# Recommendations for the Use of Polyethylene Diffusion Bag Samplers For the Long-Term Monitoring of Volatile Organic Compounds in Groundwater

# FINAL REPORT

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Prepared by

Interstate Technology and Regulatory Council Diffusion Sampler Workgroup

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# Table of Contents

1 INTRODUCTION	4
1.1 Description and Use	4
1.2 DIFFERENCES BETWEEN PDB SAMPLING AND OTHER SAMPLING METHODS	6
1.2.1 Well-Purge Sampling	6
1.2.2 Low-Flow Sampling	7
1.2.3 PDB Sampling	7
1.3 DIFFUSION SAMPLER INFORMATION CENTER	7
2 APPROPRIATE USE OF PDB SAMPLERS	8
2.1 DATA QUALITY OBJECTIVES	8
2.2 TARGET ANALYTES	9
2.3 DEPLOYMENT TIME INTERVALS	9
2.4 HYDROLOGICAL CONSIDERATIONS	10
2.4.1 Contaminant Stratification	10
2.4.2 Vertical Flow within the well	11
2.5 DETERMINING DEPLOYMENT DEPTH	12
2.6 DIFFUSION SAMPLER BAG SIZE	13
2.7 COMPLIANCE SAMPLING	14
3 CONVERSION TO PDB MONITORING	14
3.1 ACCEPTABILITY OF PDB SAMPLING	14
3.2 COMPARING PDB SAMPLING RESULTS WITH RESULTS FROM OTHER SAMPLING	
Methods	15
3.3 DEPLOYMENT OF PDBS IN WELLS WITH DEDICATED PUMPS	16
3.4 CHANGES IN REGULATORY AGREEMENTS AND DOCUMENTS	17
4 SUMMARY AND RECOMMENDATIONS	17
4.1 RECOMMENDATIONS	17
5 REFERENCES	18
APPENDIX A - ACRONYMS	20
APPENDIX B - RECOMMENDATIONS KEYED TO DOCUMENT SECTIONS.	22

# Recommendations for the Use of Polyethylene Diffusion Bag Samplers for the Long-Term Monitoring of VOCs in Groundwater

### **1** Introduction

This document is intended to facilitate the use of polyethylene diffusion bag (PDB) samplers for long-term monitoring (LTM). The guidelines presented in Sections 2 and 3 relate to appropriate implementation, data interpretation, and regulatory issues of concern. Although diffusion samplers can be useful for many different activities and have membranes composed of various materials, this discussion primarily concerns the use of low density polyethylene LDPE) bags filled with deionized water and used in LTM for specific volatile organic compounds (VOCs).

The technical basis for use of PDB samplers is presented in the U.S. Geological Survey (USGS) Water Resources Investigations Report 01-4060, 'User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells" (Vroblesky 2001a; 2001b). This document should be used in conjunction with the technical guidance in the PDB User's Guide.

#### **1.1 Description and Use**

PDB samplers, which are LDPE bags containing deionized water, are used to determine concentrations of VOCs in groundwater wells. PDB samplers are passive devices that rely on the ambient movement of groundwater from the aquifer or water-bearing zone through the well screen. VOCs in groundwater will diffuse across the bag material until constituent concentrations within the bag reach equilibrium with concentrations in the surrounding groundwater. The samplers have been used successfully at a variety of sites (Vroblesky and Hyde, 1997; Parsons Engineering Science, Inc., 1999; Church, 2000; Hare, 2000; McClellan AFB Environmental Management Directorate, 2000; Vroblesky et al., 2000; Vroblesky and Peters, 2000; Vroblesky and Petkewich, 2000).

PDB samplers are made of LDPE plastic (typically 4 mils) in the shape of a tube that is filled with deionized water and sealed at both ends. The samplers are typically about 18 to 20 inches in length and 1.25 inches in diameter; they hold between 220-350 milliliters of water. Vendors can modify the length and diameter of a sampler to meet specific sampling requirements, and bags can be filled in the field or ordered prefilled. A list of vendors for PDB samplers can be found online at the *Interstate Technology and Regulatory Council's* (ITRC's) *Diffusion Sampler Information Center* (DSIC) website (http://ds.itrcweb.org).

November 6, 2002

PDB samplers are particularly well suited to the LTM of VOCs in groundwater at wellcharacterized sites. VOCs that show a good diffusion characteristics in laboratory tests and are recommended for sampling with PDBs are listed in Table 1. Additional compounds with which there is some experience are listed in Table 2. Section 2 of this report discusses factors that should be considered when evaluating the applicability of PDB sampling at a site.

Table 1. Compounds Tested in the Laboratory.Vroblesky, D.A. and T.R. Campbell(2001), Equilibration Times, Stability, and Compound Selectivity of Diffusion Samplers for<br/>Collection of Groundwater VOC Concentrations, Adv. Env. Res., 5(1): pp.1-12.

