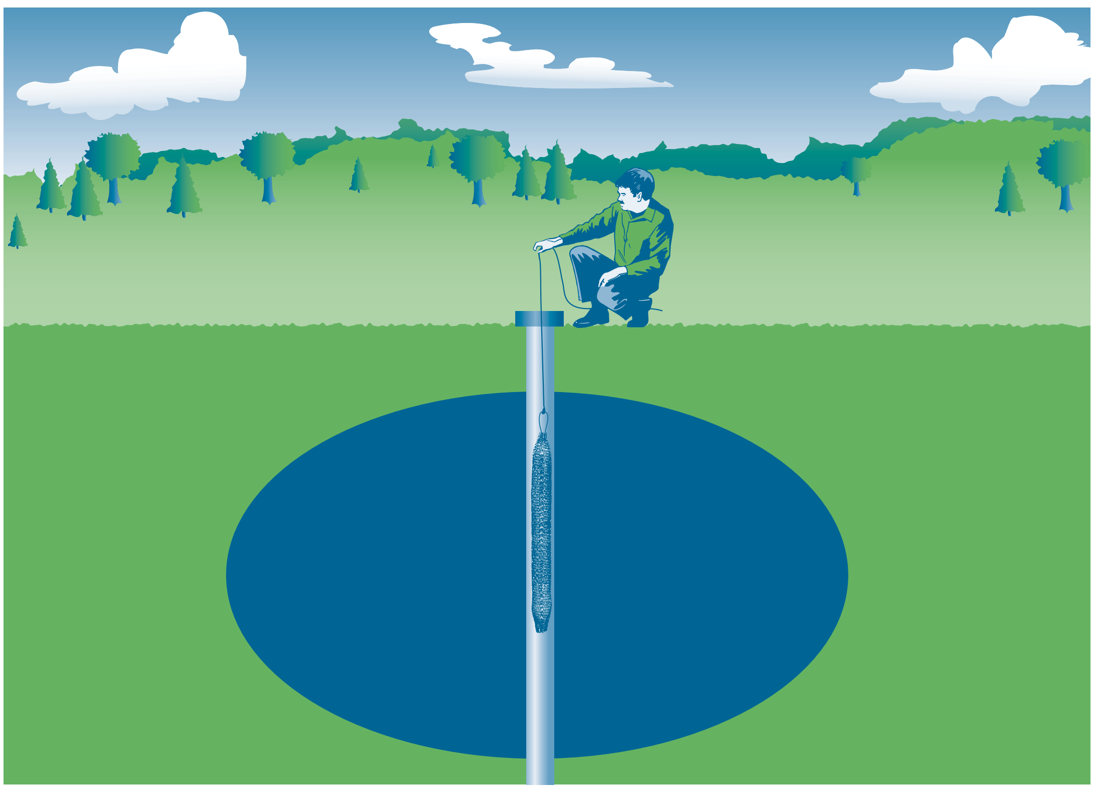
Technical/Regulatory Guidelines

Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Groundwater



February 2004

Prepared by
Interstate Technology & Regulatory Council
Diffusion Sampler Team

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EXECUTIVE SUMMARY

Polyethylene diffusion bag (PDB) samplers are low-density polyethylene bags containing deionized water, used to collect water samples in groundwater wells for laboratory analyses of volatile organic compounds (VOCs). PDB samplers are passive devices, relying on the movement of groundwater from the aquifer or water-bearing zone through the screen or open interval of a well. VOCs in groundwater diffuse across the bag material until concentrations within the bag reach equilibrium with those in the surrounding groundwater. The technical basis for use of PDB samplers is presented in the U.S. Geological Survey Water Resources Investigations Report *User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells* (Vroblesky 2001a, 2001b). The document in hand should be used in conjunction with the technical guidance in that report.

PDB samplers cannot be used to sample for all contaminants; metals and other inorganic compounds will not diffuse across the membrane. However, many VOCs have shown good diffusion characteristics in laboratory tests and are recommended for sampling with PDBs. For these common contaminants (listed in Section 1), PDB sampling is as valid as low-flow and other conventional methodologies and is often substantially less expensive over the life of a long-term monitoring (LTM) program. Cost savings in the range of 40%–70% have been achieved by replacing other sampling methods with PDB sampling. PDB samplers can also be an effective tool to characterize vertical VOC stratification in the screened or open intervals of wells and have been used to identify and delineate groundwater flow into surface waters.

This document provides a guide for regulators, technology users, and stakeholders to facilitate the use of PDB sampling, particularly for LTM. The technical guidelines for implementation in Section 2 are a consensus of the Interstate Technology & Regulatory Council (ITRC) Diffusion Sampler Team, which includes participants from nine different state regulatory agencies, as well as representatives from federal agencies, academia, and the private sector. Section 3 contains a set of sequenced questions to provide a quick preliminary screening of a site's potential for PDB sampling. Section 4 discusses regulatory issues related to PDB use, considers potential regulatory impediments to the implementation of PDB sampling, provides suggestions for expediting the process, and reports on a survey of state regulators' acceptance of the technology. No regulatory issues were identified that would restrict the application of PDBs in technically appropriate situations. The final sections provide a cost model to estimate the potential savings associated with conversion to PDB monitoring and present some case histories of the technology's implementation.

Groundwater sampling is performed to collect a sample that is representative of conditions in the aquifer. Inherent differences between various sampling techniques may produce results that generate different representations of the aquifer, but 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. PDBs may indicate contaminant concentrations higher or lower than those indicated 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 data quality objectives (DQOs), data evaluation techniques, and data end use before actual PDB deployment takes place.

Regulatory guidance documents and permits, consent orders, other agreements, and sampling and analysis plans may specify or state a preference for a specific sampling methodology. Discussions with regulators should be held before deciding to deploy PDB samplers to determine whether alternative technologies will be acceptable. Negotiations may be needed to modify or amend permits, orders, and sampling plans; in some instances, public meetings may be required. Side-by-side comparisons of sampling technologies may be necessary to establish the applicability of PDB sampling to a well; however, for 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.

Potential vertical variations in VOC concentrations (stratification) should be considered when determining placement of PDBs in a well for LTM. The deployment of a single PDB sampler should include consideration of site-specific DQOs. Deployment of a single PDB may or may not be at the depth with the highest contaminant concentration. Reprofiling wells or changing the vertical location of an established PDB monitoring point is not necessary unless evidence suggests that there have been changes in contaminant transport, hydrodynamics, or well characteristics since the initial profile was obtained. The recommended minimum equilibration period for PDBs is two weeks for water temperatures above 10ºC. No maximum deployment period has been identified, but PDBs have been successfully left in wells for three months and longer. Concentrations of VOCs in the PDB reflect the aquifer conditions one to four days prior to the recovery of the PDB.

In general, when PDBs are used to investigate vertical concentration stratification, an 18-inch-long PDB should represent no more than 5 feet of a saturated screened interval or borehole. 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 5 feet, multiple PDB monitoring points are recommended.

The ITRC Diffusion Sampler Team conducted a survey of state regulators in May 2003, primarily to identify any rules or regulations that would impede the implementation of PDB sampling. None were identified. The survey also sought the regulators' familiarity with PDBs and their views on specific applications for the technology. Based on the 54 responses received from 23 states, there is widespread regulatory support for using PDB sampling technology, particularly for LTM. Acceptance has been gained as more professionals become aware of its advantages. At the same time, awareness of its limitations justifiably results in "conditional" approval by many regulators. The application of PDBs should always be governed by site characteristics and DQOs.

This guidance document will help reduce regulatory barriers to the implementation of PDB sampling by educating regulators on the correct use, applications, and limitations of the technology; discussing issues of common concern to regulators; and providing tools (e.g., the decision tree and cost model) to aid in evaluating the potential for PDB sampling at a site.

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TECHNICAL AND REGULATORY GUIDANCE FOR USING POLYETHYLENE DIFFUSION BAG SAMPLERS TO MONITOR VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER

1. INTRODUCTION

This document provides a guide for regulators, technical and field personnel, and stakeholders to facilitate the use and implementation of polyethylene diffusion bag (PDB) sampling, particularly for long-term monitoring (LTM). The technical guidelines presented in Section 2 represent a consensus of the Interstate Technology & Regulatory Council (ITRC) Diffusion Sampler Team, which includes participants from nine different state regulatory agencies, as well as representatives from federal agencies, academia, and the private sector. This document also discusses the regulatory issues related to PDB use, considers potential regulatory impediments to the implementation of PDB sampling, and provides suggestions as to how the process might be expedited. Also included are a "decision tree" to provide a quick preliminary screening of site potential for PDB monitoring, a cost model to estimate the potential savings associated with conversion to PDB monitoring, and some case histories involving implementation of this technology. Although diffusion samplers can have membranes composed of various materials, this discussion is limited to the use of low-density polyethylene (LDPE) bags filled with deionized water and used for specific volatile organic compounds (VOCs).

The technical basis for use of PDB samplers is presented in the two-part 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). The document in hand should be used in conjunction with the technical guidance in the *User's Guide,* which is also available through the ITRC Web site (http://www.itrcweb.org) as a single volume.

1.1 Description

PDB samplers, which are LDPE bags containing deionized water, are used to collect water samples for laboratory analyses of VOCs. In groundwater wells, PDB samplers act as passive devices, relying on the ambient movement of groundwater from the aquifer or water-bearing zone through the well screen (for a detailed example demonstration of ambient flow-through, see Robin and Gillham 1987). VOCs in groundwater diffuse across the bag material until constituent concentrations within the bag reach equilibrium with concentrations in the surrounding groundwater.

PDB samplers are made of LDPE plastic (typically 4 mils thick) in the shape of a tube, filled with deionized water, and sealed at both ends (Figure 1-1). The samplers are typically about 18–20 inches in length and 1.25 inches in diameter; they hold 220–350 mL 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. The PDB shown in Figure 1-1 has a plastic mesh sock surrounding the PDB to protect it against physical damage during deployment and recovery. A list of vendors for PDB samplers can be found online at ITRC's Diffusion Sampler Information Center (DSIC) Web site (http://ds.itrcweb.org).

Figure 1-1. PDB sampler ready for deployment.

1.2 Uses, Limitations, and Application

Many VOCs have shown good diffusion characteristics in laboratory tests using PDBs submerged and equilibrated with known concentrations of selected VOCs (Table 1-1). PDB samplers have also been successfully used at a variety of field sites (Vroblesky and Hyde 1997, Parsons 1999, Church 2000, Hare 2000, McClellan 2000, Vroblesky et al. 2000, Vroblesky and Peters 2000, Vroblesky and Petkewich 2000). Other PDB sampler field studies (Parsons 2003) suggest that PDBs can be suitable for analytes beyond those listed in Table 1-1. These laboratory and field studies demonstrate the PDB sampler is an appropriate sampling technology for many VOC contaminants in groundwater. However, PDB samplers cannot be used to sample for all contaminants. For example, metals and other inorganic compounds will not diffuse across the LDPE membrane. PDBs should not be used to sample for contaminants that have not been shown to diffuse across the sampler membrane. It has also been observed that site- or well-specific conditions can adversely affect PDB performance for some analytes that performed well in laboratory testing. Section 2 discusses in detail factors that should be considered when evaluating the applicability of PDB sampling at a site.

Table 1-1. Compounds tested in the laboratory (Vroblesky 2001a)

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	Trichlorofluoromethane
2-Chlorovinylether	*cis*-Dichloropropene	1,2,3-Trichloropropane
Dibromochloromethane	1,2-Dibromoethane	Vinyl chloride
Dibromomethane	*trans*-1,3-Dichloropropene	Xylenes (total)
1,2-Dichlorobenzene	Ethyl benzene	
Unfavorable laboratory diffusion testing results		
Acetone	Methyl *tert*-butyl ether	
Methyl *iso*-butyl ketone	Styrene	

The potential for in-well flow and mixing should be considered when implementing passive sampling techniques. In some wells, vertical uniformity in VOC concentrations is observed in the screened interval of under field conditions. Figure 1-2 shows relatively uniform

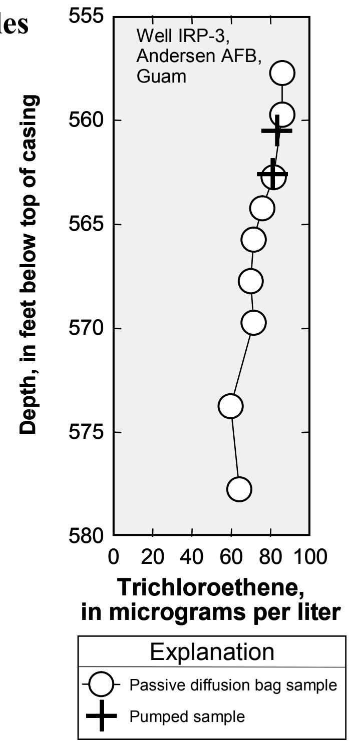

Figure 1-2. (right) Comparison of diffusion and pumped samples in groundwater showing relative uniformity in vertical distribution of trichloroethene concentrations in the screened interval of a well (modified from Vroblesky et al. 2003).

concentrations in a well where vertical flow was present in the screen. In addition, observations from a laboratory study using a sand-tank model in approximately two dimensions (Britt and Tunks 2003) imply that diffusive mixing may be an important consideration. In other wells, however, stratification in well screens is observed under natural conditions (Figure 1-3). The source of this stratification may include such factors as vertical differences in contaminant concentrations outside the well screen, vertical flow through a portion of the well screen, density contrasts, and, in wells screened at the water table, volatilization loss at the air/water interface.

Multiple PDBs deployed along the saturated screened interval or open borehole of a well can provide information on the vertical distribution of contaminants within the well (Figure 1-3). When the stratification reflects aquifer stratification or zones of inflowing

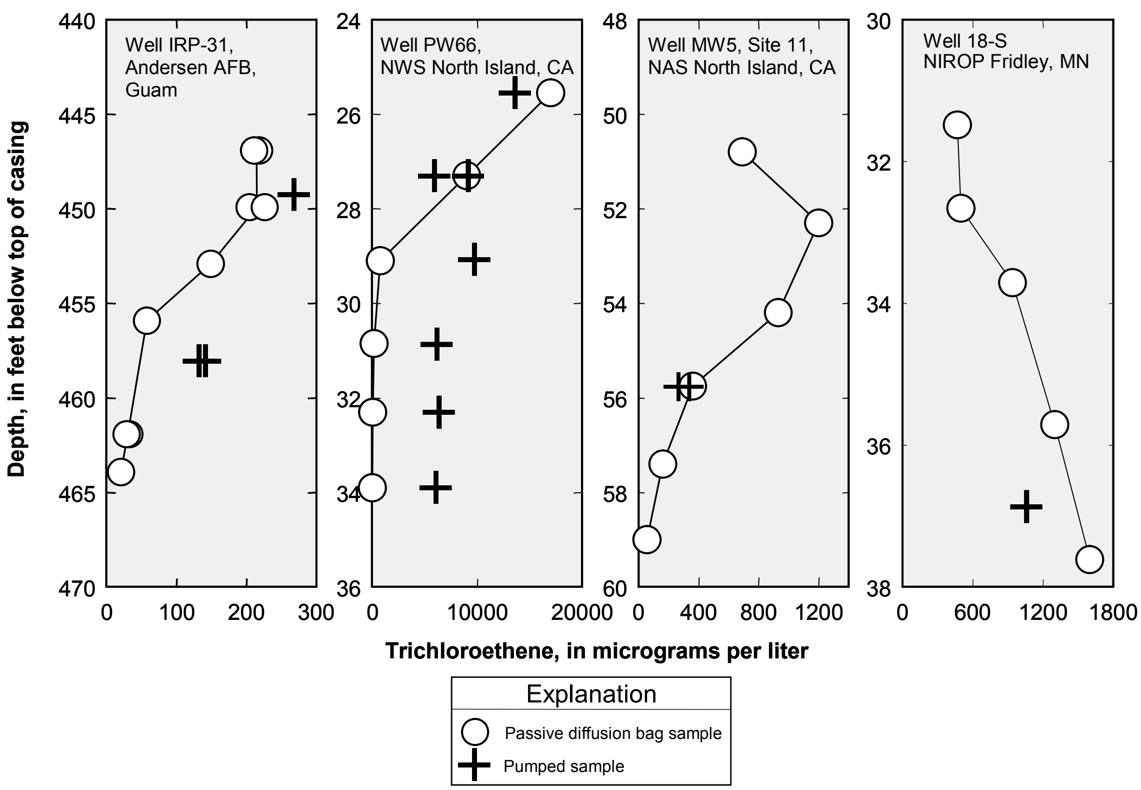

Figure 1-3. Comparison of diffusion and pumped samples in groundwater showing vertical stratification of trichloroethene in the screened interval (modified from Vroblesky and Peters 2000, Vroblesky and Petkewich 2000, Vroblesky et al. 2003).

