NEWMOA Technology Review Committee
Advisory Opinion

Innovative Technology: **Passive Diffusion Bag Samplers for VOC Sample Collection from Groundwater Monitoring Wells**[1]
Date of Opinion: **February 15, 2002**

The purpose of this Advisory Opinion is to raise awareness of the use of passive diffusion bag (PDB) sampler technology for VOC sample collection from groundwater monitoring wells and its on-site application in the Northeast.[2] This Advisory Opinion is intended to communicate Technology Review Committee (TRC) interest in the use of PDB sampling technology to potential users of hazardous waste site characterization technology, such as consultants, as well as to project managers within the various state site cleanup programs. The Advisory Opinion is also intended to educate consultants and the state regulators who oversee projects about the factors that can affect the proper use of diffusion samplers.

All seven of the Northeast states participated in the development of this Advisory Opinion consensus statement. However, it should be noted that this Advisory Opinion is not intended to be an "approval" of this technology. The appropriateness of the use of PDB samplers will need to be determined on a site-by-site basis. Potential users should contact officials in the state in which the project is located to determine if there are any state-specific requirements that could apply.

Project Background:

Recognizing the need to overcome barriers to the acceptance of technology innovation, the six New England States, EPA Region I - New England, the Northeast Waste Management Officials' Association (NEWMOA) and the New England Governors' Conference signed a Memorandum of Agreement (MOA) in March 1998 to promote interstate regulatory cooperation for waste site assessment and cleanup technologies. Subsequently, NEWMOA has worked closely with EPA Region I and the Northeast Hazardous Substances Research Center (NHSRC) to increase the understanding of the factors that discourage the use of innovative technologies. NEWMOA held meetings and conference calls with NEWMOA's Waste Site Cleanup Workgroup and co-sponsored, with NHSRC, a Stakeholders Workshop held in May 1998 called "Increasing the Use of Innovative Technologies on Small Hazardous Waste and Petroleum Sites." The focus of this Workshop was on building consensus among the stakeholders regarding measures to reduce or eliminate obstacles to the use of innovative site assessment technologies.

At the May 1998 Stakeholder Workshop, participants identified the lack of an interstate forum in the Northeast to actively review technologies and communicate both public and private sector use of innovative technologies as a major impediment to the overall marketability of the newer field analytical, characterization and monitoring technologies. To address this need, NEWMOA has established the TRC, made up of one or more staff members from each of the Northeast states to choose the technology focus, coordinate state review, issue advisory opinions and disseminate information on the use of innovative technologies.

Benefits of Innovative Site Characterization and Long-Term Monitoring Methods:

Regulatory and institutional barriers to the adoption of innovative hazardous waste site assessment and monitoring technologies and methods can result in increased expenditures to evaluate and remediate contaminated sites. Because innovative techniques have the potential to protect the environment and the public's health in a more cost-effective and efficient manner, finding ways to encourage their increased use is crucial. Some examples of the potential benefits of using innovative sample collection and field analytical technologies include:

- More Information: for the same cost, a greater number of samples can be collected and/or analyzed using innovative techniques when compared to the standard approach, providing more information upon which to base decisions. For example, PDB samplers provide a low-cost method to evaluate the distribution of VOCs in wells – multiple samples can be collected from the same well in virtually the same amount of time as an individual sample. More accurate identification of the contaminant horizon can help optimize the remedial design.

- Less Cost and Time: Innovative sample collection and analysis methods typically require less time and cost to implement than traditional methods. For example, PDB samplers can require significantly less overall labor hours for sample collection than the conventional low-flow sampling method. In addition PDB samplers significantly reduce or eliminate the generation of liquid wastes from sampler decontamination and well purging, saving handling and disposal costs.