Favorable Laboratory Diffusion Testing Results											
Benzene	1,3-dichlorobenzene	Naphthalene									
Bromodichloromethane	1,4-dichlorobenzene	1,1,2,2-tetrachloroethane									
Bromoform	Dichlorodifluoromethane	Tetrachloroethene (PCE)									
Chlorobenzene	1,2-dichloroethane	Toluene									
Carbon tetrachloride	1,1-dichloroethene	1,1,1-trichloroethane									
Chloroethane	cis-1,2-dichloroethene	1,1,2-trichloroethane									
Chloroform	trans-1,2-dichloroethene	Trichloroethene (TCE)									
Chloromethane	1,2-dichloropropane	Trichlorofluoromethame									
2-chlorovinylether	cis-dichloropropene	1,2,3-trichloropropane									
Dibromochloromethane	1,2-dibromomethane	Vinyl chloride									
Dibromomethane	trans-1,3-dichloropropene	Xylenes									
1,2-dichlorobenzene	Ethyl benzene										
<b>Unfavorable Laboratory Dif</b>	fusion Testing Results										
Acetone <sup>1</sup>	Methyl- <i>iso</i> -butyl ketone <sup>1</sup>	Methyl tert-butyl ether									
Styrene											

<sup>1</sup>T.M. Sivavec and S.S. Baghel (2000), General Electric Company, written communication.

PDB samplers are also well suited to detect contaminant stratification in a well. Multiple PDB samplers deployed along the saturated screened interval or open borehole of a well can provide valuable information on the vertical distribution of contaminants within the aquifer. This information can be useful when refining a conceptual site model, modeling contaminant fate and transport, defining source areas for treatment, or optimizing remedial system performance. However, this document is focused on the use of PDBs for LTM.

**Table 2. Compounds that have been found above detection limits in PDB demonstrations.** This listing does <u>not</u> imply favorable PDB results were obtained; individual reports must be consulted for detailed information. More information is available at <u>http://ds.itrcweb.org</u>.

Included in field demonstrations (compounds in bold are <u>not</u> in Table 1).											
Benzene	enzene 1,1-dichloroethene										
2-butanone	cis-1,2-dichloroethene	Toluene									
Chlorobenzene	trans-1,2-dichloroethene	1,1,1-trichloroethane									
Carbon tetrachloride	Dichloropropane	1,1,2-trichloroethane									
Chloroethane	Ethyl benzene	Trichloroethene (TCE)									
Chloroform	Freon 113	1,2,4-trimethylbenzene									
1,2-dichlorobenzene	Isopropyl benzene	Vinyl chloride									
1,4-dichlorobenzene	Methyl-tert-butyl ether	Xylenes									
1,1-dichloroethane	Methylene chloride	-									
1,2-dichloroethane	Naphthalene										

#### **1.2 Differences between PDB Sampling and Other Sampling Methods**

Groundwater sampling is performed to collect a representative sample from the aquifer. Many factors, including hydrogeology and well-construction, can affect groundwater sample composition. However, even when monitoring wells are properly constructed and the hydrogeology and flow regimes are understood, inherent differences in sampling techniques may produce results that generate different representations of the aquifer. No single sampling technique is <u>the</u> correct methodology—each has advantages and limitations. It is important to understand the conceptual basis and differences in sampling techniques when interpreting sampling results.

#### **1.2.1 Well-Purge Sampling**

Well-purge sampling removes a prescribed number of well volumes of water prior to sample collection. Well-purge sampling is sometimes referred to as "conventional" sampling because it has been the approach most widely employed over the past decade. In theory, this technique removes stagnant well water and brings fresh water into the well from the adjacent aquifer formation(s), thus providing a flow-weighted sample of the aquifer adjacent to the entire well screen interval or open borehole. In some instances, well-purge sampling produces samples of high turbidity that may affect sample results. The relatively high degree of pumping stress associated with well-purge sampling mixes contaminant concentrations from various contributing zones, and can induce movement of contaminants into the well from zones not adjacent to the well screen. This method generates a large volume of purge water requiring disposal, sometimes at great expense.

#### **1.2.2 Low-Flow Sampling**

Low-flow purge and sample methods were developed to minimize disturbance of the groundwater system and to reduce turbidity in samples. Turbid samples are generally not representative of the aquifer and are particularly problematic in the analysis of metals. Low-flow sampling also greatly reduces the volume of water requiring disposal or treatment compared to well-purge sampling. A low-flow sample represents a more localized volume of the aquifer affected by pumping. If there is sufficient information on hydrogeology relative to the well, the inlet of the low-flow sampler can be placed to preferentially sample a particular zone. Appropriate use of low-flow sampling should be based upon adequate vertical characterization of the well, which may include vertical profiling. In practice, however, the inlet of the low-flow sampler has often been placed at mid-screen without regard to the hydrogeology. How well low-flow samples characterize the zone targeted by the monitoring well is not fully known because concentrations can vary with depth, and vertical profiling has historically not often been required for low-flow sampling.