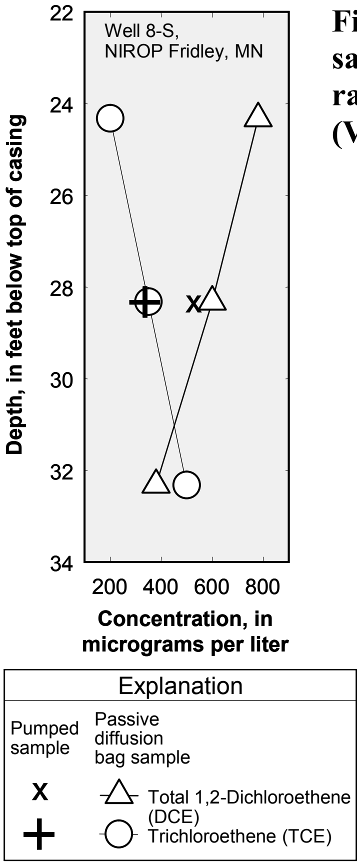

Figure 1-4. (at left) Comparison of diffusion and pumped samples in groundwater showing an apparent shift in TCE/DCE ratio between the top and bottom of the screened interval (Vroblesky and Petkewich 2000).

contamination, the information can assist in locating the zones of highest concentrations. In some cases, the data may provide information on zones of differing biodegradation potential, as implied by the change in the concentrations of the parent compound trichloroethene (TCE) to daughter products, such as 1,2-dichloroethene, across the screened interval shown in Figure 1-4. Determining the vertical distribution of contaminants also is 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 focuses on the use of PDBs for LTM.

1.3 Differences between PDB Sampling and Other Sampling Methods

The goal of groundwater sampling is to collect a sample from the aquifer that meets data quality objectives (DQOs). 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 the correct methodology—each has advantages and limitations. It is important to understand the conceptual bases of and differences between sampling techniques when interpreting sampling results.

1.3.1 Well-Purge Sampling

Well-purge sampling removes multiple well volumes of water prior to sample collection. Purge stabilization parameters—including pH, temperature, and electrical conductivity (EC)—are typically, but not always, measured after each well volume to monitor purge water stabilization. If a flow-through cell is used, dissolved oxygen and oxidation-reduction potential (ORP) can also be measured. Well-purge sampling is sometimes referred to as "conventional" sampling because it has been the approach most widely employed over the past decades. 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. Depending on the amount of water in the well, this method can generate a large volume of purge water requiring disposal, sometimes at great expense.

1.3.2 Low-Flow Sampling

Low-flow purge and sample methods were developed to minimize disturbance of the groundwater system and reduce turbidity in samples. For the low-flow method, completion of purging is based on monitoring stabilization parameters rather than on a strict well-volume prescription. Purge stabilization parameters can include temperature, pH, EC, dissolved oxygen, ORP, and turbidity (Puls and Barcelona 1996). Once some or all of these parameters have stabilized within preset criteria, sampling may commence from the pump discharge stream. Because total purge volumes may be one well volume or less in many circumstances, low-flow sampling greatly reduces the volume of water requiring disposal or treatment compared to well-purge sampling.

The dynamics of low-flow sampling is a subject of continuing study. A low-flow sample may represent a localized volume of water near the pump intake, or it may represent a flow-weighted average of the entire screen length, depending on the volume pumped. Varljen et al. (2004) suggest that low-flow purging generates inflow along the entire well screen, regardless of purge rate or pump location—indicating a flow-weighted averaging effect using common purging or low-flow techniques. Martin-Hayden (2000), however, shows that water from distant portions of a well may require relatively long purging periods to reach the pump intake. The Martin-Hayden study concluded the greatest deviation from the flow-weighted average during purging occurs during the first well volume pumped. This study also showed that in a highly stratified aquifer and unfavorable pump placement, achieving concentrations within 5% of the flow-weighted average may not occur until five well volumes are pumped.

Situations such as this do not mean that low-flow purging would not generate a sample that meets DQOs, but stabilization criteria may not be met until a flow-weighted average is achieved. Thus, purge completion criteria stabilization is critical to ensure that the flow-weighted average concentration of the contaminants is truly achieved.

1.3.3 PDB Sampling

PDB samplers rely on the passive movement of groundwater through the well and the diffusive properties of VOCs and the sampler membrane. During deployment, groundwater VOCs equilibrate with water inside the PDB sampler. PDB samples are not turbid because the membrane, having a pore size of 10 angstroms, excludes colloid-size particles. Because it can take several days for the concentrations in the PDB sampler to equilibrate with groundwater contaminant concentrations, the sample represents a time-weighted contaminant concentration, with emphasis on the last few days prior to recovery. In the absence of vertical flow or other significant mixing within the well, a PDB sample probably represents water in close proximity to the sampler deployment position and may not detect contaminants migrating through the aquifer above or below the sampler position. If head-driven vertical flow exists in the well, Church and Granato (1996) show that water in the well is dominated by water from the zone with the highest hydraulic head. PDB samples in this scenario therefore represent groundwater from the zone of highest hydraulic head. If density-driven or diffusive mixing is dominant in the well, a PDB sample represents something close to a flow-weighted average concentration of the well screen (Britt and Tunks 2003).

Table 1-2 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 possibility 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 4.2.

Table 1-2. Generalized spatial and time domains represented by three groundwater sampling methods

Sampling method	Spatial representation of sample	Temporal representation of sample
Multiple casing-volume purge	A single sample represents a flow-weighted average concentration of water brought to the well during purging. The sample potentially includes water from above or below the screen interval and artifacts from induced mobilization of contaminants from high-flow-rate pumping.	Instantaneous
Low flow	A low-flow sample represents a portion of the screen interval that can vary depending on several factors, including natural flow-through and mixing conditions in the well prior to purging, pump placement, and duration of purging relative to vertical lithologic heterogeneity and contaminant distributions. As the pumping duration increases and the monitored purge parameters approach stabilization, low-flow samples tend to approach a flow-weighted average that may be independent of pump depth.	Instantaneous
PDB	A PDB sample represents groundwater in contact with the sampler membrane, which depends on several factors, including natural flow-through and mixing conditions in the well, lithologic heterogeneity, and vertical contaminant distributions. A PDB sample can represent a mixing of the entire screen length or a more discrete interval of the well, depending on these factors. If head-driven vertical flow along the well screen is present, then the sample concentration is largely influenced by concentrations from the principal inflow sources (i.e., zones of high head).	Time-weighted average, estimated to encompass 1–4 days prior to recovery

The materials and procedures used in PDB sampling are common to groundwater monitoring and do not entail any unusual health and safety issues. However, as with any monitoring regimen, PDB deployment and recovery should comply with an approved, site-specific health and safety plan.

1.4 Diffusion Sampler Information Center

The DSIC Web site (http://ds.itrcweb.org) is maintained by the ITRC Diffusion Sampler Team to provide a centralized location for posting and exchanging information on the development and use of diffusion samplers. The Diffusion Sampler Team includes representatives from the U.S. Air Force, U.S. Navy, U.S. Environmental Protection Agency (EPA), USGS, U.S. Army Corps of Engineers, private industry, and multiple state agencies. Although some ITRC teams have public stakeholders as team members, the Diffusion Sampler Team has not attracted this interest. The team 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 diffusion sampler technology, current information on diffusion sampler training, and links to other useful information sources.

2. TECHNICAL REQUIREMENTS FOR IMPLEMENTATION

When using PDB samplers, it is important to consider DQOs, target analytes, and hydrologic concerns. It is the consensus of the Diffusion Sampler Team 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

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 method, site-specific DQOs should first be established and then used to determine 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. An explanation of the DQO process as it is used by the Department of Energy (DOE) may be found online at http://dqo.pnl.gov/why.htm.

2.2 Target Analytes

Because PDBs depend on diffusion through the polyethylene membrane to collect analytes, the ability of a target compound to readily diffuse into the PDB sampler is essential. Because most non-VOCs will not meet this criterion, PDB samplers should be used for sampling only VOCs and a few other chlorinated and aromatic compounds (Section 1.1, Table 1-1 and Section 4.2.2, Table 4-1). PDBs are generally used for LTM only after a site has been fully characterized using other groundwater sampling methods and there are sufficient data to demonstrate that specific VOCs are the only analytes of concern or when 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; the latter are not recommended for PDB sampling at this time. Table 4-1 lists compounds that have been investigated in field tests. Reports found on the DSIC may provide additional information on the suitability of PDB samplers for other compounds, but further laboratory or field studies are necessary before PDB samplers can be recommended for compounds not listed in Table 1-1 or 4-1.

2.3 Deployment Time Intervals

Many VOCs equilibrate with PDB sampler water within one to four days at temperatures of 10ºC and above, but some require longer periods, up to six days (Vroblesky and Campbell 2001). The recommended minimum deployment period for PDBs is two weeks, which allows ample time prior to retrieval for diffusion to occur between the well water and the PDB sampler. It also allows time for the restabilization of well water and formation water following any disturbance caused by sampler deployment. Restabilization typically occurs relatively rapidly in many situations, except in low-yielding wells. If the water temperature is below 10ºC, additional equilibration time may also be required.

PDBs have routinely been successfully deployed for three-month periods and longer at some sites. Bag integrity is generally not a problem. 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. A demonstration in a well of interest is recommended to verify the validity of PDB deployments longer than three months.

It is worth mentioning that, although biofouling is often raised as a potential problem in the long-term deployment of PDBs, the team does not know of a specific instance where biofouling has been documented. The potential for biofouling during very long deployments of PDBs (over three months) should be investigated on a well-specific basis.

2.4 Hydrological Considerations

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

2.4.1 Contaminant Stratification

A number of factors in a screened interval or open borehole can cause mixing and make a uniform concentration within the screened interval despite the presence of stratification in the aquifer. These include dispersion, in-well vertical flow, and thermal convection. However, studies documented in Part 2 of the *User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells* (Vroblesky 2001b) show that a high degree of variability in contaminant concentrations can sometimes occur within a 10-foot interval of well screen. Monitoring wells are commonly screened across heterogeneous material, such as sands, silts, and clays, which can influence groundwater flow and contaminant migration pathways. Therefore, in some cases, contaminant concentrations can vary or be stratified within a well-screen interval.

PDB samplers can be an effective tool for the characterization of vertical VOC stratification in the screened or open intervals of wells. PDB samplers will equilibrate with groundwater surrounding the sampler during deployment, measuring the VOC concentration at the 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 using project-specific DQOs. 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 5 feet of separation between the midpoints of adjacent PDBs. 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 5 feet or less below the groundwater surface. However, it should be noted that stratification of TCE has been observed over distances of as little as 3 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 5 feet, it is recommended that the presence or absence of vertical stratification of VOC concentrations be determined because knowledge of these gradients is necessary to optimize the placement of PDB samplers and effectively interpret PDB data.

Well-purge sampling collects a flow-weighted composite sample from some volume of aquifer over an interval that may comprise the entire well-screen 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 Team recognizes that low-flow sampling inlets have in the past often been placed midscreen without any consideration or investigation of contaminant stratification. However, the team believes such arbitrary placement is inappropriate for either low-flow or PDB sampling.

A variety of techniques can be used to determine the presence of vertical stratification. If depth-specific concentration data are available (e.g., from previous low-flow or PDB sampling, or discrete-depth sampling during the drilling of 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 on 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 PDB sampler with a nominal length of about 18 inches 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, reprofiling 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 those present when the well was originally profiled.

2.4.2 Vertical Flow within the Well

Vertical flow within a well is commonly found in bedrock aquifers but can also occur in unconsolidated formations or anywhere a screened interval or open borehole intersects zones of differing hydraulic head (e.g., Church and Granato 1996). If vertical flow is present in a well, the VOC concentration in a PDB will represent the water flowing vertically past it from another portion of the aquifer rather than the water in the adjacent formation. One means of evaluating 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 can provide a better understanding of contaminant distribution within the aquifer. Caution should be used when evaluating vertical flowmeter data from a screened interval because, while the flowmeter may provide useful data regarding zones of relatively high and low vertical flow, the data cannot be used quantitatively because part of the vertical flow moves through the annular space outside the screen.

For wells that have a 20-foot or longer saturated interval of well screen or open borehole, testing for vertical flow is recommended unless data exist to argue against it. The vertical spacing of flowmeter measurements along the saturated screened interval or open borehole should generally be every 2 feet unless there is sufficient justification for longer intervals. It is recognized that vertical flow can be of concern in wells with screens or open intervals much less than 20 feet (Hutchins and Acree 2000). As a practical matter, the team consensus is to defer the decision on making vertical flow measurements in these wells to professional judgment. Thus, the selection of the 20-foot interval as a point of differentiation is an arbitrary, although collective, decision.

2.4.3 Horizontal Flow

PDB samplers require sufficient groundwater flow to provide equilibration with the aquifer. Robin and Gillham (1987) showed that with sufficient aquifer flow conditions, groundwater will continually flow through a properly constructed well. Under these conditions, groundwater in the screen interval may be replaced in as little as 24 hours. 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 condition 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 are currently no data on the performance of PDB samplers in these situations.

Wells with sustained yields of less than 100 mL/minute have not been tested using PDB samplers, but all existing technologies have shortcomings in such environments. It is difficult to collect a water sample in low-permeability zones using any type of device, and PDB samplers may provide a practical approach if the restrictions are carefully considered. However, PDB sampling is not recommended 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.

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 decision must be made in accordance with site-specific—and even well-specific—DQOs.

It is critical that a PDB be fully submerged during the sampling period—contact with soil gas or air allows an exchange of VOCs between the PDB and the surrounding gases. Consideration must be given to potential fluctuation of the groundwater level in a well being monitored to ensure that the PDB will remain submerged during the sampling period. This care is particularly important where long deployment times are planned or where water levels are affected by tides.

The screened interval of monitoring wells often contains zones with varying rates of groundwater flow 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, but they would not be expected to contribute significantly to mass flux in the aquifer or to a pumping well.

To determine which PDB deployment interval best represents the monitoring well, site-specific DQOs should be consulted. It may be beneficial to view each well in terms of mass flux, asking the question "Where is the majority of the contaminant mass moving across the well bore under ambient stress conditions?" Other questions such as "Where is the highest concentration of contaminants?" or "Where is the zone of average contaminant concentration?" could be the guiding principles for selection of a single PDB deployment depth. It is possible the appropriate question could change over time, particularly at sites 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. As with all groundwater sampling methods, site-specific DQO should guide decision making.

These particular scenarios are presented only to illustrate that the placement of PDB samplers (or any sampler) 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 may be different and that 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, and manufacturers are generally able to accommodate a variety of well diameters and bag lengths. Factors to consider include the volume of sample needed for analysis (shorter or narrower bags provide less water) and the need for sample homogeneity (a very long bag is difficult to handle and may exhibit concentration variations along its length; some manufacturers insert a mixing ball into long PDBs to encourage efficient mixing upon retrieval). A bag length of 2 feet or slightly less is commonly used, with bag diameters that can accommodate a 2-inch-diameter well. The maximum interval sampled by a single PDB should not exceed 5 feet, so several PDBs in series may be required to sample a large well interval.

2.7 Sample Volume

The length and diameter of the PDB affect the sample volume available for analysis. The standard 18- to 20-inch-long and 1.25-inch-diameter PDB typically holds 220–350 mL of water. This is more than enough sample volume to run the typical analysis for organic volatiles by EPA Method 8260C, including all associated quality assurance/quality control (QA/QC) and any reruns that may be required. However, as the diameter and/or length of the PDB decreases, so does the available sample volume. The minimum volume of sample necessary to run EPA Method 8260C is 20 mL, assuming no method modifications and using currently accepted standard instrumentation. However, this minimum volume will not be sufficient to analyze matrix-spiked and duplicate matrix-spiked samples. Duplicate laboratory control samples may be run to provide precision data, but accuracy data would have to come from batch QC samples. Also, if sample volume is limited to 20 mL, reruns are not possible. If the sample volume will be limited, these considerations and limitations should be discussed with the regulatory agency involved with the project.

2.8 Deployment of PDBs in Wells with Dedicated Pumps

Under some circumstances, such as conducting side-by-side comparative sampling, the presence of a down-well pump is an issue. The successful deployment of PDB samplers in a 4-inch-diameter 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 4 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 saturated screen is available above the pump to expose the PDB sampler to moving groundwater. The pump should not be operated during the time interval a PDB is deployed because it would disturb the natural flow regime.

PDB samplers have been successfully deployed above dedicated pumps in 4-inch-diameter wells. Whether placement of a PDB sampler at the top of the pump proves 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 near the middle or lower portion of the screened interval, it is likely that a PDB sampler can be placed within the screened interval.

Note that, although dedicated pumps currently in use are those that fit 2-inch-diameter wells, smaller diameter pumps (as small as 3/8-inch diameter) are now being manufactured. Such smaller pumps would be less of an obstacle in conducting PDB testing.

3. TECHNICAL DECISION ANALYSIS FOR USING PDB SAMPLERS FOR LONG-TERM MONITORING OF VOCS

The following series of questions is intended to enable someone to quickly screen sites and decide whether PDB samplers might be suitable as stand-alone monitoring devices. It is not meant to be a guide for how to implement PDB sampling. However, before deploying PDB samplers, it would be useful to answer these questions, discuss the use of PDB samplers with the regulators, and complete a cost comparison. A cost analysis model is discussed in Section 5.