More information about the benefits of using innovative site characterization and monitoring approaches is contained in the January 3, 2000 article, *Improving the Cost-Effectiveness of Hazardous Waste Site Characterization and Monitoring* by the U.S. EPA Technology Innovation Office which can be found on the Internet at: www.clu-in.org/tiopersp. Additional information can be found at www.clu-in.org in the Site Characterization section. All four NEWMOA TRC advisory opinions on innovative site characterization and monitoring techniques are available at www.newmoa.org. Finally, the Interstate Technology and Regulatory Cooperation Workgroup (ITRC) website contains a section devoted to information about diffusion samplers: http://diffusionsampler.itrc.org.

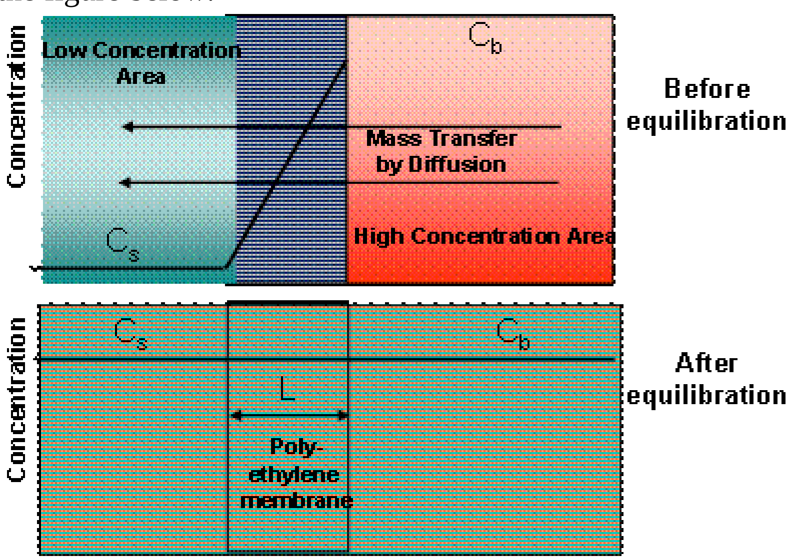
Overview of Technology:[3],[4]

Passive diffusion bag (PDB) samplers have the potential to be used for cost-effective long-term monitoring of most volatile organic compounds (VOCs) in groundwater. Generally, a PDB sampler consists of a semi-permeable membrane tube made from low density polyethylene (LDPE) that is filled with laboratory grade deionized water and placed at a specific location within the screened interval of a monitoring well. The PDB sampler is left in place for at least two weeks while contaminants in the groundwater diffuse into the water in the bag. Eventually, the concentration within the bag is the same as in the surrounding groundwater and the sampler is retrieved.

When the sampler is retrieved the water is used to fill a standard VOA vial. Therefore, PDB samplers are an innovative sampling method only. Once the PDB sampler is retrieved from the well, sample handling concerns are identical to those associated with traditional sampling methodologies, such as introduction into sample containers, preservation, chain of custody, and analytical method. None of the data collected suggest that VOCs leach from the LDPE or that there is any detrimental effect from the LDPE on the VOC sample.[5] More information detailing PDB sampler technology is included in the sections that follow.

Theory

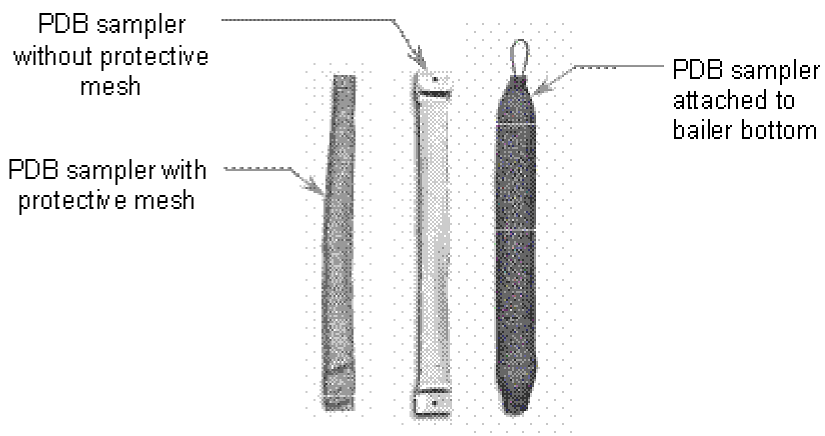
PDB sampling takes advantage of the Law of Diffusion which states that compounds will migrate from an area of high concentration to an area of low concentration until an equilibrium is achieved, as illustrated in the figure below.