#### **1.2.3 PDB Sampling**

In situations where no vertical flow occurs in the open well interval, a PDB sample represents a vertically restricted source from the section of well screen adjacent to where the sampler is positioned. Because it takes several days for the contaminant concentrations to equilibrate, the sample represents a time-integrated contaminant concentration. Lacking vertical flow within the well, a PDB sampler will not detect contaminants migrating through the aquifer above or below the sampler position. If vertical flow exists in the well, PDB sampler results likely will represent the zone with the highest hydraulic head. PDB samples are not turbid because the membrane excludes colloid-size particles.

Table 3 provides a brief qualitative summary of the spatial and temporal representation of three sampling methods. PDB results may not be identical to the results from well-purge or low-flow sampling, but this does not necessarily mean that PDBs are inappropriate for the intended application. Poor correlation between sampling methods simply means that additional work needs to be done to determine and understand the causes. Comparing PDB results with those from other sampling methods is discussed in Section 3.2.

#### **1.3 Diffusion Sampler Information Center**

The Diffusion Sampler Information Center (DSIC) website (<u>http://ds.itrcweb.org</u>) is maintained by the ITRC to provide a centralized location for posting and exchanging information on the development and use of diffusion samplers. The ITRC Diffusion Sampler Workgroup includes representatives from the U.S. Air Force, U.S. Navy, U.S. Environmental Protection Agency, USGS, US Army Corps of Engineers, private industry, and six different state agencies. It works to compile, analyze, and disseminate information on the deployment of PDB samplers on a national basis. Site users can access a current listing of deployments nationwide, news updates, and basic information on PDB sampling. The DSIC also provides

technical and information reports on PDB sampler technology, current information on diffusion sampler training, and links to other useful information sources.

Samping Meu	ilous.	
Sampling Method	Spatial Representation of Sample	Temporal Representation of Sample
Multiple Casing-Volume Purge	The flow-weighted sample concentrations represent a larger zone of influence and mixing than low flow and PDB samples. Contaminant concentrations in the aquifer not adjacent to the well screen may be incorporated into the resulting sample.	Instantaneous
	The flow-weighted sample concentration represents a portion of the open interval that can vary depending on a variety of factors. The factors include lithologic heterogeneity and pump placement relative	

to vertical permeability distributions. If vertical flow in the well screen is large relative to the pumping rate, then the sample

concentration is largely influenced by concentrations from the inflow

present and the low flow sample represents a narrow interval, then inappropriate depth placement of the pump may produce a sample

In a screened interval where chemical stratification is

Table 3. Generalized Spatial and Time Domains Represented by Three Ground	Water
Sampling Methods.	

	that does not incorporate water from the zone of highest concentration	
PDB	In a well screen dominated by horizontal flow, the sample typically represents a portion of the aquifer adjacent to the PDB sampler and a vertical zone approximately equal to the PDB length. When deployed in a part of the screened interval dominated by vertical flow, the resulting concentrations are largely influenced by concentrations from the inflow sources.	Time-integrated average of days prior recovery

# **2** Appropriate Use of PDB Samplers

When using PDB samplers, it is important to consider data quality objectives (DQOs), target analytes, and hydrologic concerns. It is the consensus of the Diffusion Sampler Workgroup that PDB sampler technology has been validated. Nonetheless, the application of the technology, as influenced by the above factors, must be evaluated.

### **2.1 Data Quality Objectives**

sources.

The decision to use PDBs must start with a review of DQOs. Each of the groundwater sampling techniques characterizes the aquifer in a different manner. With any sampling

Low Flow

ITRC Diffusion Sampler Workgroup

1-4 to

Instantaneous

method, site-specific DQOs should first be established and then it should be determined which sampling method best meets them. A general DQO—such as "collection of a representative sample"—should be refined if more specific sampling is required.

#### **2.2 Target Analytes**

Because PDBs depend on diffusion through the polyethylene membrane to collect VOCs, the ability of a target compound to readily diffuse into the PDB sampler is essential; most non-VOCs will not meet this criterion. Because of this, PDB samplers are not suitable for collecting metals or SVOCs. PDB samplers should only be used for sampling VOCs and a few other chlorinated and aromatic compounds (Tables 1 and 2). PDBs are generally used only after a site has been fully characterized using other groundwater sampling methods and once there are sufficient data to demonstrate that specific VOCs are the only analytes of concern or there is sufficient site knowledge to determine that VOCs are the only possible target analytes.