1. Is sampling being done for long-term groundwater monitoring?

- *Yes—Go to #2.*
- *No—Stop. Consider use carefully.*

> To date, the recommended use of PDB samplers has been for LTM of groundwater plumes where specific VOCs are the sole target analytes. PDB samplers also have been shown to be an effective tool for characterization of vertical VOC stratification in the screened or open intervals of wells when (1) coupled with borehole flowmeter data and (2) the VOCs are known to be quantifiable using PDB samplers.

2. Have the groundwater contaminants at the site been fully characterized?

- *Yes—Go to #3.*
- *No—Stop. Consider use carefully.*

> PDB samplers should be used for sampling only VOCs and a few other chlorinated and aromatic compounds because of the diffusive properties of these compounds. Their use should be restricted until the site has been characterized using conventional or low-flow groundwater sampling methods and there are sufficient data to demonstrate that VOCs are the only analytes of concern or there is sufficient and conclusive site knowledge that VOCs are the only possible target analytes.

3. Is groundwater sampling at the site focused on VOCs?
- *Yes—Go to #4.*
- *No—Stop. Do not deploy without alternative plans.*

> The ability of a compound to diffuse into the PDB is essential, and most non-VOCs will not meet this criterion. PDB samplers are not suitable for collecting metals or semi-VOCs. Therefore it is inappropriate to use this technology for such analytes.

4. Can all target analytes at the site be expected to be taken up by PDB samplers (see Section 1.1, Table 1-1 and Section 4.2.2, Table 4-1)?
- *Yes—Go to #5.*
- *No—Stop. Consider use carefully.*

> Although most VOCs diffuse well through polyethylene, some do not or have not been properly tested and are therefore not currently recommended for PDB sampling.
>
> Tables 1-1 and 4-1 list compounds that have been the subject of laboratory and field tests. Reports found on the ITRC database at http://ds.itrcweb.org may provide further information on the suitability of PDB samplers for specific compounds. Further laboratory or field studies may be necessary before using PDB samplers for compounds not listed in the tables.

5. Is groundwater temperature anticipated to be above 10ºC (50ºF) during all sampling events?
- *Yes—Go to #6.*
- *No—Further study may be necessary.*

> The equilibration time for PDBs is temperature dependent. Although 14 days is a sufficient period in most instances, there are no equilibrium data for water temperatures below 10ºC (50ºF). Equilibration of the PDB samplers will be slower in cold water, and longer equilibration times may be necessary. A field test should be conducted to demonstrate that temperature is not a significant factor. Figure 3.1 maps groundwater temperatures. As an additional point of reference, groundwater temperatures are generally about 1–2ºC above mean annual air temperatures.

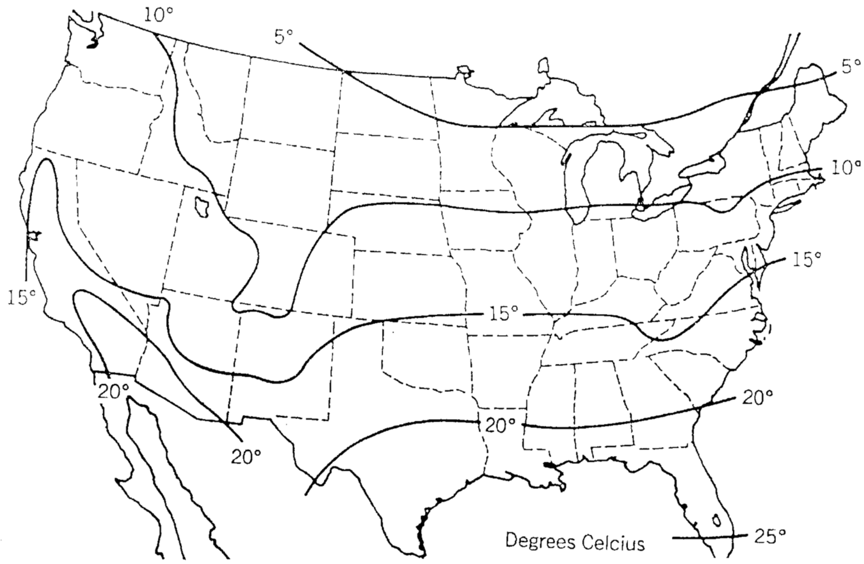

Figure 3-1. Temperature of groundwater in the conterminous United States at depths of 10–20 m (Collins 1925)**.**

6. **Have you discussed the potential use of PDB samplers with regulators?**
   - *Yes—Go to #7.*
   - *No—Stop. Discuss use of PDB samplers with regulators before deployment.*

Existing regulatory permits, consent orders, and other agreements may contain 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 whether alternative technologies will be acceptable. Significant negotiations may be needed to modify or amend permits, orders, and sampling plans, and in some instances public meetings may be required. The overhead costs of these negotiations should be considered in the decision process.

7. **Are site regulators familiar with PDB sampling technology, and will they allow the data to be used for the same purposes as those obtained by conventional sampling?**
   - *Yes—Go to #8.*
   - *No—Stop. Weigh cost and time factors before proceeding.*

Regulators may require some comparative sampling to provide evidence that the use of PDB samplers is valid at a particular site. If these requirements are extensive, costly, and burdensome, there may be no advantage to using PDB samplers. There may be reasons to employ PDB samplers in such an instance, but more information would be needed to evaluate specific situations. ITRC state points of contact (POCs) can serve as a technical resource for regulatory personnel within their own states and may be able to assist in evaluating requests to apply PDB samplers to specific sites. Section 4 of this document discusses regulatory concerns for the use of PDBs.

8. Are the monitoring wells to be sampled in an area where there is sufficient groundwater velocity? Low groundwater velocity can result from either a low hydraulic conductivity or a low hydraulic gradient.

- *Yes—Go to #9.*
- *No—Stop. Wells will need to be evaluated individually for PDB samplers.*

PDB samplers require groundwater flow sufficient to provide equilibration with the aquifer. This may not occur where groundwater is stagnant or the well has a low yield. Volatilization of VOCs in such wells may exceed the rate of replacement from groundwater flow. Wells with sustained yields of <100 mL/minute have not been tested using PDB samplers, but all existing technologies have shortcomings in such environments. It is difficult to collect a water sample in low-permeability zones using any type of device, and PDB samplers may provide a practical approach if the restrictions are carefully considered. Although definitive numbers cannot be provided, a groundwater velocity less than 0.5 feet/day, a hydraulic conductivity $<10^{-5}$ cm/sec, or a hydraulic gradient <0.001 is cause to take extra care in interpreting PDB results.

9. Are monitoring wells currently free of dedicated pumps or other sampling equipment?

- *Yes—Go to #10.*
- *No—Stop. Consider cost of removal.*

Dedicated pump systems (low flow or others) are employed at some sites to reduce costs at frequently sampled wells. They eliminate the need to decontaminate sample equipment and the collection of many types of sample blanks. Although dedicated pumps have a high initial cost, they may last up to 20 years and save money over that extended period. However, PDB samplers might be more cost-effective than dedicated pump systems if the pumps can be used elsewhere, if the pumps are near the end of their life cycle, or where the groundwater conditions significantly reduce the expected pump life. Replacement with PDB samplers might be considered on a graduated basis as old pumps need to be replaced. Deployment of PDBs in wells with dedicated pumps is discussed in Section 2.8.

10. Has a cost analysis shown PDB samplers to offer a cost savings compared to current sampling techniques?

- *Yes—PDB sampling appears to be a viable alternative.*
- *No—Stop. Retain existing sample collection program.*

A primary driving force in the use of PDB samplers is that it can be much less expensive than pump-and-sample technologies. A cost analysis is necessary to estimate whether the deployment of PDB samplers in a specific situation would result in savings. Remember to include in the cost analysis all laboratory or field tests that are likely to be required in a comparison study. Additional costs may incurred by a need to determine contaminant stratification or vertical flow. A cost model suitable for this purpose is presented in Section 5.

The largest cost savings related to the use of PDB samplers are in (1) personnel time on site and (2) the collection and disposal of purge water and the handling and disposal of decontamination fluids used on portable sampling systems. The size of the groundwater sampling operation will affect the cost savings. The cost for disposing of contaminated water and other liquids is site specific because some sites have their own resident treatment facilities. Sites that incur large costs because of off-site disposal are excellent candidates for PDB samplers even when only a modest number of wells are involved.

The above questions have been incorporated into a worksheet to be used as a preliminary screening tool. The worksheet is in Appendix C.

4. REGULATORY ISSUES

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

4.1 Acceptability of PDB Sampling

PDB samplers must be appropriate to meet the data requirements at a site or a particular well. In addition, the sampling results must be correctly interpreted. Appropriateness is determined by the DQOs of the monitoring and by the ability of the samplers to reliably meet them. 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 flows within the well, and contaminant stratification. Any proposal to use PDB samplers should consider an evaluation of these factors, as discussed in Section 2.

When considering a change in sampling methods, the question naturally arises how the results of the existing and new methods compare. It is important to remember that existing sampling methods are not necessarily “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 the same results, although each may be representative of the aquifer in its own way. Therefore, PDB sampling results should not be expected to 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 with groundwater that would not naturally flow into the well. Thus, results from purging and passive sampling techniques could be significantly different. The fact that results from PDB samplers do not agree with results from purge methods 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.

4.2 Comparing PDB Sampling Results with Results from Other Sampling Methods

Different sampling methods collect water that differs in 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 capable of producing data that meet the site-specific DQOs. 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 need and extent of sampling method comparisons are well specific. A common supposition may be that it is necessary to compare PDB sampling conduct side by side with the current sampling method. This approach may, in fact, be prudent for wells that have demonstrated considerable variability in contaminant concentrations and groundwater elevations over time. But comparison of PDB sampler results to historical sampling results may be sufficient for wells that have historically shown little variation in contaminant concentrations and groundwater elevations. LTM programs generally emphasize evaluating long-term trends, and reports should clearly identify where a change in sampling method occurred.

4.2.1 Statistical Approaches

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. A particular contaminant may compare differently in two different wells at the same site (e.g., McClellan 2000). Although statistical evaluations may provide additional insight of the sampling process, they will generally not provide a clear path to the acceptance or rejection of PDB sampling. However, this information may help to refine the conceptual site model and focus future monitoring and/or remediation on specific zones within the aquifer or well. 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 can often be 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 sampling methods. 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 further by comparing results from the conventional sample to a vertical concentration profile to determine whether the observed concentration differences are due to stratification within the well and mixing during the sampling events. If relative percent difference (RPD) is used to evaluate the comparability of sampling results, it is important to remember that variations in results for duplicate samples using conventional sampling techniques can be high. RPD is influenced by the analyte concentration, the target compound, matrix effects, and site-specific characteristics. It is also important to remember that different concentrations indicated using PDB samplers, compared to conventional sampling results, do not necessarily mean that environmental conditions are different than originally thought. The data must be interpreted within the context of the sampling method.

4.2.2 Examples of Acceptance Criteria

The implementation of PDB sampling at a site should be made in concert with the appropriate regulators. It is wise to decide upon the site DQOs and acceptance criteria beforehand. The decision to proceed may be based on comparison of results with historical data or a more comprehensive comparison study of PDB sampling and the current sampling methodology. The following are approaches that have been used in the past. These are not intended as recommended practices because there is at present no single set of criteria governing the acceptability of PDB sampling. It remains a site-specific exercise.

A demonstration using PDBs was conducted at McClellan Air Force Base in 1999 (McClellan 2000). One hundred thirty-eight PDBs were deployed in 30 wells. Each well was also sampled using conventional purge techniques at the time the PDBs were recovered. All samples were sent to the same analytical laboratory for analysis.

The McClellan report states that an acceptable variability in analytical results between an environmental sample and its paired duplicate is typically less than 30% RPD. Based on an analysis of the study's particular data, an RPD value of ≤15% was adopted as the standard of acceptable variability between PDB and conventional sampling results.

A test of means was used to determine whether the analytical results from PDB sampling and the conventional sampling could be said to represent the same statistical population. Normality tests were performed on the data using the Ryan-Joiner test to ensure the data were appropriate for use in a parametric test. Then a test of means was performed on each well-analyte pair between the two data sets, using a one-sided t-test at a 95% confidence level. Details can be found in McClellan 2000.

Another study by Parsons (2003) of 14 U.S. Department of Defense (DoD) installations developed a set of correlation criteria by which to compare PDB and conventional sampling results. Analytical results from each sampling technology were used to compute an RPD according to the equation:

$$RPD = 100 \times [abs(D - C)/(D + C)/2] \ ,$$

where

abs = absolute value,
D = PDB sample result,
C = conventional sample result.

Based on a review of standard conventions and literature RPD criteria, an RPD value of 30% was selected as a criterion to determine the acceptability of PDB sampling.

Three acceptance criteria were used to determine the suitability of PDB sampling for particular sites:

- *PDB sample results ≥ conventional sample results*—If at least one PDB sampling result for a given well is equal to or greater than the conventional sampling result, PDB sampling is deemed appropriate for use in that well.

- *RPD criterion*—If either the PDB or the conventional sample result is greater than three times the laboratory reporting limit (RL) and the PDB sampling result is less than the conventional sampling result, an RPD of 30 is used as the acceptance criterion.

- *RL criterion*—If both the PDB and conventional sampling results are less than or equal to three times the laboratory RL, a value of ± the RL is used as the range of acceptance between the two values. If the RLs for the conventional and PDB samples are different, the lower RL is used to determine the acceptance range.

The Parsons study included 332 wells and 1199 PDB samplers. Compounds were considered to have shown "acceptable" analytical results if they met the above correlation criteria in at least 70% of the comparison samples (Table 4-1). The Parsons study suggests that PDBs can be suitable for analytes beyond those that have been investigated in the laboratory (cf. Table 4-1 and Table 1-1). This study also suggests that site- or well-specific conditions may adversely affect PDB performance for some analytes that performed well in laboratory testing. Laboratory studies indicate the ability of an analyte to diffuse through the PDB, which is a requirement for effective PDB sampling, but field conditions introduce other variables that are not accounted for in the laboratory.

4.2.3 Reasons for Low Correlations

Sometimes there is not good agreement between PDB and conventional sampling results. PDB sampling should not be summarily dismissed in such cases. Rather, an attempt should be made to discover the reason for the discrepancy. Parsons (2003) compiled the following list of potential reasons that PDB samples and conventional samples might not agree:

- Low-magnitude concentrations where a small difference of a few micrograms per liter could result in a large percentage difference and failure of the RPD criterion.
- Inappropriate (too short or too long) deployment period.
- Excessive time lag between PDB and conventional sampling events.
- Laboratory- or field-induced contamination that may be present at varying levels in different samples but are not representative of site-related contamination.

Table 4-1. Field experience sampling VOCs with PDBs (Parsons 2003)

Data suggest that PDB sampling may be useful for these target compounds (see text)		
Benzene	1,2-Dichlorobenzene	1,1,2,2-Tetrachloroethane*
Bromobenzene*	1,3-Dichlorobenzene	Tetrachloroethene
Bromochloromethane*	1,4-Dichlorobenzene	Toluene
n-Butylbenzene	Dichlorodifluoromethane	1,2,3-Trichlorobenzene*
sec-Butylbenzene	1,1-Dichloroethane	1,2,4-Trichlorobenzene*
tert-Butylbenzene	1,2-Dichloroethane	1,1,1-Trichloroethane
Carbon disulfide	1,1-Dichloroethene	1,1,2-Trichloroethane
Carbon tetrachloride	*cis*-1,2-Dichloroethene	Trichloroethene
Chlorobenzene	*trans*-1,2-Dichloroethene	Trichlorofluoromethane
Chloroethane	1,2-Dichloropropane	1,1,2-Trichloro-1,2,2-trifluoroethane
Chloromethane	Ethylbenzene	Vinyl chloride
Dibromochloromethane	Hexachlorobutadiene*	*m,p*-Xylene
1,2-Dibromoethane*	*p*-Isopropyltoluene	*o*-Xylene
Dibromomethane*	1-Methylethylbenzene	Xylenes, total
Data suggest that PDB sampling may be problematic for these target compounds (see text)		
tert-Amyl methyl ether*	Naphthalene	1,2,4-Trimethylbenzene
Bromoform*	*n*-Propylbenzene	1,3,5-Trimethylbenzene

* The data set for this compound was relatively small (fewer than five instances of comparison), so the power of the classification (i.e., acceptable or unacceptable) is fairly low.

