample typically is greater than for the PDB sampler and the potential for mixing of stratified layers is higher. When pumping three or more casing volumes of water prior to collecting a sample, chemical concentrations in the discharging water typically change as the well is pumped (Keely and Boateng, 1987; Cohen and Rabold, 1988; Martin-Hayden and others, 1991; Robbins and Martin-Hayden, 1991; Reilly and Gibs, 1993; Barcelona and others, 1994; Martin-Hayden, 2000), due to mixing during pumping and other factors, such as the removal of stagnant water in the casing and changing patterns of inflow and outflow under ambient and pumping conditions (Church and Granato, 1996). The induction of lateral chemical heterogeneity during pumping also may produce variations in the sampled concentrations. The amount of mixing during purging can be highly variable (Barber and Davis, 1987; Church and Granato, 1996; Reilly and LeBlanc, 1998; Martin-Hayden, 2000), and may result in concentrations that are not locally representative (Reilly and Gibs, 1993). Substantial vertical hydraulic gradients, even in shallow homogeneous aquifers, have been observed to bias sampling using conventional purging because the majority of the pumped water may come from a particular horizon not related to the contaminated zone and because the intra-well flow that intruded the aquifer may not be adequately removed during purging (Hutchins and Acree, 2000). Thus, differences may be observed between concentrations obtained from a pumped sample and from a PDB sample in a chemically stratified interval if the pumped sample represents an integration of water collected from multiple horizons and the PDB sampler represents water collected from a single horizon.

Low-flow purging and sampling (Barcelona and others, 1994; Shanklin and others, 1995) disturbs the local ground water less than conventional purge-and-sample methods. Thus, samples obtained by PDB samplers are likely to be more similar to samples obtained by using low-flow purging than to those obtained by using conventional purge-and-sample methods. Even under low-flow conditions, however, purging still can integrate water within the radius of pumping influence, potentially resulting in a deviation from VOC concentrations obtained by PDB sampling. One investigation found that in low hydraulic conductivity formations, low-flow sampling methodology caused excessive drawdown, which dewatered the screened interval, increased local ground-water velocities, and caused unwanted colloid and soil transport into the ground-water samples (Sevee and others, 2000). The authors suggest that in such cases, a more appropriate sampling methodology may be to collect a slug or passive sample from the well screen under the assumption that the water in the well screen is in equilibrium with the surrounding aquifer.

Isolating a particular contributing fracture zone with straddle packers in an uncased borehole allows depth-discrete samples to be collected from the target horizon (Hsieh and others, 1993; Kaminsky and Wylie, 1995). Strategically placed straddle packers often can minimize or eliminate the impact of vertical gradients in the sampled interval. However, even within a packed interval isolating inflowing fracture zones, deviations between VOC concentrations in water from PDB samplers and water sampled by conventional methods still may occur if the conventional method mixes chemically stratified water outside the borehole or if the packed interval straddles chemically heterogeneous zones.

The use of multilevel PDB samplers and other types of multilevel samplers (Ronen and others, 1987; Kaplan and others, 1991; Schirmer and others, 1995; Gefell and others, 1999; Jones and others, 1999) potentially can delineate some of the chemical stratification. Diffusion sampling and other sampling methodologies, however, can be influenced by vertical hydraulic gradients within the well screen or the sand pack. When vertical hydraulic gradients are present within the well, water contacting the PDB sampler may not be from a horizon adjacent to the PDB sampler. Rather, the water may represent a mixing of water from other contributing intervals within the borehole. In a screened well, even multilevel samplers with baffles to limit vertical flow in the well cannot prevent influences from

vertical flow in the gravel pack outside the well screen. Such vertical flow can result from small vertical differences in head with depth. A field test conducted by Church and Granato (1996) found that vertical head differences ranging from undetectable to 0.49 ft were sufficient to cause substantial flows (as much as 0.5 liters/minute) in the well bore.

QUALITY CONTROL AND ASSURANCE

The sources of variability and bias introduced during sample collection can affect the interpretation of the results. To reduce data variability caused during sampling, a series of quality-control samples should be utilized.

Replicate samples are important for the quality control of diffusion-sampler data. Sample replicates provide information needed to estimate the precision of concentration values determined from the combined sample-processing and analytical method and to evaluate the consistency of quantifying target VOCs. A replicate sample for water-filled diffusion samplers consists of two separate sets of VOC vials filled from the same diffusion sampler. Each set of VOC vials should be analyzed for comparison. Approximately 10 percent of the samplers should be replicated.

The length of the PDB sampler can be adjusted to accommodate the data-quality objectives for the sampling event. The length can be increased if additional volume is required for collection of replicate and matrix spike/matrix spike duplicate samples.

Trip blanks are used to determine whether external VOCs are contaminating the sample due to bottle handling and/or analytical processes not associated with field processing. Trip blanks are water-filled VOA vials prepared offsite, stored and transported with the other bottles used for collecting the environmental sample, and then submitted for analysis with the environmental sample. Consideration also should be given to the collection of a predeployment PDB trip blank to determine if the PDB samplers are exposed to extraneous VOCs prior to deployment. The predeployment trip blank should be a PDB sampler that is stored and transported with the field PDB samplers from the time of sampler construction to the time of deployment in the wells. An aliquot of the predeployment blank water should be collected from the PDB sampler in a VOA vial and submitted for analysis at the time of sampler deployment.

Water used to construct the diffusion samplers should be analyzed to determine the presence of background VOCs. Although many VOCs accidentally introduced into the diffusion-sampler water probably will reequilibrate with surrounding water once the diffusion samplers are deployed, some VOCs may become trapped within the diffusion-sampler water. For example, acetone, which is a common laboratory contaminant, does not easily move through the polyethylene diffusion samplers (Paul Hare, General Electric Company, oral commun., 1999). Thus, acetone inadvertently introduced into the diffusion-sample water during sampler construction may persist in the samplers, resulting in a false positive for acetone after sampler recovery and analysis.