While most VOCs diffuse well through polyethylene, some do not, or have not been adequately tested; therefore, those VOCs are not recommended for PDB sampling at this time. Table 2 lists compounds that have been or are planned to be the subject of laboratory or field tests. Reports found on the DSIC may provide additional information on the suitability of PDB samplers for these compounds. Further laboratory or field studies may be necessary before PDB samplers can be used for these compounds and for other compounds not listed in Tables 1 and 2.

#### **2.3 Deployment Time Intervals**

Although many VOCs equilibrate with the PDB sampler water within 48 to 72 hours at temperatures of 10°C and above, the recommended minimum equilibration period for PDBs is two weeks. This time period allows ample time for diffusion to occur between the stabilized well water and the PDB sampler. It also allows time for the restabilization of well water and formation water following disturbance. Restabilization may occur relatively rapidly in many situations. However, in low-yielding wells or colder water, additional time may be required.

PDBs have routinely been successfully deployed for three-month periods and longer at some sites. Therefore, in most situations, samplers can be retrieved and deployed for the next quarterly monitoring round during the same mobilization. The advisability of longer deployment times is determined by individual well characteristics, although generally bag integrity is not a problem. A demonstration in a well of interest is recommended to verify the validity of PDB deployments longer than three months.

#### 2.4 Hydrological Considerations

In order to correctly interpret sampling results, it is important to know if there is stratification of contaminant concentrations in the well, as well as to what extent vertical and horizontal flows within the well affect the sample collected.

#### 2.4.1 Contaminant Stratification

Studies documented in the 'User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells" (Vroblesky, 2001b) clearly show that a high degree of variability in contaminant concentrations can occur within a 10-foot interval of well screen. Monitoring wells are typically screened across heterogeneous material such as sands, silts, and clays that can influence groundwater flow and contaminant migration pathways. Therefore, contaminant concentrations can vary or be stratified within a well-screen interval.

PDB samplers are an effective tool for the characterization of vertical VOC stratification in the screened or open intervals of wells. PDB samplers will equilibrate with groundwater immediately adjacent to the well screen, measuring the VOC concentration along the screen interval where the PDB sampler is deployed. Therefore, it is recommended that if contaminant stratification is present in a well the appropriate depth for any planned single sampler deployment be determined. Initially, any well having more than 5 feet of well screen or open borehole below the groundwater surface should be evaluated for potential contaminant stratification. If multiple PDBs are deployed for this evaluation, there should be no more than five feet of separation between the midpoints of adjacent PDBs. In contrast, well-purge sampling will provide a composite VOC concentration over an interval that may comprise the entire well-screen length. Generally, the determination of vertical contaminant concentration gradients will be neither practical nor necessary if a well has a screen or open area length of five feet or less below the groundwater surface. However, it should be noted that stratification of trichloroethylene (TCE) has been observed over distances of as little as three feet (Vroblesky, 2001b). A single PDB sampler deployed in such a short interval can practically represent the limited interval of the aquifer that is in direct communication with the well. However, in wells with screens or an open area length of more than five feet, it is recommended that the presence or absence of vertical stratification of VOC concentrations be determined because knowledge of these gradients is necessary for the effective interpretation of PDB data and to optimize the placement of PDB samplers.

In contrast to PDB sampling, well-purge sampling collects a flow-weighted composite sample from some volume of aquifer over an interval that may comprise the entire wellscreen length and beyond. Because low-flow and PDB sampling are more depth-specific, a somewhat more detailed knowledge about the contaminant distribution and flow regime within the well is needed to interpret these results within the context of a well-defined conceptual site model. The Diffusion Sampler Workgroup recognizes that low-flow sampling

November 6, 2002

inlets have in the past often been placed mid-screen without any consideration or investigation of contaminant stratification. However, the Workgroup does not support this practice for the deployment of PDB samplers.

A variety of techniques can be used to determine the presence of vertical stratification. If depth-specific concentration data are available from low-flow methods, discrete-depth sampling during the drilling of the well, or some other type of depth-discrete sampling within the well, it may be possible to use such data to identify the optimum location for placement of one or more PDB samplers. At individual wells where substantial historical data indicate that the flow system and plume configuration are relatively stable or predictable over time, it may be possible to profile a well using PDB samplers placed at different depth intervals during successive sampling events to develop a complete vertical profile while keeping initial deployment costs low. In all cases, detailed stratigraphic information, lithologic or grain-size data, geophysical logs, flowmeter data, and other available information should be considered in addition to contaminant concentration data; in this way, the decision regarding where and how many PDB samplers should be deployed is based on an understanding of the hydrogeological context rather than only contaminant concentrations.