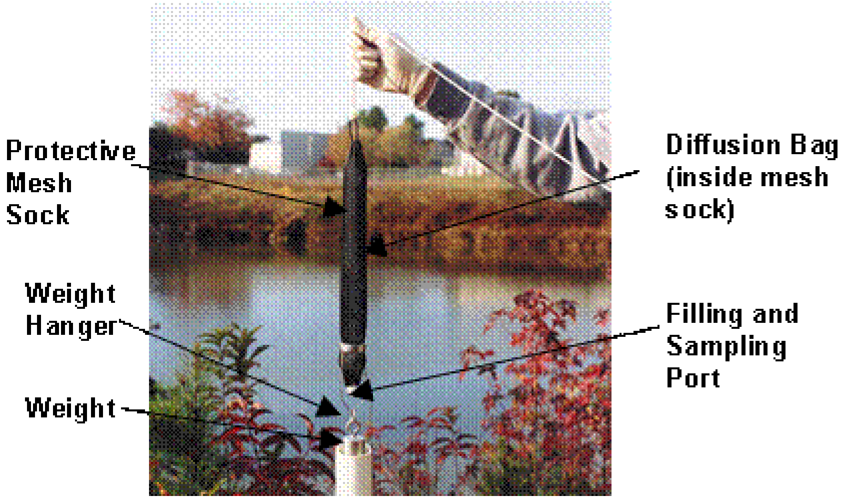
For many VOCs of interest, the VOC concentration in water within the PDB sampler approaches the VOC concentration in water outside of the PDB sampler over an equilibrium period. The rate at which equilibrium is established is governed by Fick's Law which states that the rate of diffusive mass transfer through a unit area (J) is proportional to the difference in concentrations (C_b-C_s) divided by the distance separating those concentrations (L): $\mathbf{J = D (C_b - C_s) \div L}$, where D is the constant of proportionality, also known the diffusivity or the diffusion coefficient.

Description and Deployment

A typical PDB sampler consists of a semi-permeable membrane lay-flat tube made of LDPE between 12 and 24 inches long. PDB samplers are patented, and therefore must be obtained from an authorized distributor, or potential users must negotiate a nonexclusive license for sampler construction from the United States Geological Survey (USGS).[6] The tube is closed at both ends and contains laboratory-grade deionized water that is free of VOCs.[7] The typical diameter of a PDB sampler used in a 2-inch diameter well is 1.2 inches. An LDPE mesh on the outside of the tube is sometimes used to protect against abrasion in open boreholes and also as a means to attach the sampler to the suspension line. Examples of PDB samplers with and without the protective mesh are shown below.