- Inherent differences between PDB and conventional sampling methods (i.e., the fact that some conventional samples are drawn from a much larger volume of the aquifer than are PDB samples).
- Water table above the top of the well screen. This cause is related to the preceding one and may be particularly significant at fuel-contaminated sites, where fuel concentrations may be highest near the water table. These higher concentrations might be drawn into the well during a conventional purge but would not be detected by PDBs deployed in the screen interval.
- Significant contaminant stratification in which dissolved contaminants are localized in discrete layers that may not be sampled by PDBs. Also, nonuniform distribution of dissolved contaminants in the aquifer (e.g., among the benzene, toluene, ethylbenzene, and xylenes [BTEX] compounds) due to differences in solubility, density, sorptive, and degradation properties.
- Aeration of PDBs during the deployment period due to a declining water table or deployment above the water table.
- Deployment of the PDBs above or below the screened interval of the well, where natural groundwater flow through the well does not occur.
- Vertical flow in the well resulting from the presence of vertical hydraulic gradients.
- Aquifer characteristics such as hydraulic conductivity, groundwater velocity, and lithology that might limit natural flow of groundwater through the well screen.
- Well-specific conditions that would limit groundwater flow through the well, such as where the filter-pack permeability is lower than that of the aquifer, causing groundwater flow lines to diverge around the well.

- Compound incompatibility with PDBs. Some compounds (e.g., methyl *tert*-butyl ether [MTBE], acetone, 4-methyl-2-pentanone, and styrene) have been shown to have poor diffusivity across the PDB membrane (Vroblesky 2001a).
- Physicochemical properties of the compound. This cause is related to the preceding one and includes compounds that are not listed in Vroblesky 2001a) but have had less favorable field results (see Section 4.2.2, Table 4-1).
- Laboratory-induced variability resulting from the PDB and conventional samples' being analyzed in different sample delivery groups and therefore being potentially analyzed on different days, by different operators, on different equipment.

4.3 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 whether alternative technologies will be acceptable. Negotiations may be needed to modify or amend permits, orders, and sampling plans; in some instances, public meetings may be required.

4.4 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 water-quality goals. Given that PDB sampling is a valid and defensible technique that produces representative samples, it is the Diffusion Sampler Team's judgment that PDBs are an acceptable means for collecting site closeout data. There is no reason to expect that other sampling techniques produce results that are either superior to 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 uncontaminated wells located beyond areas of contamination and used to monitor the advance of contaminated groundwater, or to provide warning of contaminant migration toward production wells and potential receptors. The leading edge of an advancing contaminant front would most likely be within a zone of higher hydraulic conductivity, which would contribute substantially to a pumped sample. PDB samplers might be advantageous in that they could potentially detect VOC contamination that would be diluted below detection limits using well-purge sampling techniques. However, if the screened interval of the well is greater than about 5 feet, a single PDB might not detect contamination that would appear above or below the placement depth of the bag. In such cases, multiple PDBs would be needed in each sentinel well for each sampling event to ensure timely detection of advancing contaminants at all depths across the entire screened interval. This requirement could make PDBs less cost-effective if adequate coverage of a long screened interval is to be ensured. Again, DQOs and knowledge of site characteristics, special requirements, or overriding considerations at a site should determine whether PDBs are appropriate for sentinel wells.

4.5 Survey of State Regulators

The ITRC Diffusion Sampler Team conducted a survey of state regulators in May 2003. In total 54 responses were received from 23 different states. The primary purpose of the survey was to identify any rules or regulations that would impede the implementation of PDB sampling. None were identified. The survey also sought the views of regulators on specific applications for PDBs and their familiarity with the technology. PDB sampling is being implemented across the country: all but two of the 23 states reporting had sites using the technology. Appendix D contains a compilation of the survey results.

Contact with regulators was initiated by the ITRC state POCs. The survey was Internet-based; responses were entered and recorded online. Multiple responses were allowed within any state, without regard to specific agencies. A complete analysis of the survey results will be published and be made available on the DSIC Web site. The focus of this discussion is on the potential impact of state and federal rules and regulations on the use of PDBs, as well as the existing regulatory climate and attitudes that could affect applications of this new technology.

One question on the survey asked respondents to identify any state rules or regulations that could hinder the use of PDBs for groundwater monitoring. Three responses suggested potential problems; however, further investigation revealed that the situations cited did not represent a roadblock. One comment was in reality a technical comment related to appropriate use, and a second comment indicated a variance would be required because the methodology is not currently in the state's sampling manual. Notably, this particular state will soon publish a new manual that does include PDB sampling. The third comment concerned sites monitoring for a broader list of contaminants that were not all amenable to PDB sampling. Again, this is more of a technical issue than a regulatory problem. In summary, the survey did not identify any barriers to the use of PDBs for groundwater sampling based in state rules and regulations. A similar question concerning federal rules and regulations likewise identified no hindrances.

Regulators from nine of the 23 states surveyed stated they had guidance on PDB technology. However, such guidance was generally not a state-specific document but an external publication such as the *User's Guide* (Vroblesky 2001a, 2001b). At this writing only a single state (New Jersey) has drafted specific guidance related to PDB sampling. The New Jersey guidance will be published in March 2004 and will be included in a revised version of the state's *Field Sampling Procedures Manual*, to be published later in 2004.

One series of questions in the survey sought to identify what regulators considered to be acceptable uses for PDB sampling. Respondents were asked to identify in which of the following scenarios they felt PDBs could be implemented, assuming all contaminants of concern would be adequately monitored with PDBs: LTM, compliance monitoring, sentinel well plume detection, site closeout, and site characterization (Figure 4-1).

Use of PDB sampling for LTM had widespread support among the regulators. There were no objections, although some specified support was conditional on site-specific characteristics. There were few objections to using the PDB technology for either compliance monitoring or sentinel well plume detection. Again, some regulators cautioned that site-specific characteristics had to be considered.

The use of PDB sampling for site closeout was more controversial. Twenty-six percent of the respondents said they would support this use, and an additional 54% said they would support it with conditions. Twenty percent of the regulators stated they would not use PDBs for site closeout. Of the five PDB uses queried, this one had the least support. The use of PDBs for site characterization was supported by 41% of the regulators, as well as an additional 44% who would do so conditionally. Thirteen percent did not favor the use of PDBs for site characterization.

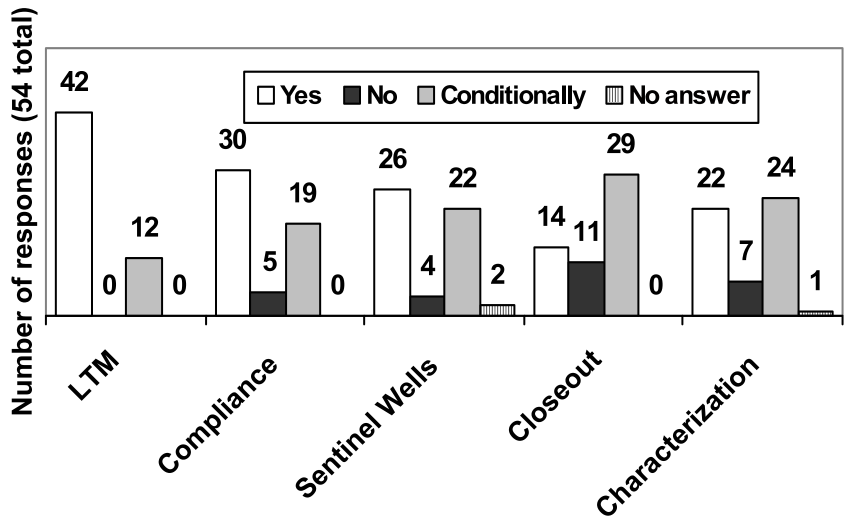

Figure 4-1. Regulator responses regarding the use of PDBs for various purposes.
(The 54 responses came from 23 different states.)

Analysis of these data by state is complicated by the fact that ten states had multiple responses, sometimes from separate agencies. It is not surprising that there was some disagreement within a single state. Figure 4-2 is an attempt to summarize the results on a state basis. To achieve this end, the most liberal use of PDB technology has been reflected. For example, if one regulator in the state would permit the use of PDBs for site closeout, then that opinion is the one entered, even though others from that state may not favor that use. It is recognized this treatment skews the results, and Appendix D contains a complete compilation of the results for anyone who wishes to perform a different analysis.

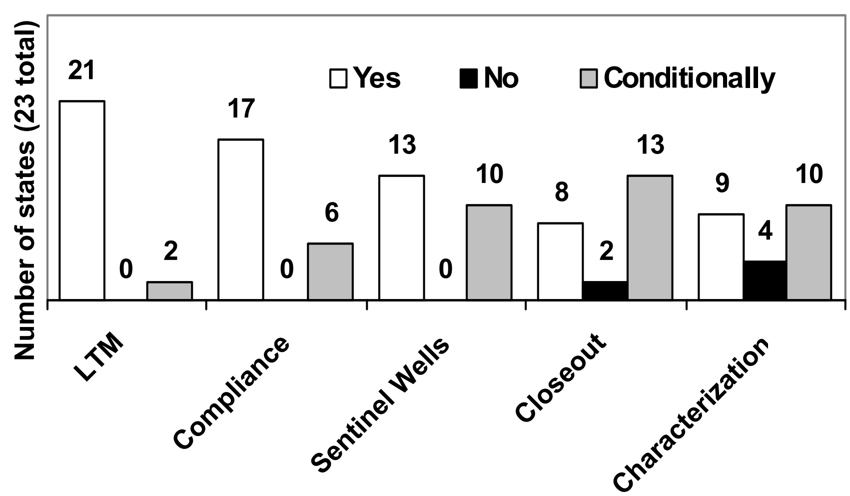

Figure 4-2. PDB survey results from 23 states indicating regulator support for specific uses of PDBs.
(Note that the responses reflect not an official state policy but only the proclivity of individual regulators.)

This survey of state regulators identified widespread support for the use of PDB sampling technology, particularly for LTM. Acceptance has been gained over time as more professionals become aware of the advantages of the technology. At the same time, awareness of its limitations justifiably results in "conditional" approval by regulators. The application of PDBs should always be governed by site-specific characteristics and DQOs.

5. COST ESTIMATES

PDBs offer many advantages, including significant cost reductions over purge sample-collection techniques. This section provides information, tools, and case studies to help compare the cost of using PDBs to collect monitoring well samples with other common sample-collection techniques, such as low-flow and whole-well-purge methods. An interactive spreadsheet that compares costs associated with PDBs with other sample collection techniques can be downloaded from the DSIC at http://ds.itrcweb.org.

This section also discusses the cost to convert to PDB sampling from another sample-collection technique. The degree of testing required and the anticipated costs vary widely. Implementation costs are discussed to make the reader aware of potential costs that may be incurred in converting to PDB sampling. Some alternative approaches are presented that might reduce implementation costs. The type of testing required to demonstrate PDBs at a specific site depends on the quality and quantity of site historical data, site groundwater and contaminant dynamics, regulatory requirements, and the willingness of responsible parties to work at risk without explicit regulatory approval.

The case studies provided here are an attempt to communicate practical experience obtained from the field. A cross section of examples from private, DOE, and Air Force sites is provided. More examples are available at the DSIC.

5.1 Estimating PDB Implementation Costs

It is generally desirable to perform an evaluation of the implementability of PDB sampling in a well prior to conversion to PDB sampling. The scope and cost of this evaluation can vary significantly depending on site-specific conditions and regulatory requirements. In some instances, the implementation cost may exceed the return on investment, such that further consideration of PDB sampling is not warranted. Conversely, the cost savings realized through conversion to PDB sampling may validate the investment in the implementability evaluation.

Several considerations applicable to PDB implementation are discussed below. Although not all of these considerations may be applicable for each application, they provide useful guidance for estimating implementation costs.

The complexity of an implementation evaluation may vary depending on the application. For example, a simple pilot evaluation may involve placing a zip-lock bag filled with distilled water in a well for two weeks, retrieving it, analyzing the contents for VOCs, and comparing those results to historical VOC data from the same well. Alternatively, a more rigorous evaluation may involve development of a work plan, extensive field and laboratory investigations (e.g., vertical contaminant profiling and vertical-flow measurement), data analysis and evaluation, development of recommendations, reporting, regulatory interaction, document revision (e.g., sampling program guidance documents), and consecutive follow-up evaluations. As a conservative approach to determining the implementation cost, a moderately rigorous implementation evaluation is described in detail below.

A common approach for determining the implementability of PDB sampling is to perform a side-by-side comparison of PDB and conventional sampling results. Additionally, vertical contaminant profiling of each well is recommended to identify the optimal deployment depth of the PDB sampler. This type of investigation might involve the following activities:

- <u>Work Plan Development</u>—A document detailing the objectives and scope of a PDB sampling evaluation should be developed. This document can be used to initiate regulatory interaction and potential later acceptance of the PDB method and also to provide direction to the field scientists performing the implementation evaluation. Depending on the type of work plan developed, this cost can vary from a few hundred to several thousand dollars. As a guide, it would not be unreasonable to assume labor costs of approximately 1–2 hours per well to develop a work plan.

- <u>Field Equipment Procurement</u>— Table 5-1 is a list of equipment, supplies, and laboratory analytical services typically required to perform a PDB evaluation, along with their typical costs. Costs for field equipment, including laboratory analysis, can vary from a few hundred to a few thousand dollars per well and are heavily dependent on the number of samples needed to obtain the vertical profile. Note that laboratory VOC analytical costs will be the same regardless of sampling method.

- <u>Field Sampling</u>—If coordinated with a scheduled conventional sampling event, an initial PDB sample collection involves two mobilizations to the site/well: one to deploy the PDB samplers and a second to retrieve them during the coincidental conventional sampling event. The field labor required to complete the PDB sampling portion of this phase varies depending on site and well characteristics. During a large-scale PDB sampling demonstration performed for the Air Force (Parsons 2003), the labor required to perform field sampling ranged 1.8–9.5 hours per well and averaged approximately 3 hours per well (see Table 5-2). For subsequent samplings, consideration can be given to deploying the

Table 5-1. Nonlabor direct costs associated with implementation of PDB sampling

Item	Cost
Stainless steel weight (extra heavy)	$15.00
1000-foot spool of 0.125-inch poly rope	$19.75
Diffusion sampler	$14.00
Plastic sheeting (per roll)	$6.00
Purified water (per gallon)	$1.00
Nitrile gloves (box)	$11.50
Water-level meter rental (per day)	$20.00
Vehicle rental and gas (per day)	$65.00
Photoionization detector (per day)	$60.00
Photoionization detector calibration gas	$35.00
Zip ties (each)	$0.03
Sample labels (per well)	$0.20
Laboratory analyses (SW8260B, per sample)	$135.00
Shipping field equipment and supplies	$50.00
Sample shipment (per cooler)	$50.00

samplers following recovery of the previously deployed samplers, thereby eliminating a separate deployment trip. In addition, subsequent samplings typically involve a single PDB sampler deployed at a depth determined from initial vertical profiling. Recovery of a single PDB sampler should require a substantially shorter time than the average of 3 labor hours per well previously cited.

- *Data Analysis/Evaluation and Reporting*—This task involves sample tracking, database development and management, data validation, data analysis/evaluation, and reporting. The cost of this task can vary significantly depending on the scope of the implementation evaluation.

- *Recommendations*—This task involves reviewing the results of the PDB sampling evaluation and developing well-specific recommendations for optimal PDB placement depths for those wells approved for PDB deployment. Additionally, anomalous situations may require further evaluation and study. If additional field evaluations are necessary, this cost will be increased.

- *Regulatory Interaction*—Some regulatory interaction costs would likely be incurred to gain approval for switching from the current sampling technique to PDB sampling. Before going through all the permit modifications and revising the sampling and analysis plan and the quality assurance project plan, discuss with your regulator the possibility of a variance to evaluate the use of PDBs at the site. If the evaluation indicates that PDBs are appropriate for monitoring the contaminants at the site, then proceed to modify the appropriate permits and documents.

- *Document Revision*—If the groundwater sampling method is changed to PDB sampling, some revision of sampling-related documents will be required as indicated above.

Table 5-2 provides a summary of implementation costs at 14 Air Force installations, including minimum, maximum, average, and median values. While these data indicate a significant variability in cost from one installation to the next, the reduction in costs using PDB technology as opposed to conventional sampling techniques is consistently in the range of 60%–80%.

In summary, there are many items and tasks to consider prior to implementation of a PDB sampling program. These costs can vary significantly depending on the scope of the sampling program. Although some examples of typical costs have been presented above, each item should be considered individually on a site- or well-specific basis to estimate an implementation cost specific to the application.

5.2 Offsets to Implementation Costs

Implementation costs can sometimes be offset or reduced by careful planning and coordination. The following sections discuss some aspects to consider.