If available data are insufficient to adequately characterize contaminant stratification in a particular well, multiple PDB samplers may be deployed along the saturated screened interval to develop a vertical contaminant profile. For profiling purposes, as a general rule, a single 1.5- to 2-foot long PDB sampler should not represent more than 5 feet of screened interval. If multiple lithologic units with contrasting hydraulic conductivities or multiple fracture zones are present within a 5-foot interval, more than one PDB sampler may be required to adequately determine the contributions of the various horizons. When possible, the deployment depths of the PDB samplers in the profile should target horizons determined from examination of the existing data. Placing PDB samplers at regular default intervals along the well screen may result in data that cannot be attributed to any specific unit or zone because they were located at the interface between units, making interpretation of the results more difficult.

After a vertical contaminant concentration profile has been established for a well, the need to repeat the profiling process after a period of time will depend on the dynamics of the groundwater system. Generally, re-profiling wells should not be necessary. A well may need to be profiled again if contaminant concentrations at that particular sampling location vary widely over time or if water-level data indicate that the hydraulic stresses on the system at that location have changed substantially from the stresses present when the well was originally profiled.

#### 2.4.2 Vertical Flow within the Well

Vertical flow within a well is more commonly found in bedrock aquifers, but can occur in unconsolidated formations, or anywhere a screened interval or open borehole intersects zones

of differing hydraulic head. If vertical flow is present in a well, the VOC concentration in the PDB will be representative of the water flowing vertically past it from another portion of the aquifer rather than of the groundwater quality in the adjacent formation. One means of accomplishing this evaluation of vertical flow in a well is to use a borehole flowmeter to collect measurements across the entire well screen interval or open borehole. Using flowmeter data in conjunction with vertical profiling will provide a better understanding of contaminant distribution within the aquifer.

For wells that have a 20-foot or longer saturated interval of well screen or open borehole, testing for vertical flow is recommended. The vertical spacing of measurements along the saturated screened interval or open borehole should generally be made no less than one measurement every 2 feet unless there is sufficient justification for longer intervals. Similar testing for wells having a saturated interval of well screen or open borehole of 10–20 feet should be considered if piezometric or other data indicate vertical flow may be of concern.

#### 2.4.3 Horizontal Flow

PDB samplers require sufficient groundwater flow to provide equilibration with the aquifer. For water in the well to be representative of the aquifer, the rate of solute contribution from the aquifer to the well must equal or exceed the rate of in-well contaminant loss, such as by volatilization or convection. This may not occur where groundwater velocities are very low or the well has a low-yield, which is commonly the result of a very low gradient or a very low hydraulic conductivity. There is currently no data on the performance of PDB samplers in these situations.

PDB sampling is probably unsuitable for wells in which water in the screened interval becomes effectively stagnant. Less suitable wells also include those that are poorly designed, constructed, or developed. Wells so inefficient that they are pumped dry during conventional sampling are unlikely to be suitable candidates for PDB sampling. Of course, sampling from such wells is problematic regardless of sampling method.

#### 2.5 Determining Deployment Depth

The depth at which a PDB sampler is deployed should not be arbitrary. The decision must be made based on knowledge of the aquifer, contaminant distribution, well construction, flow within the well, and historical sampling results. After the user has an adequate understanding of the hydrogeologic environment and contaminant distribution at a given monitoring well, there remains the question of the depth at which a PDB sampler should be deployed to collect samples that are appropriate for the purposes of the monitoring program. That decision must be made in accordance with site-specific—and even well-specific—DQOs.

It is critical that a PDB remain submerged during the sampling period. Contact with the air will allow an exchange of VOCs between the PDB and the atmosphere. Consideration must

be given to the potential fluctuation of groundwater levels in the well being monitored to assure the PDB will remain submerged during the sampling period. This is particularly important where long deployment times are planned.

The screened interval of monitoring wells often contains intervals with varying degrees of groundwater yield and varying levels of contamination. The highest contaminant concentrations may be observed in a highly conductive interval that represents a preferential pathway for migration of contaminants away from a source area. Conversely, some very fine-grained intervals may contain high contaminant concentrations; they would not be expected to contribute significantly to mass flux in the aquifer, or to a pumping well.

To determine which depth interval is the most critical to monitor with a PDB sampler, it may be beneficial to view the system in terms of mass flux, asking the question "where is the majority of the contaminant mass moving through the well under ambient stress conditions?" The PDB sampler should then be positioned to monitor the interval that is representative of the largest portion of the total contaminant mass. In most cases, that will mean monitoring the interval with the highest contaminant concentration that is also capable of yielding a significant amount of flow under stressed conditions. However, that could change over time, particularly at sites that are undergoing active remediation efforts.

If much of the contaminant mass has been removed from the more productive zones within the aquifer, localized fine-grained intervals of the overall aquifer may contain the majority of the remaining contaminant mass and may act as a source of continuing mass loading to the groundwater through desorption of contaminants. If continuing remediation efforts are focused on removing the sorbed contaminants from the fine-grained materials, it would be consistent with the remediation objectives to place PDB samplers adjacent to those strata, at least in those areas where the removal efforts are taking place. Wells located on the perimeter of the plume may need to be monitored in higher conductivity zones that represent migration pathways away from the treatment area.