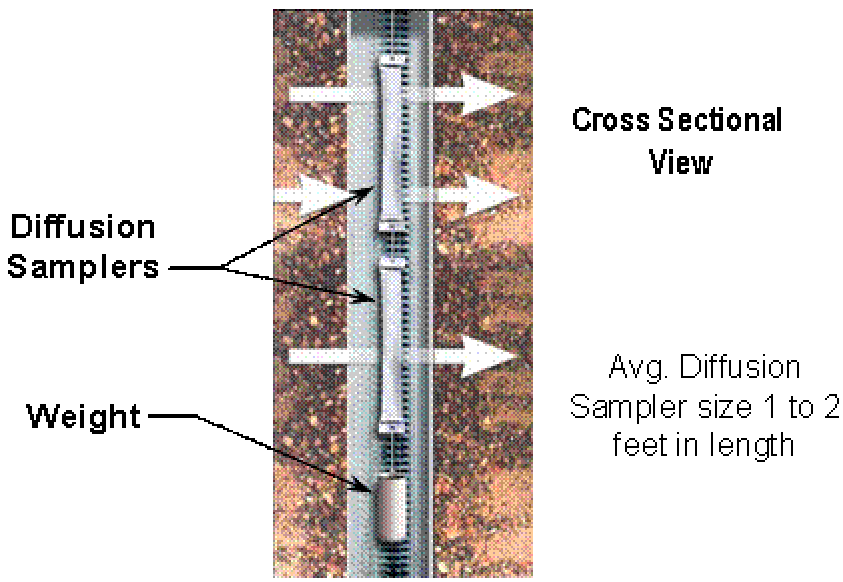
A variety of approaches can be used to deploy the PDB samplers in wells. A typical deployment approach is to attach the PDB samplers to a weighted line and then position and secure the line so the PDB is at the target horizon within the well. A stainless steel line is preferable, but a non-buoyant non-stretch line could be used. The line should not be reused in differing wells to prevent carryover of contaminants. However, stainless steel line could be reused if thoroughly decontaminated. An alternate deployment approach is to attach the PDB sampler to a fixed pipe in the well. In order to counterbalance the buoyancy of the PDB sampler, sufficient weight should be added. Weights can be attached directly to the PDB sampler if the attachment point is of sufficient strength to support the weight. If the weights are stainless steel they can be reused after sufficient decontamination. A typical deployment is illustrated in the following figure.



The amount of time that the samplers should be left in the well prior to recovery depends on both the time required by the PDB sampler to equilibrate with ambient water and the time required for the environmental disturbance caused by sampler deployment to return to ambient conditions. With most tested VOCs, the PDB samplers equilibrated within 48 hours. However, the well water may require a substantially longer time to restabilize following the disturbance of sampler deployment. Results of several studies indicate that approximately two weeks of equilibration should be adequate for water PDB samplers in most wells screened in sandy formations. In less permeable formations, longer equilibration times may be required and PDB samplers might not be appropriate for use in poorly yielding formations. As a general rule, PDB samplers should not be used in water-bearing zones with a hydraulic conductivity of less than 1 x 10^{-6} centimeters per second.

There is no specified maximum time for sampler recovery. Samplers have been left in place in VOC-contaminated groundwater for three months and up to a year without any loss of bag integrity. However, the effects of long-term (greater than one month) deployment on bag and sample integrity have not yet been thoroughly tested for a broad range of compounds and concentrations. In some environments, a biofilm can develop on the outside of the bag, reducing the transfer of some compounds through the bag. In all cases, the user must demonstrate that the chosen equilibrium time is appropriate for the situation in each monitoring well.

If there are vertical components of intra-borehole flow, multiple intervals of the formation contributing to flow, or varying concentrations of VOCs vertically within the screened interval, then the deployment of multiple PDB samplers within a well could more fully characterize the contaminated horizon(s) and would be more appropriate than a single sampler. However, if vertical flow is found to be occurring, then the VOC concentration in the PDB sampler cannot be correlated with the position of the sampler in the well nor can it be assumed to be representative of the entire screened interval, and therefore, PDB sampling might not be the most appropriate technique for sample collection. A visual example of multiple PDB samplers in a well is included below.



Recommendations for PDB sampler deployment vary with screen length:

- **5 feet or less**: PDB sampler in the center. Note that contaminant stratification has been observed in wells with screens of less than 5 feet.

- **5-10 feet**: initially use multiple PDB samplers to ascertain the presence or absence of contaminant stratification.

- **10 feet or more**: for anything other than qualitative reconnaissance purposes, PDB samplers should be used only in conjunction with borehole flow meters or other techniques to characterize vertical flow, and vertical variability in hydraulic conductivity and contaminant distribution.