Table 5-2. Cost of implementing PDB sampling at 14 DoD facilities (adapted from Parsons 2003)

Installation	Number of wells evaluated	Implementation labor hours—total / per well[a] (hours)	Other direct implementation costs—total / per well ($)	Total estimated implementation costs per well[b] ($)	Long-term cost of conventional sampling per well, per event ($)	Long-term cost of PDBs per well, per event ($)	Cost advantage of PDB sampling over conventional sampling per well, per event ($)	Percentage cost savings of switching to PDB sampling	Return on investment (%)
Andrews AFB	26	90 / 3.5	16,276 / 626	2,381	332	78	254	77	213
Bolling AFB	10	25 / 2.5	3,705 / 370	4,256	186	68	118	63	1
Buckley AFB	16	48 / 3	6,149 / 384	2,619	336	74	262	78	200
Columbus AFB	20	60 / 3	1,240 / 602	2,417	343	70	273	80	407
Dover AFB	20	47 / 2.3	10,399 / 520	2,267	323	68	255	79	459
Edwards AFB	38	108 / 2.8	20,783 / 547	1,808	218	72	146	67	324
Keesler AFB	17	50 / 2.9	8,562 / 504	2,809	474	106	368	78	260
Shaw AFB	24	43 / 1.8	9,339 / 389	1,597	304	67	237	78	613
Vandenberg AFB	56	150 / 2.7	32,198 / 575	1,653	296	75	221	75	583
George AFB	34	71 / 2.1	21,954 / 646	1,812	414	95	319	77	704
March AFB	20	51 / 2.6	17,284 / 864	2,100	209	62	147	70	472
Norton AFB	17	64 / 3.8	17,776 / 1,046	2,900	297	71	226	76	500
Williams AFB	10	95 / 9.5	22,975 / 2,298	5,315	813	182	631	78	258
DDJC-Sharpe	25	85 / 3.4	16,233 / 649	2,308	227	62	167	74	232
Minimum	10	25 / 1.8	3,705 / 370	1,597	186	62	118	63	1
Maximum	56	150 / 9.5	32,198 / 2,298	5,315	813	182	631	80	704
Average	24	70 / 3.3	15,405 / 716	2,589	341	82	259	75	373
Median	20	62 / 2.9	16,255 / 588	2,345	314	72	246	77	366

[a] Using a two-person field team.

[b] Implementation cost includes work plan development, vertical profiling (one PDB per 3 feet of saturated screen) of each well, field equipment and laboratory analyses, field sampling labor, data analysis/evaluation and reporting, recommendation development, regulatory interaction, and revision of existing sampling program documents (e.g., sampling and analysis plan, quality assurance project plan).

5.2.1 Purge Water

Most sampling situations require purged well water to be contained and disposed of, requiring labor (to purge the well, transport the water, and transfer it to either a treatment facility or a contractor for transport to its disposal destination), transportation, storage (e.g., Baker tank rental), and disposal costs. Since virtually no wastewater is generated with PDB sampling, these costs would likely be greatly reduced or entirely avoided.

5.2.2 Reduced Sampling Time

In cases where the number of sampling days is expected to decrease, there should be a reduction in the number of QA/QC samples. Labor costs can be reduced approximately 15 minutes per QA/QC sample eliminated. In addition, lower analytical and shipping costs should be expected. QA/QC samples include the following:

- trip blanks—typically one per cooler shipped, usually one per sampling day;
- duplicate samples—typically 10% of the total primary samples collected;
- matrix spike and matrix spike duplicate—typically 5% each of the total number of primary samples collected; and
- equipment blank (e.g., equipment rinsate)—typically 5% of the total number of primary samples collected, or a minimum of one per day.

Rather than making a special unscheduled trip to the site to install/remove PDBs, attempt to coordinate placement or removal of the PDBs at the same time the sampling crew normally is at the well locations (e.g., during times of water level measurement or other sampling).

5.2.3 Coordination of Sampling

When discussing implementation of the PDBs with your regulator, discuss ways to implement PDBs without significantly increasing your implementation costs. For example, at a site that has been well characterized, has been conducting routine groundwater monitoring for several years, and is currently using low-flow sampling techniques, you may want to discuss placing one diffusion bag sampler in each monitoring well during the next scheduled sampling event at the same depth interval from which low-flow samples have been previously collected to see how well they correlate to historical VOC concentration ranges at those wells. This approach would enable PDBs to be evaluated without a side-by-side comparison of PDB to contemporary conventional sample results and would effectively cut the implementation cost in half. For those wells where PDB results are outside the historical concentration range for a particular well, additional vertical profiling may need to be conducted. It should be noted, though, that if the site is not well characterized and PDB results differ from those obtained using conventional sampling techniques, it may be more difficult to convince a regulator that PDBs are adequate for monitoring VOCs at those wells.

5.2.4 Phased Sampling

If vertical profiling is necessary because the saturated well screen length is greater than 5 feet or the existing site characterization (e.g., historical record) is inadequate, it may be attractive to phase in the vertical profile or implementation evaluation. For example, for a site with 20 wells sampled quarterly, the PDB evaluation and vertical profiling could be performed in five wells each quarter. Then the evaluation for the entire site would be completed within one year, but the PDB implementation costs would be distributed evenly through four different sampling events.

5.3 Cost Model

The potential cost savings of implementing PDB sampling in place of other sampling methods is a driving force in the deployment of PDBs. A cost model has been developed that enables cost implications to be evaluated in the assessment of PDB deployment on a site-specific basis. It may be downloaded from the DSIC at http://ds.itrcweb.org. The cost comparison technique used by the spreadsheet is a standard "present value" calculation to represent the total, present-day cost of future sample collection expenses. The spreadsheet model sometimes uses default values based on data collected during previous field demonstrations of PDBs, but the user is encouraged to use site-specific cost data so that the cost comparison is more accurate. Certain site-specific conditions, such as whether well purge water is treated on site without cost or is transported off site and treated at an additional cost, can have a substantial impact on the cost analysis.

The intent of the cost model is to enable the comparison of sampling costs for the current sampling method, PDBs, and another alternative sampling method. The alternative scenario can be used to compare costs with a third sampling technique or with the modification of certain parameters previously defined in one of the other two scenarios (akin to a sensitivity analysis for selected parameters). An example would be to evaluate the impact of reducing the sampling frequency.

The cost model is an Excel spreadsheet with defined formulas to calculate net present value (NPV) of up to three sampling scenarios. The cells in the spreadsheet are color-coded: a blue font indicates user input is required; a red font indicates a calculated value. When an override value is entered by the user, the cell background changes to blue. The "economic evaluation" spreadsheet requires the user to enter costs by category (discussed further below), which are used to calculate a "cost per event." This value is multiplied by the number of events per year for up to 30 years to calculate a total annual cost. Using a provided discount rate, the NPV for up to three sampling alternatives is calculated, providing a comparison over a time interval of up to 30 years. These results are presented in the spreadsheet titled "Year by Year NPV."

The user input fields are described in Table 5-3. Each cost category has extra fields to enable costs not included in the defined cost fields to be included on a site-specific basis.

Table 5-3. Input fields for the PDB implementation cost model

Category	Description
Number of field personnel	Field personnel required for sampling.
Sampling days (per event)	The number of days required to sample all wells included in the sampling event. As guidance, it would be reasonable to expect sampling at least 20 wells per day when each well has a single PDB and is less than 50 feet deep. This estimate would be influenced by an event in which vertical profiling is conducted or situations where PDBs are not used for all sampling events because occasionally analyses for analytes may be required that PDB samplers cannot collect.
Length of sampling day (hours)	Hours of sampling activity per day; an integer 1–16.
Labor cost (hourly per person)	Hourly labor rate for field personnel. This may be an average blended rate if sampling personnel change throughout a project, as they frequently do.
Per diem (daily per person)	The daily cost per person for food and lodging.
Travel and transportation costs (per event)	Travel for field personnel and transportation of equipment, per event.
Equipment rental/disposables	Costs associated with equipment rental and disposable items. Specify all sampling equipment costs here (whether rented or owned). If equipment or pumps can be redeployed to another location, you may enter a negative dollar amount. The cost of all PDB equipment needs to be included here. Detailed site-specific costs are preferred, but for estimation guidance, see Section 5.1, Table 5-1.
Miscellaneous sampling cost 1	User-identified supplemental cost. Credits may be entered as negative values.
Miscellaneous sampling cost 2	Same as above.
One-time cost for PDB sampling (first year only)	Additional costs experienced during the initial year of PDB sampling. Refer to estimates of implementation costs in Section 5.1.
VOC analysis cost	The cost of laboratory VOC analyses.
Number of wells	The number of wells sampled.
Number of samples per well	The number of samples collected per well. This is generally one unless vertical profiling is being done.
Shipping	The cost of shipping samples to the analytical laboratory. A default value is $50 per day (assuming one cooler per day).
Number of duplicate samples	The default value is 10% of the total number of samples taken, but value may be user defined.
Number of equipment/field blanks	The default value is one per day of sampling, but the value may be user defined.
Number of matrix spike and matrix spike duplicate samples	The default value is 10% of the total number of samples taken, but the value may be user defined.

Category	Description
Number of trip blanks	The default value is one per sampling day, but the value may be user defined.
Miscellaneous analytical cost 1	User-identified supplemental cost. Credits may be entered as negative values.
Miscellaneous analytical cost 2	Same as above.
Waste treatment cost (per event)	Cost to treat waste produced by sampling.
Waste disposal cost (per event)	Cost to dispose of waste produced by sampling.
Waste transportation cost (per event)	Cost to transport waste produced by sampling.
Miscellaneous waste disposal cost 1	User-identified supplemental cost. Credits may be entered as negative values.
Miscellaneous waste disposal cost 2	Same as above.
Number of events (annually)	Number of sampling events scheduled per year.
Inflation rate (percentage)	Assumed rate of inflation. Default value is 3%.
Discount rate (percentage)	Assumed discount rate. Default value is 7%.
Number of years to run model	User defined for up to 30 years. Default value is 30.
Tax rate (percentage)	Assumed tax rate. Default value is 0%.

5.4 Examples/Case Studies

The following specific examples provide data on the cost savings realized when the sites changed groundwater monitoring protocols to incorporate PDBs.

5.4.1 A Private Facility

A private facility conducting LTM of groundwater exclusively for VOCs using either low-flow or bailer sampling methods had over eight years of groundwater monitoring data. PDB sampling was evaluated, and all contaminants of concern (COCs) were measurable by the PDB method. There were 20 wells (all generally less than 40 feet in depth) in the LTM program that historically required five days to sample (including mobilization and demobilization). Since converting to PDB sampling, these 20 wells are now sampled in one day, saving four days of labor and per diem costs for a two-person sampling crew per sampling event. The annual cost of this quarterly monitoring program was reduced 52%, from $18,800 to $9,860 based on labor and per diem savings only.

5.4.2 Kansas City Plant

This DOE facility previously conducted semiannual LTM for VOCs using micropurge and traditional bailing (Baker et al. 2000). By converting mostly to the PDB sampling method (221 of 316 total samples), annual LTM costs were reduced 54%, from $32,415 to $14,835. Concurrently, sampling labor was reduced 35%, from 133 to 87 hours, and annual wastewater generation was reduced 98%, from 783 to 19 gallons. Solid waste (disposable materials and equipment) associated with groundwater sampling was reduced 85%, from about 886 to 129 pounds.

5.4.3 McClellan AFB

McClellan AFB is a nearly 3,000-acre facility near Sacramento, California. More than 400 wells are presently being used to monitor the migration of multiple VOC-contaminated groundwater plumes. A 1999 demonstration study (McClellan 2000) deployed multiple PDB samplers in 30 monitoring wells and compared their performance to conventional purge and sampling. The consequent report also compared costs of sampling using PDBs, conventional purge and sampling, and low-flow sampling. Based upon sampling 125 wells, the annual recurring costs were estimated to be $98,098 for PDB sampling, $236,572 for conventional purge and sampling, and $289,172 for low-flow sampling. These estimates represent about a 60% reduction in recurring costs when PDB sampling is used. A one-time cost of $32,500 was added for PDB and low-flow sampling to determine optimal sampler position. Capital costs were approximately the same for all methodologies. The majority of the savings related to decreased labor costs associated with purging during the sampling events.

6. CASE STUDIES

The following examples demonstrate the value of PDBs at a variety of sites. Additional case studies have been documented in the *User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells, Part II: Field Tests* (Vroblesky 2001b). Other references are Ballestero, Silva, and Newman (2002); Gefell, Hamilton, and Stout (1999); Harte (2002); and Parker and Clark (2002). A case study database maintained on the DSIC (http://ds/itrcweb.org) provides a search function as well as the opportunity to remotely submit contributions.

6.1 PDBs Approved for Long-Term Monitoring

Site name: Cape Canaveral Air Force Station (CCAFS), Pilot Study Sites Space Launch Complex 11 (SLC-11) and SLC-12

Site location: Cape Canaveral, Florida

Date of study: October 2000

Hydrogeological setting: Shallow (within 5 feet of the ground surface) water table conditions, medium- to fine-grained sands

Well construction: Wells screened across the water table, screened intervals of 10 feet, no dedicated pumps

Contaminants of concern: Chlorinated solvent VOC compounds including TCE, 1,1-dichloroethene (DCE), *cis*-1,2-DCE, *trans*-1,2-DCE, and vinyl chloride. Source—historical on-site handling/disposal of solvents.

Remedial operations: Under the Resource Conservation and Recovery Act (RCRA) process, the two pilot study sites have progressed through the RCRA facility investigation (RFI) and the corrective measures study (CMS). LTM of chlorinated solvent compounds was selected as the remedial action for the two sites. LTM has been ongoing since 1998.

Point of contact: John R. McGann, PG, BEM Systems, Inc., SE Regional Operations, 930 Woodcock Road, Suite 101, Orlando FL 32803

Costs: Field collection costs using PDB samplers—One-time setup costs of $30/well, and field sampling costs of approximately $125/sample.

Regulatory status/approval: Florida Department of Environmental Protection and EPA approval for use of PDB samplers at six CCAFS VOC sites was granted. Subsequently, no further action (NFA) was granted at two of the LTM VOC sites where PDB samplers were used for sampling/monitoring.

Narrative: A pilot study was performed in October 2000 on 11 monitoring wells located at the two inactive launch complexes. A comparison of the analytical results obtained through side-by-side collection of samples using low-flow procedures and PDB samplers indicated that the PDB and low-flow results were comparable. Since regulatory approval was granted for the use of PDB samplers at the CCAFS VOC LTM sites, two of the sites were granted NFA and closed. PDB samplers are currently used at four CCAFS VOC LTM sites: SLC-11, SLC-12, FT-17, and Facility 84920.

Site-specific references: *Cost-Efficient Long-Term Monitoring (LTM) of Chlorinated VOC Plumes through the Utilization of Passive Diffusion Bag (PDB) Samplers* (June 2001); annual reports for LTM at SLC-11, SLC-12, SLC-18 (closed), SLC-19 (closed), FT-17, and Fac. 84920.

6.2 PDBs Used to Investigate Contamination in Fracture Zones

Site name: City of Pittsville Municipal Well PMW-6 Investigation

Site location: Pittsville, Wisconsin

Date of study: 2002

Hydrogeological setting: PMW-6 is a municipal water supply well constructed on 8/30/99. The soil consists of sand and gravel to 42 feet below ground surface, underlain by granite to 300 feet. PMW-6 can produce approximately 105 gallons per minute.

Well construction: The well is constructed with 61 feet of grouted 8-inch steel casing followed by an open borehole. The well has a dedicated pump that was removed prior to the PDB sampling.

Contaminants of concern: A raw water sample taken from PMW-6 in early March 2001 contained benzene at concentrations exceeding state standards and maximum contaminant levels. The well site investigation report and wellhead protection plan showed no indication of a VOC source within a reasonable distance from the site.

Remedial operations: The well was temporarily taken off line. The well was put back on line after sampling confirmed remedial measures were adequately addressing the elevated benzene. The remediation system consists of two air-stripping towers (initially installed to address elevated iron concentrations) and carbon polishing.

Points of contact: Jennifer J. Ronk, Applied Environmental Solutions, Inc. N62 W37644 Parkview Drive, Oconomowoc, WI 53066, jennifer@AppliedEnvironmentalSolutions.net, 414-331-5570; Tom Hvizdak, Wisconsin Department of Natural Resources, 473 Griffith St., Wisconsin Rapids, WI 54494, hvizdt@dnr.state.wi.us, 715-421-7850

Costs: PDB samplers were chosen for sampling at this site because they provide a reliable method of collecting samples from the identified fracture zones. The samplers are easy to install, samples are easy to collect, and only limited investigative-derived waste is generated. While a cost/benefit analysis was not completed, this method is less expensive than a more traditional approach of installing packers in the borehole and pumping from the selected zones.

Regulatory status/approval: PDB samplers have not been formally approved in Wisconsin for LTM. However, this method was approved by the Wisconsin Department of Natural Resources at this site as meeting the screening-level DQOs.

Narrative: PMW-6 is completed in fractured bedrock. Samples collected from the municipal well had reported benzene concentrations above state and federal drinking water standards. The source of the benzene is unknown. To evaluate the source of the benzene contamination, the borehole was taped with a video camera to locate fracture zones in the borehole. A colloidal borescope was then used to evaluate the groundwater flow velocity in the fracture zones. Based on the results of this investigation, several primary fracture zones were identified. PDB samplers were then deployed at the levels of the fracture zones in an attempt to identify the zones that were contributing the highest contaminant loads.

The resulting groundwater samples did not have reportable concentrations of benzene. However, they did have reportable concentrations of chloromethane in a distinct concentration gradient, and concentrations increased with depth. Chloromethane can be a by-product of chlorinating a well and has a specific gravity greater than 1.