These particular scenarios are presented only to illustrate that the placement of PDB samplers has to be consistent with the specific monitoring objective for a particular monitoring well, noting that the objectives for different wells in the monitoring system will be different, and the monitoring objectives for a particular well may change during the life of the project.

#### 2.6 Diffusion Sampler Bag Size

A variety of PDB lengths and diameters can be employed during field demonstrations. Factors to consider include the volume of sample needed for analysis (shorter or thinner bags provide less water) and the need for sample homogeneity (a very long bag is difficult to handle and may exhibit concentration variability along its length). A bag length of 2 feet or slightly less is commonly used with bag diameters accommodating a 2-inch well. The

maximum interval sampled by a single PDB should not exceed 5 feet, so that several PDBs in series may be required to sample a large well interval. Manufacturers are generally able to accommodate a variety of well diameters and bag lengths.

#### **2.7 Compliance Sampling**

Although the major use of LTM results is to track temporal changes in the extent and degree of aquifer contamination, there are other monitoring applications for PDB samplers. Monitoring for site closeout entails evaluating groundwater quality against specific waterquality goals. Given that PDB sampling is a valid and defensible technique that produces representative samples, it is the Diffusion Sampler Workgroup's judgment that it is an acceptable means for collecting site closeout data. There is no reason to expect that other sampling techniques produce results that are either superior or more protective than PDB sampling. DQOs and knowledge of the site should guide the decision on the most appropriate sampling technology to employ.

Sentinel wells are another potential application for PDBs. These wells are placed between areas of contamination and drinking-water wells to provide an early warning of any contamination migrating toward the drinking-water wells. PDB samplers might be advantageous in that they could potentially detect contamination that would be diluted below detection limits using well-purge sampling techniques. However, if a sentinel well has a screened interval longer than five feet, a single PDB might not detect contamination flowing above or below the placement depth of the bag. Multiple PDBs would be needed at these wells. Furthermore, because sentinel wells may be sampled less frequently than LTM wells, the effectiveness of PDBs over the longer deployment times would need to be demonstrated at specific wells. Again, DQOs and knowledge of the site should dictate whether PDBs are appropriate for sentinel wells.

# **3** Conversion to PDB Monitoring

There are a number of technical and regulatory issues that must be addressed if PDB sampling is substituted for other sampling methods for LTM. These issues must be examined within the context of the particular project objectives, data needs, and site conditions of each potential application.

### 3.1 Acceptability of PDB Sampling

To be acceptable to regulators PDB samplers have to be appropriate to meet the data requirements at a site or a particular well. In addition, regulators are concerned that the sampling results be correctly interpreted. Appropriateness is determined by the DQOs of the monitoring, and by the ability of the samplers to reliably obtain a representative sample. Correct interpretation of sampling results requires the evaluation of factors that affect the ability of a PDB sampler to obtain a suitable sample, including target contaminants, well

construction, vertical and horizontal flow within the well, and contaminant stratification; these factors are discussed in Section 2. Any proposal to use PDB samplers should consider an evaluation of these factors.

When considering a change in sampling methods, a natural question that arises is how the results using the new and existing methods compare. It is important to remember that existing sampling methods are not "correct" simply because they have been in place for a time. Comparison of results obtained using different sampling methods is problematic because the different methods seldom produce similarly representative samples. Therefore, regulators should not expect that PDB sampling results will duplicate results from other sampling techniques.

It must be kept in mind that there are inherent limitations with every groundwater sampling method. When pumping a well, contaminants could be drawn into the well from locations that would not naturally flow into the well. As such, results from purging and passive sampling techniques could be significantly different. If results from PDB samplers do not agree with results from purge methods, it does not necessarily mean the bags are inappropriate for the intended application. Poor correlation between sampling methods means that additional work needs to be done to determine why the discrepancy exists.

# **3.2** Comparing PDB Sampling Results with Results from Other Sampling Methods

Different sampling methods collect water that differs in its contributory source—vertically and horizontally, as well as temporally. Therefore, differences in analytical results between PDB sampling and other methods should be expected. Similar results are not required for PDB data to be acceptable. The sampling method should be compatible with the appropriate site-specific DQO. The results must be consistent, coherent, and interpretable in context with all available information. There is no specific definition of "comparable" at present. It is essential that all parties involved in the deployment of PDBs at regulated sites identify and agree on DQOs, data evaluation criteria, and data end use before the PDBs are deployed.