PDB samples are removed from the well using the attached line. Excess water should be removed from the outside of the sampler prior to sample collecting in order to minimize the potential for cross contamination or dilution of the sample. The sample is transferred from the PDB into 40 mL volatile organic analysis (VOA) vials using one of several methods. Some commercially available PDB samplers come with a discharge device. For samplers with a fill plug, the plug can be removed for sampling. The sampler can be pierced near the bottom with a small-diameter tube. Lastly, decontaminated scissors can be used to cut open the bag at one end. In all cases, care should be taken to minimize the potential for volatilization losses.

Applicable Contaminants[8]

PDB samplers are appropriate for many, *but not all*, VOCs. Therefore, PDB samplers are appropriate for use at well-characterized sites where the target chemicals are known and have been determined appropriate for PDB samplers. PDB samplers are not appropriate for inorganic compounds. They also have a limited applicability for the very soluble and the very insoluble organic compounds, such as acetone, MTBE, most semi-volatiles, and most ions. Hydrophobic compounds can have an affinity to the LPDE plastic and do not diffuse into the water inside the bag. The VOCs that have been tested and shown good correlation between the results from PDB sampler water and test-vessel water (11 percent or less difference) are listed below:

benzene	DBC chloromethane	trans-1,2-dichloroethene	1,1,2-trichloroethane
BDCmethane	dibromomethane	1,2-dichloropropane	trichloroethene
bromoform	1,2-DCbenzene	cis-dichloropropene	TCFmethane
cholorobenzene	1,3 – DCbenzene	EDB	1,2,3-TCPA
carbon tetracholoride	1,4-DCbenzene	trans-1,3-DCPE	1,1,2,2-PCD
chloroethane	DCFmethane	ethyl benzene	tetrachloroethene
chloroform	1,2-dichloroethane	naphthalene	vinyl chloride
chloromethane	1,1-dichloroethene	toluene	xylenes
2-chlorovinylether	cis-1,2-dichloroethene	1,1,1-trichloroethane	

The tested compounds showing poor correlation (>20 percent difference) are:

acetone
MTBE
styrene
MIBK

In addition, PDB samplers are not appropriate for sampling iron, sulfate, nitrate, and manganese, and therefore PDB samplers are not recommended for use to evaluate the natural attenuation process unless the necessary natural attenuation parameters can be collected in another manner.

Comparison of PDB Sampling to Traditional High Volume Purge and Low Flow Techniques

A general comparison of PDB, high volume purge and low flow sampling is presented below:

- **PDB Samplers**: Generally, diffusion samplers constitute a point sample that represents ambient conditions better than conventional methods because there is no mixing. PDB samplers are useful for targeting high concentrations within a screen interval. Average concentrations for a screen interval are obtained by using multiple samplers. Multiple samplers can also be used to characterize contaminant stratification within a well. Eliminates or substantially reduces the amount of water removed from the well that requires management and the amount of decontamination waste generated.

- **High Volume Purge Sampling** (≥ 3 casing volumes): Provides a flow-weighted sample, meaning that more permeable zones provide proportionally more water than less permeable zones. Integrates water over a relatively large area and alters concentrations by mixing, and can sometimes induce flow from horizons not in the vicinity of the well screen that would not enter the well under ambient conditions. A substantial quantity of water is removed from the well and a significant amount of equipment decontamination waste is generated, both of which require proper management.

- **Low-flow Sampling**: Depending on geology, can consist of a mixed sample that mixes concentrations over varying intervals like a purge sample, or can approximate a point sample similar to a PDB sample. However, the pipe intake must be at the proper depth to insure that the contamination is intercepted correctly. Less water is removed from the well than from high volume purging, but still much more water than from PDB sampling, and a significant amount of equipment decontamination waste is generated, both of which require proper management. Please note that a peristaltic pump should never be used for VOC sampling. Only a positive displacement pump placed in the well should be used for VOC sample collection.