Based on the results of the PDB sampling, Applied Environmental Solutions concluded that the benzene previously reported in the well is present only when the well is being actively pumped. Subsequent sampling confirmed this result. Based on the chloromethane gradient, it was hypothesized that the majority of the water produced in the well was from a shallow fracture zone. Therefore, when the well was chlorinated, the dense chloromethane sank to the bottom of the well and stagnate while fresh water was being contributed from above.

Based on these results, there are two fracture zones that are suspected to be contributing to the reported benzene contamination in PMW-6. Using the information collected to determine the depth and orientation of these fracture zones, locations are currently being chosen for piezometers. These piezometers will be used to aid in the ultimate identification of the source of the benzene.

Site-specific references: The project is still in the investigative stage, and final documents have not yet been produced.

6.3 Performance Monitoring Using PDB Sampling

Site name: Somersworth Municipal Landfill Superfund Site
Site location: Somersworth, New Hampshire
Date of study: 2001
Hydrogeological setting: About 15–75 feet of sand and gravel overlie fractured bedrock. Groundwater flows NW through the overburden and WNW through bedrock.
Well construction: There are 30 wells at the site, most of which have 2-inch diameters.
Contaminants of concern: PCE, TCE, *cis*/*trans*-1,2-DCE, 1,1-DCE, and benzene
Remedial operations: A zero-valent iron permeable reactive barrier is in place at the downgradient edge of the landfill. LTM for VOCs is conducted three times a year and will continue for decades.
Point of contact: Karen Berry-Spark, GeoSyntec Consultants, Inc., 130 Research Lane, Suite 2, Guelph, Ontario N1G 5G3, Canada, kberryspark@geosyntec.com, 519-822-2230

Costs: Savings are estimated at $8,000 per sampling event even without considering waste disposal cost savings. Implementation costs of about $18,000 were recovered in less than three sampling events.

Regulatory status/approval: The New Hampshire Department of Environmental Services and EPA have approved use of PDBs for LTM at the site. Twenty-eight wells have been regularly sampled using this technology since the winter of 2001.

Narrative: A comparison study of PDB and conventional purge sampling was conducted at the 26-acre Somersworth Landfill site to demonstrate the appropriateness of PDBs for LTM at the site. Comparability was confirmed for 20 of the wells. Poor comparability of the data at the remaining three wells was attributed to the nonuniform distribution of VOCs in bedrock fractures at the depths and does not appear to be related to the geochemical environment of the permeable reactive barrier or the landfill. PDBs are currently being used to monitor the performance of the zero-valent iron permeable reactive barrier at this site.

Site-specific references: *Performance Monitoring Using PDB Samplers at the Somersworth Superfund Site*, RDTF Permeable Reactive Barriers Action Team Meeting, November 6–7, 2002, Washington, D.C.

7. SUMMARY AND RECOMMENDATIONS

PDB sampling technology has been validated by both laboratory and field tests. Although it is not capable of meeting all types of monitoring needs at remedial sites, specific applications of this technology can be effective both technically and economically. No regulatory issues have been identified that would restrict the application of PDBs in technically appropriate situations.

The ITRC Diffusion Sampler Team 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 as valid as low-flow and other conventional methodologies for sampling certain VOCs, and regulators should actively consider the use of this technology where appropriate. 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 higher or lower than those indicated by other sample collection methods. Therefore, it is essential that all parties involved in the implementation of PDBs at regulated sites identify and agree on DQOs, data evaluation techniques, and data end uses 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 saturated well screens 5 feet or less in length, a single 18-inch-long PDB should suffice to characterize the saturated screened interval. In general, if PDBs are used to investigate vertical concentration stratification, an 18-inch-long PDB should represent no more than 5 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, unless data exist to argue against it. 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. 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 made with site-specific DQOs in mind. Deployment may be at a depth corresponding to the zone of highest contaminant mass flux or highest concentration or at a depth of average concentration within the well.

7. Reprofiling wells or changing the vertical location of 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 10ºC. 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 5 feet, multiple PDB monitoring points are recommended.

8. REFERENCES

Ballestero, T. P., G. P. Silva, and K. S. Newman. 2002. “Comparison of Bedrock Well Water Sampling Methods,” pp. 142–46 in *Proceedings, National Ground Water Association Fractured-Rock Aquifers Symposium*, Denver, March 13–15.

Baker, J., S. Ramm, B. Heacock, and J. Wyckoff. 2000. *Team #B0010161 Groundwater Sampling Efficiency Improvements*. Kansas City, Mo.: Department of Energy, Kansas City Plant.

Britt, S. L., and J. Tunks. 2003. “Thorough Mixing of Contaminant Stringers in Monitoring Wells Demonstrated in Sand Tank Ground Water Model: Results Support Expanded Use of No-Purge Sampling Techniques,” in *Proceedings of the NGWA Conference on Remediation: Site Closure and the Total Cost of Cleanup*, New Orleans, November 13–14.

Church, P. E. 2000. *Evaluation of a Diffusion Sampling Method for Determining Concentrations of Volatile Organic Compounds in Groundwater, Hanscom Air Force Base, Bedford, Massachusetts.* U.S. Geological Survey Water Resources Investigations Report 00-4242.

Church, P. E. and G. E. Granato. 1996. “Bias in Ground Water Data Caused by Well-Bore Flow in Long Screen Wells,” *Ground Water* **34**(2): 262–73.

Collins, W. D. 1925. *Temperature of Water Available for Individual Use in the United States*. U.S. Geological Survey Water Supply Paper 520-F, pp. 97–104.

Gefell, M. J., L. A. Hamilton, and D. J. Stout. 1999. “Comparison Between Low-Flow and Passive-Diffusion Bag Sampling Results for Dissolved Volatile Organics in Fractured Sedimentary Bedrock,” pp. 304–15 in *Proceedings, National Ground Water Association Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Symposium*. Houston, November 17–19.

Hare, P. W. 2000. “Passive Diffusion Bag Samplers for Monitoring Chlorinated Solvents in Groundwater,” pp. 377–86 in *Proceedings, Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. Monterey, Calif., May 22–25.

Harte, P. T. 2002. “Comparison of Temporal Trends in VOCs as Measured with PDB Samplers and Low-Flow Sampling Methods,” *Ground Water Monitoring and Remediation* **22**(2): 45–47.

Hutchins, S. R., and S. D. Acree. 2000. “Ground Water Sampling Bias Observed in Shallow, Conventional Wells,” *Groundwater Monitoring Review* **20**(1): 86–93.

Martin-Hayden, J. M. 2000. “Sample Concentration Response to Laminar Wellbore Flow: Implications to Ground Water Data Variability,” *Ground Water* **38**(1): 12–19.

Martin-Hayden, J. M., and G. A. Robbins. 1997. “Plume Distortion and Apparent Attenuation Due to Concentration Averaging in Monitoring Wells,” *Ground Water* **35**(2): 339–46.

McClellan (McClellan AFB Environmental Management Directorate). 2000. *Technology Application Analysis Report for Passive Diffusion Membrane Samplers*. Sacramento, Calif.

Parker, L. V., and C. H. Clark. 2002. *Study of Five Discrete Interval-Type Groundwater Sampling Devices*. ERDC/CRREL TR-02-12. Cold Regions Research and Engineering Laboratory, U. S. Army Corps of Engineers, Engineer Research and Development Center.

Parsons (Parsons Engineering Science, Inc.). 1999. *Technical Report for the evaluation of Groundwater Diffusion Samplers*. Prepared for Air Force Center for Environmental Excellence Technology Division.

Parsons. 2003. *Final Comprehensive Results Report for the Passive Diffusion Bag Sampler Demonstration*.

Puls, R. W., and M. J. Barcelona. 1996. *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*. United States Environmental Protection Agency, Publication No. EPA/540/s-95/504.

Puls, R. W., and C. J. Paul. 1998. “Discrete-Level Ground-Water Monitoring System for Containment and Remedial Performance Assessment Objectives,” *Journal of Environmental Engineering* **124**(6): 549–53.

Robin, M. L. J., and R. W. Gillham. 1987. “Field Evaluation of Well Purging Procedures,” *Ground Water Monitoring Review* **7**(4): 85–93.

Varljen, M., M. J. Barcelona, J. Obereiner, and D. Kaminski. 2004. "Numerical Simulations to Assess the Monitoring Zone Achieved During Low-Flow Purging and Sampling," in *Proceedings of the Nielsen Environmental Field School 2004 North American Environmental Field Conference and Exposition*, Tampa, Fla., January.

Vroblesky, D. A. 2001a. *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*. U.S. Geological Survey Water Resources Investigations Report 01-4060.

Vroblesky, D. A. 2001b. *User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells: Part 2. Field Tests*. U.S. Geological Survey Water Resources Investigations Report 01-4061.

Vroblesky, D. A., J. W. Borchers, T. R. Campbell, and W. Kinsey. 2000. *Investigation of Polyethylene Passive Diffusion Samplers for Sampling Volatile Organic Compounds in Groundwater at Davis Global Communication, Sacramento, California, August 1998 to February 1999.* U.S. Geological Survey Open-File Report 00-307.

Vroblesky, D. A., and T. R. Campbell. 2001. "Equilibration Times, Stability, and Compound Selectivity of Diffusion Samplers for Collection of Groundwater VOC Concentrations," *Advanced Environmental Restoration* **5**(1): 1–12.

Vroblesky, D. A., and W. T. Hyde. 1997. "Diffusion Samplers as an Inexpensive Approach to Monitoring VOCs in Groundwater," *Ground Water Monitoring and Remediation* **17**(3): 177–84.

Vroblesky, D. A., M. Joshi, J. Morrell, and J. E. Peterson. 2003. *Evaluation of Passive Diffusion Bag Samplers, Dialysis Samplers, and Nylon-Screen Samplers in Selected Wells at Andersen Air Force Base, Guam, March–April 2002*. U.S. Geological Survey Water Resources Investigations Report 03-4157.

Vroblesky, D. A., and B. C. Peters. 2000. *Diffusion Sampler Testing at Naval Air Station North Island, San Diego County, California, November 1999 to January 2000*. U.S. Geological Survey Water Resources Investigations Report 00-4182.

Vroblesky, D. A., and M. D. Petkewich. 2000. *Field Testing of Passive Diffusion Bag Samplers for Volatile Organic Compound Concentrations in Groundwater, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999 and May 2000*. U.S. Geological Survey Water-Resources Investigations Report 00-4246.

Vroblesky, D. A., and T. Pravecek. 2002. *Evaluation of Passive Diffusion Bag and Dialysis Samplers in Selected Wells at Hickam Air Force Base, Hawaii, July 2001*. U.S. Geological Survey Water Resources Investigations Report 02-4159.

APPENDIX A

Acronyms

ACRONYMS

CCAFS	Cape Canaveral Air Force Station
CMS	(RCRA) corrective measures study
COC	contaminant of concern
DCE	dicholoroethene
DNAPL	dense, nonaqueous-phase liquid
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DQO	data quality objective
DSIC	Diffusion Sampler Information Center (ITRC Diffusion Sampler Team Web site)
EC	electrical conductivity
EPA	U.S. Environmental Protection Agency
ITRC	Interstate Technology & Regulatory Council
LDPE	low-density polyethylene
LTM	long-term monitoring
MTBE	methyl *tert*-butyl ether
NFA	no further action (required)
NPV	net present value
ORP	oxidation-reduction potential
PCE	perchloroethene (tetrachloroethene)
PDB	polyethylene diffusion bag
POC	point of contact
RCRA	Resource Conservation and Recovery Act
RFI	RCRA facility investigation
RL	reporting limit
RPD	relative percent difference
QA/QC	quality assurance/quality control
TCE	trichloroethene
USGS	U.S. Geological Survey
VOC	volatile organic compound

APPENDIX B

Recommendations Keyed to Document Sections

Matrix of Recommendations and Applicable Sections

Recommendation	Applicable sections														
	1.1	**1.2**	**1.3**	**2.1**	**2.2**	**2.3**	**2.4.1**	**2.4.2**	**2.4.3**	**2.5**	**3**	**4.1**	**4.2**	**4.4**	**4.5**
1. PDB sampling is as valid as low-flow and other conventional methodologies for sampling certain VOCs, and regulators should actively consider the use of this technology where appropriate. 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.	X	X	X	X	X		X	X	X			X	X		X
2. PDBs may indicate contaminant concentrations that are higher or lower than those indicated by 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.		X	X	X			X			X			X		
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 5 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 stratification, an 18-inch-long PDB should represent no more than 5 feet of a saturated screened interval or borehole.							X			X					
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, unless data exist to argue against it. For screened well intervals less than 20 feet, an assessment should be considered if other site data suggest that significant vertical flow may exist.								X							

Recommendation	Applicable sections														
	1.1	**1.2**	**1.3**	**2.1**	**2.2**	**2.3**	**2.4.1**	**2.4.2**	**2.4.3**	**2.5**	**3**	**4.1**	**4.2**	**4.4**	**4.5**
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										X	X		
6. The deployment of a single PDB sampler should be made with site-specific DQOs in mind. Deployment may be at a depth corresponding to the zone of highest contaminant mass flux or highest concentration or a depth of average concentration within the well.							X			X					
7. Reprofiling wells or changing the vertical location of 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.							X								
8. The recommended minimum equilibration period for PDBs is two weeks for water temperatures above 10ºC. No maximum deployment period has been identified, but PDBs have been successfully left in wells for three months and longer.						X					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 5 feet, multiple PDB monitoring points are recommended.														X	

APPENDIX C

Screening Worksheet for PDB Implementation

Screening Worksheet for PDB Implementation

A negative answer to any of the following questions will require further action or investigation before PDB samplers can be deployed. If all answers are affirmative PDB, sampling is likely to be a viable option for the site.

Question	YES	NO
1. Is sampling being done for long-term groundwater monitoring?		
2. Have the groundwater contaminants at the site been fully characterized?		
3. Is groundwater sampling at the site focused on VOCs?		
4. Can all target analytes at the site be expected to be taken up by PDB samplers? (Section 1.1, Table 1-1 and Section 4.2.2, Table 4-1)		
5. Is groundwater temperature anticipated to be above 10ºC (50ºF) during all sampling events?		
6. Have you discussed the potential use of PDB samplers with regulators?		
7. Are site regulators familiar with PDB sampling technology, and will they allow the data to be used for the same purposes as those obtained by conventional sampling?		
8. Are the monitoring wells to be sampled in an area where there is sufficient groundwater velocity? Low groundwater velocity can result from either a low hydraulic conductivity or a low hydraulic gradient.		
9. Are the monitoring wells currently free of dedicated pumps or other sampling equipment?		
10. Has a cost analysis shown PDB samplers to offer a cost savings compared to current sampling techniques?		

APPENDIX D

Survey of State Regulators

Diffusion Sampler State Regulator Survey, May 2003

√ = yes; N = no; C= conditional; D= don't know; na= no answer

States (23)	**AL**	**AZ**	**CA**	**CO**	**FL**	**IN**	**KS**	**KY**	**MA**	**ME**	**MO**	**NE**	**NJ**	**NM**	**NV**	**NY**	**OR**	**PA**	**RI**	**SC**	**TN**	**TX**	**VT**
Responses (54)	**1**	**1**	**11**	**2**	**2**	**1**	**1**	**2**	**1**	**1**	**1**	**1**	**13**	**1**	**1**	**2**	**1**	**2**	**2**	**2**	**3**	**1**	**1**
In your state is there currently guidance with respect to PDB technology?	N	N	2√ 7N 1D	1N 1D	1√ 1D	N	√	2N	N	D	N	D	8√ 2N 1D	N	N	2N	N	2N	1√	1√ 1N	1√ 1N 1D	N	√
From your own perspective, as well as your perception of your department or agency, do you feel that any rules or regulations could hinder the implementation of PDBs for groundwater monitoring?																							
• State rules or regulations	N	N	1√ 4N 6D	1N 1D	1N 1D	D	D	2N	N	N	N	N	2√ 8N 2D	N	N	2N	N	1√ 1N	2N	1N 1D	3N	D	N
• Federal rules or regulations	N	N	6N 5D	1N 1D	2D	D	D	2N	N	N	N	N	5N 8D	N	N	2N	N	1N 1D	1N 1D	1N 1D	2N 1D	N	N
Are there sites in your state that are currently using PDB technology?	√	N	11√	2√	2√	√	√	2√	√	√	√	√	13√	√	√	2√	√	2D	2√	2√	3√	√	√
Are there sites in your state that are currently considering the use of PDB technology?	√	√	11√	2√	1N 1D	√	D	2√	√	√	√	√	13√	√	√	2√	√	2D	2√	2√	3√	√	√
Assuming all contaminants of concern would be adequately monitored with PDBs, do you feel they could be implemented for …																							
• Long-term monitoring?	√	√	8√ 3C	1√ 1C	1√ 1C	√	√	1√ 1C	√	√	√	√	12√ 1C	√	√	1√ 1C	√	1√ 1C	1√ 1C	2C	3√	√	√
• Compliance sampling?	√	C	6√ 3N 2C	√ 1C	1√ 1C	√	√	1√ 1C	√	√	C	√	9√ 1N 3C	C	√	1√ 1C	√	2C	1√ 1C	2C	1√ 1N 1C	C	√
• Sentinel well plume detection?	√	C	5√ 5C 1na	2C	2C	C	√	1√ 1C	√	√	C	√	6√ 4N 3C	√	C	2√	C	2√	1√ 1C	2C	3√	C	√
• Site closeout?	C	C	5√ 6C	2C	2N	C	C	1√ 1N	√	C	C	C	4√ 5N 4C	√	C	1√ 1C	√	2C	2C	1N 1C	1√ 1N 1C	N	C
• Site characterization?	C	√	6√ 4C 1na	1N 1C	2N	C	C	2C	N	C	N	√	8√ 5C	√	√	1√ 1C	√	2C	2C	2C	2√ 1C	N	C

APPENDIX E

Response to Technical Comments

NOTE: Specific pages and line numbers mentioned in the comments refer to a review draft of this document. In many instances those references do not correspond to the published version.