The desirable extent and frequency of sampling methodology comparisons are often dependent on the results from a specific well. A common supposition may be that it is necessary to conduct a side-by-side comparison of PDB sampling with the current sampling method. While this approach would be prudent for wells that have demonstrated considerable variability in contaminant concentrations and groundwater elevations over time, for wells that have historically shown little variation in contaminant concentrations and groundwater elevations, comparison of PDB sampler results to historical sampling results may provide enough information to determine whether PDB samplers are appropriate for the application. LTM programs generally emphasize evaluating trends, and reports should clearly identify where a change in sampling method occurred.

Statistical approaches that have been used for comparisons include an evaluation of the relative percent deviation between the results of two different sampling methods and calculated correlation coefficients between results obtained by two different sampling methods. The results are seldom clear across the board but vary by well and contaminant. Often, a particular contaminant will behave differently in two different wells at the same site. Although they may provide additional insight of the sampling process, statistical evaluations will generally not provide a clear path to the acceptance or rejection of PDB sampling. It is likely that long-term trend analysis will provide the most useful information.

Statistical regressions of PDB sampling data versus data from other sampling methods are often misleading. Outlying data can produce a high correlation coefficient that is virtually meaningless. Therefore, statistical regressions should not be required for the comparison of PDB sampling with other technologies. A simple plot of PDB sampling data and other sampling data in relation to a 1:1 concentration line may provide a meaningful visual interpretation. Wells exhibiting outlying data on a scatter plot should be examined by comparing the conventional sample to a vertical profile to evaluate the possibility that the observed concentration differences are due to mixing. If relative percent deviation is used to evaluate the comparability of sampling results, it is important to remember that variations in results for <u>duplicate</u> samples using the same sampling technique are often 50 percent or more. It is also important to remember that higher concentrations indicated by PDB samplers over conventional sampling results do not mean that environmental conditions are worse than originally thought. The data must be interpreted within the context of the sampling method.

#### 3.3 Deployment of PDBs in Wells with Dedicated Pumps

The successful deployment of PDB samplers in a four-inch well with a dedicated pump is unlikely if the PDB needs to be placed below the pump. The best chance for successful deployment below the pump is in wells that are straight and plumb with diameters of at least four inches. Further, the wire and tubing in the well should be tightly bundled, under tension, and have no protruding ties or wires. It is unlikely that the PDB sampler can be placed *below* the pump unless the well diameter is much larger than the pump diameter and the well is plumb. Because dedicated pumps are generally sized to the well, it is unlikely that there will be sufficient space between the pump and the wall of the well to allow for passage of the PDB sampler. Thus, for deployment of PDBs, it is essential that the pump is located within the screened interval and that sufficient screen is available above the pump to expose the PDB sampler to moving groundwater. Pumps should not be operated during the time interval a PDB is deployed because they would disturb the natural flow regime.

PDB samplers have been successfully deployed above dedicated pumps in 4 inch wells. Whether placement of a PDB sampler at the top of the pump will prove adequate for monitoring depends upon the length of the pump, the pump intake, and the position of the

pump relative to the screened interval. For wells with pumps placed near the middle or lower portion of the screened interval, it is likely that a PDB sampler can be placed within the screened interval.

#### **3.4 Changes in Regulatory Agreements and Documents**

Existing regulatory permits, consent orders, and other agreements may contain model language and/or sampling and analysis plans that stipulate a specific methodology for the collection of groundwater samples. In addition, agency guidance documents may also state a preference for a specific sampling methodology. Discussions with regulators should be held prior to the decision to deploy PDB samplers to determine if alternative technologies will be acceptable. Negotiations may be needed in order to modify or amend permits, orders, and sampling plans; in some instances, public meetings may be required.

### **4 Summary and Recommendations**

PDB sampling technology has been validated by both laboratory and field tests. Although it does not provide a single solution to monitoring needs at remedial sites, specific applications of this technology can be effective both technically and from a cost-savings standpoint. Regulators should support the use of this technology where appropriate.

#### 4.1 Recommendations

The ITRC Diffusion Sampler Workgroup makes the following recommendations regarding the application of PDB sampling to LTM. It is worth noting that many of these recommendations have broad application to all groundwater sampling techniques and are not restricted to PDB sampling.

- 1. PDB sampling is equally as valid as low-flow and other conventional methodologies for certain VOCs. Results obtained from each of these sampling methods may differ. As with other sampling technologies, PDB sample collection must be matched to site-specific DQOs.
- 2. PDBs may indicate contaminant concentrations that are higher or lower than those obtained using other sample collection methods. Therefore, it is essential that all parties involved in the implementation of PDBs for LTM at regulated sites identify and agree on DQOs, data evaluation techniques, and data end use before actual PDB deployment takes place.
- 3. Potential vertical variations in VOC concentrations (stratification) should be considered when determining placement of PDBs in a well for LTM. For saturated well screens five feet or less, a single 18-inch long PDB should suffice to characterize the saturated screened interval. In general, if PDBs are used to investigate vertical concentration

November 6, 2002

stratification, an 18-inch long PDB should represent no more than five feet of a saturated screened interval or borehole.