SUMMARY

Water-filled passive diffusion bag (PDB) samplers described in this report are suitable for obtaining a variety of VOCs in ground water at monitoring wells. The suggested application for PDB samplers is for long-term monitoring of VOCs in ground-water wells at well-characterized sites. Where the screened interval is greater than 10 ft, the potential for contaminant stratification and/or intra-borehole flow within the screened interval is greater than in screened intervals shorter than 10 ft. It is suggested that the vertical distribution of contaminants be determined in wells having 10-ft-long well screens, and that both the vertical distribution of contaminants and the potential for intra-borehole flow be determined in wells having screens longer than 10 ft. A typical PDB sampler consists of a 1- to 2-ft-long low-density polyethylene lay-flat tube closed at both ends and containing deionized water. The sampler is positioned at the target horizon by attachment to a weighted line or fixed pipe.

The amount of time that the samplers should be left in the well prior to recovery depends on the time required by the PDB sampler to equilibrate with ambient water and the time required for environmental disturbances caused by sampler deployment to return to ambient conditions. The rate that water within the PDB sampler equilibrates with ambient water depends on multiple factors, including the type of compound being sampled and the water temperature. Concentrations of benzene, *cis*-1,2-dichloroethene, tetrachlorethene, trichloroethene, toluene, naphthalene, 1,2-dibromoethane, and total xylenes within the PDB samplers equilibrated with the concentrations in an

aqueous mixture of those compounds surrounding the samplers under laboratory conditions within approximately 48 hours at 21 °C. A subsequent laboratory study of mixed VOCs at 10 °C showed that tetrachloroethene and trichloroethene were equilibrated by about 52 hours, but other compounds required longer equilabration times. Chloroethane, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, and 1,1-dichloroethene were not equilibrated at 52 hours, but appeared to be equilibrated by the next sampling point at 93 hours. Vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane were not equilibrated at 93 hours but were equilibrated by the next sampling point at 166 hours. Different equilibration times may exist for other compounds. Differences in equilibration times, if any, between single-solute or mixed-VOC solutions have not yet been thoroughly examined.

The samplers should be left in place long enough for the well water, contaminant distribution, and flow dynamics to restabilize following sampler deployment. Laboratory and field data suggest that 2 weeks of equilibration probably is adequate for many applications. Therefore, a minimum equilibration time of 2 weeks is suggested. In less permeable formations, longer equilibration times may be required. When deploying PDB samplers in waters colder than previously tested (10 °C) or for compounds without sufficient corroborating data, a side-by-side comparison with conventional methodology is advisable to justify the field equilibration time.

Following the initial equilibration period, the samplers maintain equilibrium concentrations with the ambient water until recovery. Thus, there is no specified maximum time for sampler recovery after initial equilibration. PDB samplers have routinely been left in ground waters having concentrations of greater than 500 ppm of TCE for 3 months at a time with no loss of bag integrity, and at one site, the PDB samplers were left in place in VOC-contaminated ground water for 1 year with no reported loss of sampler integrity. The effects of long-term (greater than 1 month) PDB-sampler deployment on sampler and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations. In some environments, development of a biofilm on the polyethylene may be a consequence of long-term deployment. Investigations of semipermeable membrane devices (SPMDs) have shown that the transfer of some compounds across a heavily biofouled polyethylene membrane may be reduced, but not stopped. If a heavy organic coating is observed on a PDB sampler, it is advisable to determine the integrity of the sample by comparing sampler results to a conventional sampling method concentrations before continuing to use PDB samplers for long-term deployment in that well.

PDB methodology is suitable for a broad variety of VOCs, including chlorinated aliphatic compounds and petroleum hydrocarbons. The samplers, however, are not suitable for inorganic ions and have a limited applicability for non-VOCs and for some VOCs. For example, although methyl-*tert*-butyl ether and acetone and most semivolatile compounds are transmitted through the polyethylene bag, laboratory tests have shown that the resulting concentrations were lower than in ambient water. The samplers should not be used to sample for phthalates because of the potential for the LDPE to contribute phthalates to the water sample.

When attempting to determine whether the use of PDB samplers is appropriate at a particular well, a common approach is to do a side-by-side comparison with a conventional sampling method. This approach is strongly suggested in wells having temporal concentration variability. In a well having relatively low temporal concentration variability, comparison of the PDB-sampler results to historical concentrations may provide enough information to determine whether the PDB samplers are appropriate for the well. In general, if the two approaches produce concentrations that agree within a range deemed acceptable by the local, state, and Federal regulatory agencies, then use of a PDB sampler in that well will provide VOC concentrations consistent with the historical record. If concentrations from the PDB sampler are higher than concentrations from the conventional method, then it is probable that the concentrations from the PDB sampler are an adequate representation of ambient conditions. If, however, the conventional method produces concentrations that are substantially higher than the concentrations found by using the PDB sampler, then the PDB sampler may or may not adequately represent local ambient conditions. In this case, the difference may be due to a variety of factors, including mixing or translocation due to hydraulic and chemical heterogeneity of the aquifer within the screened or open interval of the well and the relative permeability of the well screen.

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USER'S GUIDE FOR POLYETHYLENE-BASED PASSIVE DIFFUSION BAG SAMPLERS TO OBTAIN VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN WELLS

PART 1: DEPLOYMENT, RECOVERY, DATA INTERPETATION, AND QUALITY CONTROL AND ASSURANCE

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