EPA Groundwater Forum PDB Workgroup

1. Table 1-2: Clarification is needed regarding how this table is to be used, perhaps more importantly whether analytes that appear here but are not on Table 1-1 should undergo laboratory testing to determine just how good (favorable) PDBs are for monitoring these analytes. See also comment # 14.

   Table 1-2 was included to indicate that PDBs can be successfully used to sample compounds beyond those in Table 1-1 that were subjected to laboratory tests. The "favorable" compounds in Table 1-2 have shown good correlation with other sampling methods, which suggests that they are good candidates for PDB sampling. Laboratory testing of these compounds would, of course, provide more direct evidence of their suitability. For clarity the word "favorable" has been replaced, and the latter table has been moved to Section 4.2.2 as Table 4-1.

2. Section 2.8: It is unclear whether the discussion of PDB deployment with dedicated pumps is related just to the testing of PDBs suitability in individual wells, the long-term use of both devices in a well for different types of analytes, or both. Note that the dedicated pumps that are commonly used are those that fit in 2-inch wells. However, smaller diameter bladder pumps are now being manufactured (down to 3/8-inch diameter), so the apparent use of both in a well may no longer be an issue.

   The use of PDBs in wells with dedicated pumps is primarily of interest where side-by-side comparison sampling is desired. This might be required by regulators at some sites or for particular wells. We will note the availability of smaller pumps. However, many existing configurations employ larger pumps.

3. P.4, L.24: Clarify what time period the sample concentration is supposed (thought) to represent (see Table 1-3).

   Table 1-3 has been revised to indicate the sample represents a time-weighted average concentration of the 1-4 day period prior to sample recovery.

4. P.4, L.35. Please provide the basis for the recommendation that wells with 20 feet or longer well screens or open hole are tested for vertical flow.

   The literature confirms that vertical flow in wells is not uncommon, and it is recognized that vertical flow can be of concern in wells with screens or open intervals much less than 20 feet. Wording has been added in Section 2.4.2 to indicate that the selection of the 20-foot interval as a point of differentiation was an arbitrary, although collective, decision. Professional judgment should prevail whenever there is reason to believe vertical flow may be present in a well regardless of the well screen length.

5. P.5, L.18: If the guidance is primarily about using PDBs as stand-alone samplers for VOCs, clarify what the function of the pump is.

   Please refer to the response to Comment #2.

6. P.6, L.4: Clarify why sentinel wells should be monitored by multiple PDBs (for all sampling events?).

   Multiple PDB samplers are recommended in a sentinel well when the well screen or saturated portion of the borehole is greater than 5 feet, following the general recommendation that a single PDB should not represent more than 5 feet of water column. In an uncontaminated sentinel well, contaminants might enter the well in a stratified manner that could elude a single PDB. Therefore the conservative approach for a sentinel well would be to deploy multiple bags as appropriate. Section 4.4 has been revised to clarify this point.

7. P.10, L.26: Change "with which there was favorable field experience" to " for which there were sufficient field data." Existing text suggests unfavorable data were not used.

   The designation of a compound as having "favorable" or "unfavorable" results was not driven by a sufficiency of data. The criteria used in the referenced study are discussed in Section 4.2.2. The text has been reworded.

8. P.11, Table 1-2: The table indicates that bromoform and napthalene had "less favorable results in field sampling comparison study," yet these analytes are shown as having "favorable laboratory diffusion testing results" in Table 1-1. This is likely to be confusing to the reader. Some discussion is needed with regard to which table should "carry more weight" in guiding the reader. This reviewer believes that while the data in Table 1-2 are instructive, they should be viewed as "preliminary." These data should not be used as a substitute for laboratory testing to evaluate PDB performance for specific VOCs, as shown in Table 1-1.

   The intent of the table of field sampling results was to indicate that the list of analytes to which PDB sampling is applicable is larger than those tested in the laboratory (Table 1-1). The field data also show that site- or well-specific conditions may adversely affect PDB performance for some analytes that performed well in laboratory testing. Laboratory studies indicate the ability of an analyte to diffuse through the PDB, which is a requirement for effective PDB sampling, but field conditions introduce other confounding factors that are not accounted for in the laboratory. To lessen any confusion between these two tables, the field data has been moved to Section 4.2.2 as Table 4-1.

9. P.11, L.8: Change first part of sentence to "Sand-tank experiments by Britt (2003) seem to show significant dispersion of solutes along a well bore under conditions of uniform lateral flow."

   This sentence was removed during document revision.

10. P.11, L.11-16: The intent of the discussion regarding Figure 1-2 is not apparent. Either the last sentence should be omitted or the thought process behind the last statement should be clearly presented. As it stands, the discussion provides two possibilities to explain the data in Figure 1-2, then dismisses the second possibility without explanation.

    The last sentence has been removed.

11. P.20, L.14: It is stated here that well with screen lengths or open boreholes of 20 feet or longer should be tested for vertical flow. Yet, on page 18, it is recommended that any well with greater than 5 feet of well screen or open borehole be evaluated for contaminant stratification. The results of stratification can only be appropriately evaluated within the context of knowing whether or not vertical flow is occurring. These two recommendations should apply to the same well screen/open borehole length.

    It is true that the presence of vertical flow would affect interpretation of PDB sampling results. Explanation of the 20-foot criterion for conducting vertical flow testing is addressed in the response to Comment #4. The criterion of investigating for stratification when the well screen or borehole is greater than 5 feet in length relates to the length of the typical PDB in relation to the open interval. Professional judgment should prevail at any well where there is data to support another approach.

12. P.20, Sec.2.5: In this or some other appropriate section, discuss procedures to be used to suitability of PDBs and determination of PDB deployment depths in new wells where there are no sampling information.

    If there are indeed no sampling data, then the site investigation is probably at a preliminary level, and PDBs would not be appropriate. If the wells are part of a new LTM program, then the decision analysis presented in Section 3 would be a good starting point. The technical requirements are already covered in Section 2. The determination of deployment depths is specifically addressed in Section 2.5.

13. P.24 and Appendix C: This decision analysis is intended to provide the basis to determine whether or not PDB samplers might be suitable for a site. Although there is a statement that recommends that before deploying the samplers the use of the samplers is discussed with the regulators and a cost comparison is made, nowhere is it stated that there may be a need to determine contaminant stratification and vertical flow prior to determining how many and where the samplers are deployed. The document does discuss this issue, but it is strongly recommended that it is reiterated here so that a person unfamiliar with the various issues associated with the use of the samplers does not proceed strictly on the basis of "yes" from this list of questions.

    The decision analysis is a preliminary screening tool to quickly screen sites that warrant further consideration for using PDB sampling. It is not meant to be a guide for how to implement PDB sampling. The potential necessity for additional work to evaluate stratification and/or vertical flow is something to be considered before actual

implementation. The cost analysis model in Section 5 can incorporate these costs. A note to this effect has been added to the text box associated with question #10 in the decision analysis.

EPA National Risk Management Research Laboratory

14. Pages 3, Lines 30-31 and Page 10, Lines 12-14: It would be informative to users to offer more detail of the mechanism of the PDB and why "Metals and other inorganic compounds will not diffuse across the membrane." In the literature available on PDBs, this is only stated, but not explained—just simple diffusion. Parsons study states that PDBs can't be used for sulfate. However, current research I am conducting showed sulfate in some samples collected with PDBs although they were not as high as those obtained with conventional samplers. Also, there was no consistent trend among the data.

    This document is focused on the implementation of PDB sampling rather than the specific mechanism(s) by which they work. More technical information may be found in the *User's Guide* (Vroblesky 2001a) and related articles.

15. Page 4, Line 21 and Page 17, Line 36: Please define "colder water" (i.e., <10°C).

    The text has been clarified.

16. Page 4, Lines 23-24 and Page 18, Lines 1-4: Some discussion should be included regarding consistency of time deployed for data comparison purposes. Also, a statement here that PDB samples are "time averaged."

    There is no need for strict consistency in PDB deployment times for comparative purposes or to obtain comparable results. The essential requirement is that the deployment time allow for contaminant equilibration and well stabilization. The recommended minimum deployment time is two weeks. Beyond that, at least up to intervals of three months, there is no effect. The contaminant concentrations in the PDB will generally be a time average of the one to four days prior to collection. A PDB deployed for two weeks should produce the same results as one deployed for two months if they are retrieved the same time.

17. Page 5, Lines 5-10 and Page 21, Lines 6-10: While I understand this section, the wording is initially confusing. Some rewording or clarification of ". . . a PDB remain submerged during the sampling period." The PDB should be deployed in a location to allow for fluctuations in the water table and still be submerged.

    This passage has been reworded for clarity.

18. Page 5, Line 18 and Page 22 Section 2.8: Why would a PDB be used if a dedicated pump is in place? If it can be justified, please explain. Use of a PDB in conjunction with a pump would only increase sampling costs.

Please refer to the response to Comment #2.

19. Page 6, Line 8: Should this read ". . .was to identify **any** (rather than **and**) rules or regulations . . . "?

    This typographical error has been corrected.

20. Pages 12, 13, 14, Figures 1-2, 1-3, and 1-4: Fonts on all three graphics should be the same (i.e., axes, etc.).

    New figures have been substituted.

21. Figure 1-2: Statement "The pump produces a mixture of contaminated and uncontaminated water." This statement also be included in Figure 1-3. While it is true that more of an averaged value is obtained with pumps, this effect is less with PDBs although they don't seal off a specific zone within a screened interval, particularly in a 4-inch well (PDB diameter is 1.25 inches).

    New figures have been substituted.

22. Page 14, Line 20: ". . . over the past decade" should read ". . . over the past several years or decades" (either works). It has been much longer than the past decade.

    The passage has been changed.

23. Page 15, Lines 2-7: Provide references.

    NOTE: Comment refers to Section 1.2.1.

24. Lines 24-29: ". . .a PDB sample represents a vertically restricted source. . ." is not a completely true statement, nor are lines 28 and 29 completely true (see above comment on Figure 1-2). If justification is available for these statements, please provide references.

    This description has been revised.

25. Page 16, Table 1-3: Why is the section "Low Flow" column 2 indented with a "•" in front (with no explanation)? Also the last sentence ("In a screened. . .") should also be included in the section on PDBs as this is true for both methods.

    The formatting of the table (now Table 1-2) has been corrected and the text revised.

26. PDB section, column 3: "Time-integrated average of 1-4 days prior to recovery"—the statement has been made that minimum deployment time is 2 weeks for most constituents. How is the "1-4 days" determined? Please reference.

Laboratory experiments (Vroblesky and Campbell 2001) have shown that the contaminant concentrations in the PDB will equilibrate with the exterior solution within 48 hours for many compounds that are amenable to PDB sampling. However, the equilibration time is compound dependent, and the diffusion times for compounds such as vinyl chloride and 1,1-dichloroethene are much longer. Depending on the analyte, the PDB sample represents a time average of the one to six days prior to collection. The recommended minimum deployment of two weeks provides adequate time for both contaminant equilibration and well stabilization. The estimate of a one to four day average of contaminant concentrations (probably better stated as one to six days) is merely an estimate and indication of the dynamic nature of the sampling.

27. Page 18, Lines 32-33:Please provide references for this section.

    The specific sentence referenced (in Section 2.4.1) concerns the sample obtained by purge sampling. There is no specific reference cited, but the statement represents a consensus opinion of the team.

28. Page 20, Sec. 2.4.2: Please provide references for this section.

    The section referenced concerns the potential for vertical flow within a well. This section has been revised and references added.

29. Page 21, Lines 13-18: Please provide references for this section.

    Section 2.5 concerns determining the appropriate deployment depth for PDB samplers. Although there is no specific reference cited, the guidance provided is based upon the field experience of team members and represents a consensus opinion.

30. Page 22, Line 5: Can it be verified that longer bags may exhibit concentration variability along its length? Some mixing will occur simply in retrieving the PDB and then during sampling.

    Anecdotal evidence indicates that stratification within a long PDB can occur. Retrieval could induce mixing, depending on the particular circumstances. Some manufacturers insert a mixing ball into long PDBs to encourage efficient mixing upon retrieval.

31. Page 30, Line 22: ". . . similarly representative samples." What is a representative sample? Any references would be helpful.

    The term "representative" is often ill-defined; it has been removed. After all, every sample is representative of something. It is the job of the investigator to select a sampling method that will provide meaningful data in light of specific DQOs.

32. Page 31, Lines 22-26: Please provide references.

    That a target analyte can behave differently in two different wells at the same site has been documented in field reports. See McClellan (2000) and Parsons (2003).

33. Page 31, Lines 35-38: [provide] references to verify the 50 percent difference in duplicate samples.

    The specific reference to 50% has been deleted. However, the precision associated with analysis of field samples is variable. Selection of a low RPD criterion may result in an unfair test of the comparability of sampling techniques.

34. Page 31, Lines 38-41: Please explain what is meant by ". . . environmental conditions are worse than originally thought" and offer more explanation regarding impact on PRPs and decision making.

    This sentence has been reworded. The salient point is that sampling results can differ and must be interpreted within the context of the sampling method.

35. Page 34, Line 10,12: Proper reference for Vroblesky and Pravecek, 2002.

    The correction has been made.

36. Page 36, Line 6: The question asked to be paraphrased and not quoted. Where is the reference to Figure 4-1? Figure 4-1 on page 37 should follow this section on page 36.

    This paragraph has been modified and reference to the figures clarified.

37. Page 38, Lines 5-7 and Figure 4-2: It is misrepresenting the states' responses to include only one positive response to closeout while a majority may have rejected it.

    There is no best way to condense multiple responses from a given state. The approach taken—to display the response most favorable to PDB sampling—is not a misrepresentation but one alternative that was clearly presented as such. The reader is free to consult the data in Appendix D to conduct his own analysis. The caption for Figure 4-2 has been modified to call attention to the assumptions stated in the text.

38. Figure 4-2 Caption: Too many prepositions. Reword "PDB survey results from 23 states indicting regulators acceptability to specific uses. . . ."

    The caption has been reworded.

39. Page 43, Table 5-2: First column width need adjusted. What are the two notes at the bottom of the table referring to? There is no matching symbol in the table itself.

    Formatting changes have been made and the symbols entered.

40. Page 45, Lines 2-3: Please clarify ". . . reduce the implementation cost by a factor of 50 percent."

    The sentence has been modified to clarify that PDB costs would be approximately half that of conventional sampling.

41. Page 56, Lines 10-12: This reference is not used in the text - delete.

    The Vroblesky and Campbell (2001) study is now referenced in Section 2.3.

42. Page 59: Appendix B and Table B-1 are not referenced in the text. This should be done with some discussion on the table. Also, why are the sections listed as ".1, .2, etc.? Shouldn't it be 1.1, 1.2, etc.? The last column of the entire table should have a border.

    Formatting on the draft copy did not display the full margins. The integer number refers to the recommendation number, consistent with the summary in Section 7. Section referrals do include subsections. The table formatting has been changed for clarity.

43. Page 67: First section, the "✓" should moved down under IN. KS is left blank - please fill in.

    These changes have been made.

<u>State of California</u>

44. The title of the document is misleading. The Interstate Technology & Regulatory Council (ITRC) should stay only with the technical guidance (and not the regulatory guidance). Without legal advice the ITRC cannot prepare the regulatory guidance. The title of document should be revised to read, "Technical Guidance for Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Groundwater."

    The principal objective of ITRC technical work teams is to develop guidance documents to meet the information needs of regulatory staff, technology vendors, and environmental consultants. These products help state environmental agencies gain valuable technical knowledge and develop consistent regulatory approaches for reviewing and approving specific technologies. State regulators lead ITRC technical teams, which rely on broad-based participation from federal agencies, industry, academia, and other stakeholders in building collective knowledge and collaborative products. It is the responsibility and purview of the individual states to develop official policy and regulatory guidance on all matters within their political jurisdiction.

    The title of this document correctly reflects its contents and purpose. It not only provides technical guidance but also identifies regulatory issues and suggests possible approaches or solutions.

45. The document emphasizes the long-term monitoring (LTM) with the polyethylene diffusion bag samplers (PDB). The document should be presented in such a way that the PDB can be used for groundwater monitoring (both short and long term). All the references to LTM should be replaced with “monitoring.”