- 4. If a well has a saturated screened interval or open borehole of 20 or more feet, it is recommended that a flowmeter or other comparable means be used to assess vertical flow. For screened well intervals less than 20 feet, an assessment should be considered if other site data suggest that significant vertical flow may exist.
- 5. "Side-by-side" comparisons of sampling technologies may be necessary to establish the applicability of PDB sampling to a well. In wells where there has historically been little variation in contaminant concentration and groundwater elevation, comparison of PDB sampler results to the historical record may provide enough information to determine whether PDB sampling is appropriate for the well.
- 6. The deployment of a single PDB sampler should be at a depth corresponding to the zone of highest contaminant mass flux. This may be the depth with the highest contaminant concentration.
- 7. Re-profiling wells or changing an established PDB monitoring point is not necessary unless there is evidence to suggest that there have been changes in contaminant transport, hydrodynamics, or well characteristics since the initial profile was obtained.
- 8. The recommended minimum equilibration period for PDBs is two weeks for water temperatures above 10°C. No maximum deployment period has been identified, but PDBs have been successfully left in wells for three months and longer.
- 9. PDB sampling may be used for compliance purposes, including sentinel well monitoring and site closeout. If PDBs are used in sentinel wells with saturated screen or borehole lengths greater than five feet, multiple PDB monitoring points are recommended.

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# **APPENDIX A**

# Acronyms

# Acronyms

DQO	Data quality objective
DSIC	Diffusion Sampler Information Center (ITRC website)
ITRC	Interstate Technology and Regulatory Council
LDPE	Low-density polyethylene
LTM	Long-term monitoring
PDB	Polyethylene diffusion bag
SVOC	Semivolatile organic compounds
TCE	Trichloroethylene
USGS	U.S. Geological Survey
VOC	Volatile organic compound

# **APPENDIX B**

# **Recommendations Keyed to Document Sections**

November 6, 2002

#### Table B-1. Matrix of Recommendations and Applicable Sections.

Re	Recommendation Section												
#	Description	1.1	1.2	2.1	2.2	2.3	2.4.1	2.4.2	2.5	2.7	3.1	3.2	3.4
1	PDB sampling is equally as valid as low-												
	flow and other conventional methodologies												
	for certain VOCs. Results obtained from												
	each of these sampling methods may differ.	Х	Х	Х	Х					Х	Х	Х	
	As with other sampling technologies, PDB												
	sample collection must be matched to site-												
	specific DQOs.												
2	PDBs may indicate contaminant												
	those obtained using other sample collection												
	methods. Therefore, it is essential that all												
	parties involved in the implementation of		v	v								v	v
	PDBs for LTM at regulated sites identify and		Λ	л								Λ	Λ
	and data end use before actual PDB												
	deployment takes place.												
3	Potential vertical variations in VOC												
	concentrations (stratification) should be												
	considered when determining placement of												
	PDBs in a well for LTM. For saturated well												
	screens five feet or less, a single 18"-long												
	PDB should suffice to characterize the						Х						
	saturated screened interval. In general, if												
	PDBs are used to investigate vertical												
	concentration stratification, an 18"-long												
	PDB should represent no more than five feet												
	of a saturated screened interval or borehole.												
4	If a well has a saturated screened interval or												
	open borehole of 20 or more feet, it is												
	recommended that a flowmeter or other												
	comparable means be used to assess vertical												
	flow. For screened well intervals less than							X					
	20 feet, an assessment should be considered												
	if other site data suggest that significant												
	vertical flow may exist.												

Re	commendation	Section											
#	Description	1.1	1.2	2.1	2.2	2.3	2.4.1	2.4.2	2.5	2.7	3.1	3.2	3.4
5	"Side-by-side" comparisons of sampling technologies may be necessary to establish the applicability of PDB sampling to a well. In wells where there has historically been little variation in contaminant concentration and groundwater elevation, comparison of PDB sampler results to the historical record may provide enough information to determine whether PDB sampling is appropriate for the well.		X								х	х	
6	The deployment of a single PDB sampler should be at a depth corresponding to the zone of highest contaminant mass flux. This may be the depth with the highest contaminant concentration.								Х				
7	Re-profiling wells or changing an established PDB monitoring point is not necessary unless there is evidence to suggest that there have been changes in contaminant transport, hydrody namics, or well characteristics since the initial profile was obtained.						x						
8	The recommended minimum equilibration period for PDBS is two weeks for water temperatures above 10°C. No maximum deployment period has been identified, but PDBs have been successfully left in wells for three months and longer.					x							
9	PDB sampling may be used for compliance purposes, including sentinel well monitoring and site closeout. If PDBs are used in sentinel wells with saturated screen or borehole lengths greater than five feet, multiple PDB monitoring points are recommended.		х							х			