PDBs have a number of applications under various sampling scenarios. The emphasis of this document is indeed upon the use of PDB sampling for long-term monitoring, as stated in the introduction. Interest in PDB sampling is often related to LTM because of the potentially large cost savings in that application.

46. Executive Summary, page iii, 3rd para: “No regulatory or policy issues were identified that would restrict the application of PDBs in technically appropriate situations.” This sentence is misleading and should be deleted from the document.

A primary purpose of the survey of regulators was to identify regulatory hindrances to the appropriate use of PDBs for groundwater monitoring. Obviously there are technical limitations in using PDBs; for example, some target contaminants are simply not amenable to PDB sampling. However, responses to the survey did not, in fact, identify any regulatory obstacles that would preclude the use of PDB sampling under appropriate conditions.

47. Section 1.1, Description, Table 1-1: The table refers to “xylenes.” However, the referenced publication uses “total xylenes.”

The correction has been made.

48. Section 1.1, Description, page 2, 3rd para: “Sand-tank experiments by Britt (2003) seem to show widespread dispersion of solutes through a well bore under conditions of uniform flow.” This statement should be deleted from the document for the following reasons: The so-called in-well mixing of groundwater contamination has not been proved by any analytical model studies. The Lab Model (Sand-tank) study consists of 4-inch-wide screen for the height of the tank (both upstream and downstream side) is a rectangular screen. A no-flow boundary exists on the other two sides of the so-called well bore. Such a setup cannot remotely represent well bore. In fact, the setup represents a rectangular gate with a screen. The conventional definition of pore volume for a well bore does not apply to the Lab Model study. The Lab Model study cannot represent any field conditions.

Although we are retaining a reference to the work as a professional presentation, we have deemphasized it and clarified some of the potential uncertainties. Section 1.2 now notes that “…observations from a laboratory study using a sand-tank model in approximately two dimensions (Britt and Tunks 2003) imply that diffusive mixing may be an important consideration.”

49. Section 2.4.1, page 9, 3rd para: "For profiling purposes, as a general rule, a single 1.5- to 2-foot-long PDB . . . ." Delete the reference to 2-foot PDB. The Executive Summary indicates 1.5-foot PDB. The PDB length should be maintained consistently through out the document.

    PDBs are available in many sizes and can be custom made. Lengths of 5 feet and more have been deployed successfully. The point being made here is that a single PDB in the range of 18–24 inches length should not represent more than 5 feet of vertical well space. The text has been changed.

50. Section 2.4.2: Please include reference to "flowmeter."

    Please see the response to Comment #28.

51. Section 2.4.3, Horizontal Flow: "PDB samplers require sufficient groundwater flow . . . ." Diffusion plays important role with the PDB and not the groundwater flow. Moreover, the phrase "sufficient groundwater flow" is more confusing. Can any one define what is sufficient (or insufficient) groundwater flow? This section needs revision.

    Some groundwater flow is necessary for the PDB sample to represent groundwater conditions rather than stagnant well conditions. This is why conventional purge sampling methods were originally developed. There is no precise definition of what constitutes sufficient flow. Some guidelines, however, are provided in the discussion of item #8 in Section 3.

52. Section 7, Summary and Recommendation Item 1: "PDB sampling is as valid as . . . and regulators should support the use of this technology where appropriate." It is not the regulator's responsibility to support any technology. The role of regulators is to review the technology that can satisfy the requirements of the regulations. The phrase "regulators should support" can be replaced with "regulators should give considerations for . . . ."

    The workgroup was, in fact, using the term "support" in the sense of seriously evaluating PDB sampling at a site on its merits. Certainly there is no suggestion that this technology, or any other, be blindly implemented. The wording has been changed to recommend "active consideration" of PDB sampling.

53. The ITRC Diffusion Sampler Team (DST) should consist of members from various disciplines such as hydrogeologists, hydrologists, geotechnical engineers, and chemical engineers. Various disciplines can bring the best from their profession for the technical guidance.

    Agreed. As Appendix F shows, members of the Diffusion Sampler Team represent a broad spectrum of professional areas and occupational realms. The development of this guidance document, as well as a myriad of other workgroup activities, has benefited immensely from the diversity of backgrounds and views brought to bear on the subject by our membership.

54. [On] page 2 the reference to sand tank experiments should be deleted. The experiment with sand tanks conducted by Britt were two-dimensional and did not account for boundary conditions. If the reference is included the sentence should read: "Two-dimensional experiments by Britt (2003) seem to show widespread dispersion of solutes in sand tanks under conditions of uniform flow."

    The text has been modified. Please see the response to Comment #48.

55. The guidance document should mention the net "sock" that is used to hold the bag's shape in the well.

    Actually, the "sock" is not used to maintain the shape of the bag but serves as a protective shield against mechanical damage during deployment and recovery. This information has been added to the description in Section 1.1.

56. Section 1.1. The sand tank work by Sandy Britt has not been extensively peer-reviewed and should not be cited within the ITRC document. The observation by Britt of widespread distribution of solutes within a well bore may be an artifact of the experiment design rather than due to dispersion.

    The text has been modified. Please see the response to Comment #48.

57. Section 1.2. The work by Parker and Clark (2002) should be mentioned in the ITRC document. Their work supports the conclusion that a PDB sample is a time-weighted average and that analytical differences between PDBs and conventional sampling is due to natural solute variation.

    This reference has been added.

58. Section 2.3. This section contains the only reference to biofouling within the entire document. The issue of biofouling should be further explained. If PDBs are biofouled, how should be situation be addressed? Can PDBs still be used for LTM if biofouling occurs? Should the deployment time be decreased to reduce the possibility of biofouling? What degree of biofouling causes a concern? Is the PDB sample still usable if upon retrieval it is coated with slime?

    Despite actively seeking such information, the team has found no record of biofouling of PDBs. If biofouling were encountered in a specific situation, it would be cause for concern but would have to be evaluated at that time and in context.

59. Section 4.2.1. A literature reference should be provided for the "50%" number given as an acceptable percent relative difference for duplicate samples.

    Please see the response to Comment #33.

60. Section 4.4. For compliance monitoring, the ability of PDBs to yield long-term representative samples should be periodically checked by conducting side-by-side evaluations with conventional or low-flow purging techniques. Likewise, for site closeouts, the PDBs should be checked with conventional techniques before final decisions are made about the achievement of water quality objectives. Hence, for RCRA and CERCLA corrective action, potentially 85% of the groundwater monitoring could be done with PDBs. The first 10% of the groundwater monitoring would be done with conventional techniques to establish a baseline. The next 85% of the samples would be PDBs if the results agreed with the initial baseline. Then, upon the completion of the project, the last 5% of the sampling would be conventional sampling to demonstrate compliance to the water quality goals.

    This is a valid approach. As discussed in Sections 4.1 and 4.2, there are several alternatives. The issues should be explored and decided upon in advance of deployment.

61. Section 4.5. For RCRA interim status facilities subject to groundwater monitoring, 40 CFR Section 265.92 requires semiannual sampling for pH, specific conductance, total organic carbon, and total organic halogen. Likewise, CCR Title 22 Section 66265.97 has a similar requirement for temperature, electrical conductivity, turbidity, and pH at interim status facilities. Hence, this is a federal and state impediment for the use of PDBs at RCRA interim status facilities. However, there is no comparable requirement for RCRA-permitted facilities in both the federal and state regulations.

    The Diffusion Sampler Team does not regard RCRA status as a regulatory impediment, as the related regulations do not preclude the use of PDB sampling. Obviously, as at all sites, specific concerns and requirements will determine whether or not PDB sampling is a useful or economic approach. PDBs can be used in conjunction with other technologies, e.g., as outlined in Section 5.2.3.

62. Section 6. There are other published studies beside Vroblesky (2001) which can be cited as case studies, such as Harte (2002), Parker and Clark (2002), Ballestero et al. (2002), and Gefell et al. (1999).

    The references provided have been added.

63. Section 7, Bullet 9. PDBs should be used for compliance and sentinel monitoring only if the PDBs are periodically checked by conventional methods. Likewise, for site closeout, the PDBs should be checked by conventional methods.

    The team has stated its opinion that PDB sampling is technically valid for compliance and sentinel sampling. The exact requirements need to be negotiated with the cognizant regulatory authority.

64. Comment #61 should be modified to include CCR Title 22, Sections 66265.97(e)13 and 66264.97(e)13 that require temperature, electrical conductivity, turbidity, and pH be sampled each time groundwater is sampled. So, this regulation exists for both interim status and permitted hazardous waste landfills, surface impoundments, waste piles, land farms, and

other facilities to which Article 6 groundwater monitoring requirements apply. 40 CFR section 265.92 also requires annual sampling for chloride, iron, manganese, phenols, sodium, and sulfate.

San Diego County does allow for diffusion bags, but with conditions. See page 5-43 for definition of discrete point-interval sampling that includes PDBs and page 5-52 and 5-53 for the conditions in the attached section of the county's SAM manual. Note: SAM allows closeout sampling with PDBs but requires vertical profiling to be repeated at that time. Also requires sampling depth at highest concentrations for routine monitoring. Must also establish that wells have demonstrated net flow or measured flow through the well.

If I'm not mistaken, I believe that I indicated that San Diego County had included sections on alternative sampling devices that placed restrictions on the use of devices such as PDBs. The manual states that there are better alternatives but that, if used/approved, would require demonstration of a net positive flow through the well screen before being implemented. It recognized that these "passive" devices rely on the positive flow from the aquifer through the screened interval to bring the contaminants to the sampler device (unlike active sampling devices that purge the sampling point).

Please see the response to Comment #61. The suitability of PDB sampling must be decided on a site specific basis. There are technical reasons that PDB sampling is not appropriate for some sampling needs, such as for metals. At the same time, PDBs can be used in conjunction with other technologies, as outlined in Section 5.2.3.

State of New Hampshire

65. Oxygenates such as MtBE, TAME do not diffuse well through the PDB membrane. As a result, this technology is not appropriate for most LUST sites. I think more research needs to be done on alternative membranes if the technology is to be viable for most petroleum sites. The other membrane issue is the inability to get accurate results for naphthalene. The petroleum sites where oxygenates are not a concern typically have naphthalene as a COC. As a result, it is hard to see a petroleum site application for the technology.

    As discussed in Sections 1.1, 2.2, and 4.2.2 of the document (with special reference to Tables 1-1 and 4-1), an acknowledged limitation of PDB sampling is that the polyethylene membrane does not allow rapid diffusion of all compounds. Target analytes are primarily VOCs. Research is currently under way on membranes that can encompass non-VOCs.

66. The report does not have a lot of data in it on how long the PDB samplers can be left in wells. The technology would be desirable as a low-cost replacement for traditional sampling. I would envision the PDB samplers being collected and then a new PDB being put in the well for the next round of sampling. This would avoid the two-trip scenario and is how the technology is likely to be used by budget-conscious consultants. If this becomes a common practice, we would need to know whether the PDB can be left in for up to six months

(semiannual sampling is common) without compromising the sample via biologic growth, etc.

Deployment intervals are discussed in Section 2.3. Current practice often deploys new PDBs at the same time existing ones are retrieved. To our knowledge there are no documented instances of biological fouling or other deterioration of polyethylene membranes during deployments of the length mentioned.

State of Nevada

67. Page 2, paragraph 2: Correlation criteria of 70% were considered favorable. This seems low to me. Additional brief discussion in this section or in an appendix would give greater reassurance to the skeptical regulatory who may be accustomed to 95% levels of statistical significance.

    The results from PDB sampling and other sampling techniques should not be expected to be identical. Comparison of sampling results is discussed in Section 4.2. Details of the specific study in question are available in the full report (Parsons 2003).

68. Page 3, Figure 1-2: The conclusion(s) that should be drawn from this figure is/are not clear to me. I suggest redrawing it, omitting one of the two curves included, or omitting the entire figure. Simply including a reference to the statement that "contamination stratification has been observed" may suffice.

    The figures have been changed to better demonstrate the stratification concepts being discussed.

69. Page 7, Paragraph 1, Last sentence: Change the word "above" to "below" or "following."

    Editorial changes have rendered this comment moot.

70. Page 21: Length of deployment is not included as an issue in this bulleted list; however, it was discussed previously. Was it intentionally omitted?

    The discussion of low correlations has been shifted to Section 4.2.3. The length of the PDB deployment is generally not an issue as long as the minimum equilibration time is provided. Limited data are available on very long deployments (greater than six months). The time lag between PDB and conventional sampling events is mentioned as a potential factor in low correlations, as is water table fluctuation over the deployment period.

71. Page 28, Table 5-2: (a) Is this table labeled correctly? In all cases, the long-term cost of PDBs are HIGHER than conventional costs; however, the cost advantages are of PDB are listed as greater than conventional sampling. (b) How was the last column, "Return on

investment," calculated? It is not clear to me why ID #2 had only a 1% cost advantage. Perhaps including the formulas used as footnotes or in an appendix would suffice.

The column headings for Table 5-2 have been corrected.

The return on investment is calculated by dividing the anticipated cost savings from PDB sampling by the implementation costs. This is calculated for the entire long-term monitoring period and includes the variables associated with each site, such as the number of wells and frequency of sampling. When the number of wells being converted is small, or the remaining monitoring period is short, the return on investment can be low. More detail is available in the original report (Parsons 2003).

72. Page 29, Paragraph 4, Last sentence: Rephrase. The notion that an "overall" reduction in costs was "consistent" despite "significant variability" is confusing to me.

    The wording has been changed to clarify the statement.

73. What studies have been done on degradation of the PDB in the environment, and how that may or may not affect the analyses.

    No mechanical degradation of the PDB has been found over long deployments or even in contact with pure product. Chemical contamination is not really an issue because the sample equilibrates with groundwater over the deployment interval.

74. [An] item that does not appear to be addressed is seasonal water level variations. It would seem to me that the user of PDBs would need to sample for at least a year with PDBs to understand where the "hot spot" is for each season. Perhaps historical data could be used to estimate the theoretical location of this "hot spot"; however, the document does not seem to address this issue.

    It is prudent to analyze data for seasonal trends regardless of the sampling method employed. At some sites the seasonal water levels can vary markedly. Under such circumstances it might take longer to establish clear trends.

75. The document included some discussion about long-term deployment of the samplers; however, there was no discussion about the long-term quality of the wells in which the bags are used. Without purging of the wells, does sediment accumulation become a problem, i.e., does the usability of the wells decrease faster than in wells that are purged as a part of sampling?

    Unless the well screen is at the bottom of the well casing, normal purging will not clear sediment from the bottom of a well. Moreover, PDBs will not permit the transfer of particulates into the sample bag. Long-term well quality issues exist independently of the sampling technique.

State of Texas

76. Two compounds on Table 1-1 (bromoform and napthalene), shown under "Favorable laboratory diffusion testing results" are also listed on Table 1-2 under the heading "Less favorable results in field sampling comparison study." Since both of these tables are recommended for use in determining appropriate compounds for use of PDB samplers, this apparent contradiction needs to be addressed in some manner.

    Table 1-1 reflects the results of a laboratory study indicating that both bromoform and naphthalene diffuse readily through the PDB membrane. Table 4-1 (formerly Table 1-2, but now in Section 4.2.2) reflect the specific experience with sampling VOCs in the field, as evaluated according to specific criteria. Less than satisfactory performance was judged against certain criteria, and possible reasons for such performance are detailed in Section 4.2.3.

77. While the discussion under Section 4.5 Survey of State Regulators is useful in describing the different views of state regulators on the acceptability of PDB sampling for certain activities, it does not address why the state regulators held those views, especially where a significant number indicated they would not use PDB sampling for a specific purpose, e.g., closeout and site characterization. A better fleshed-out understanding of regulator concerns could lead to further research needs, etc.

    The survey did allow for comments by those completing it, but such comments were not always provided. A more thorough discussion of the survey results is being prepared separately.

78. On Table 5-2, it appears that the data under the column of "Long-term cost of conventional sampling per well, per event" should actually be under the next column "Long-term cost of PDBs per well, per event" and vice versa. Otherwise, it appears the cost of PDB sampling exceeds conventional sampling costs in every case which is not true.

    These changes have been made.

Commonwealth of Virginia

79. If a "proof of method" demonstration were required, then it seems reasonable to simply deploy both sampling methods in all the wells at a site during the initial sampling. If the analytical results indicated that the paired sampling was within the 30% relative percent difference (RPD) that ITRC notes on page 20, then it is likely that diffusion sampling is viable for the site.

    This is a valid approach. As discussed in Sections 4.1 and 4.2, there are several alternatives. The issues should be explored and decided upon in advance of deployment.

State of West Virginia

80. Page 16: "8. Are the monitor wells to be sampled in an area where there is sufficient groundwater velocity? Low groundwater velocity can result from either a low hydraulic conductivity or a low hydraulic gradient." This should be "monitoring wells," and low velocity can also result from a small quantity of groundwater.

    Editorial changes have been made.

APPENDIX F

ITRC Contacts, Fact Sheet, and Product List

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