However, before PDB samplers replace low flow or high volume purge groundwater sampling techniques, a side by side comparison should be completed. For well screen lengths greater than five feet multiple PDB samplers should be used as discussed on page 6. A comparison can be obtained by previously deploying the PDB sampler and retrieving it from the well just prior to placing the pump in the well. Another method is to place both the PDB sampler and the pump in the well simultaneously with the PDB sampler directly below the pump inlet, leaving the PDB sampler in the well after the pumped sample is collected. The comparison is particularly important in wells with high temporal chemical variability. In wells with low temporal chemical variability, comparison of PDB sampler results to historical concentrations could be adequate.

Generally, disagreement between the results from different sampling methods can be attributed to wells that connect zones of significantly different hydraulic head or contaminant concentration. PDB sample concentrations reflect the groundwater concentration at the sample location, whereas purging a well might draw in contamination from another area. If concentrations from the PDB sampler are higher than concentrations from the conventional method, then it is probable that the concentrations from the PDB sampler represent ambient conditions. With pumping methods, water from areas not adjacent to the screened interval can be drawn in, for example along inadequate well seals or through fractured clay. If that drawn-in water contains a lower contaminant concentration than the ambient water it would dilute the sample.

If the conventional method produces concentrations that are significantly higher than the concentrations found by using PDB sampling, then the PDB sampler may or may not adequately represent local ambient conditions. The difference may be due to a variety of factors, including hydraulic and chemical heterogeneity within the screened or open interval of the well, and the relative permeability of the well screen. PDB samplers can be more locally representative if pumped samples mix chemically stratified zones. As mentioned above, with pumping methods, water from areas not adjacent to the screened interval can be drawn into the well. If that water has a higher contaminant concentration, it would increase the concentration found in the pumped sample. A borehole flowmeter and multiple PDB samplers can be used to determine which of the methods better reflects the local conditions. A borehole flowmeter can assess whether intra-borehole flow is present and multiple PDB samplers can be used to determine if contaminant stratification is present.

The relative advantages and limitations of PDB samplers are outlined below.

Advantages:

- Eliminates or substantially reduces the amount of purge water associated with sampling that has to be managed.

- Inexpensive method to obtain groundwater samples. Typical costs are $16.50 to $22 per sampler.

- Relatively easy to deploy and recover – a minimal amount of labor and field equipment are required. Practical for use where access is a problem and where discretion is desirable.

- Samplers are disposable, so there is little downhole equipment to decontaminate between wells and minimal decontamination waste to manage.

- The use of multiple samplers can be helpful in delineating contaminant stratification in the open or screened intervals of monitoring wells. This is difficult to accomplish using conventional methods.

- The pore size of LDPE is about 10 angstroms or less, so sediment does not pass through the membrane into the bag. Therefore, the samplers are not subject to interferences from turbidity. However, turbidity by itself does not affect the concentration of VOCs in a sample.

- Alkalinity-contributing solutes do not pass through the membrane, allowing for collection of VOCs in a non-alkaline matrix, and thereby eliminating the VOC losses associated with the foaming that occurs when using acid to preserve the sample in highly alkaline water.[9]

Limitations:

- Integrates over time - would be a limitation in an aquifer where VOC concentrations change more rapidly than the samplers equilibrate and the goal of sampling is to collect a representative sample of a particular point in time.

- Water-filled LDPE PDB samplers are not applicable for all compounds. The samplers are not appropriate for inorganic compounds. They also have a limited applicability for the very soluble and the very insoluble organic compounds, such as acetone, MTBE, most semi-volatiles, and most ions.

- PDB samplers cannot be used to measure parameters such as pH, temperature, and redox potential. However, these parameters are typically not necessary to meet the goals of a sampling event where the use of PDB samplers is appropriate. The purpose of measuring pH, temperature, and redox potential is typically to document that the well has been adequately purged before sample collection, or for use in evaluating natural attenuation. Well purging is not an issue when PDB samplers are used, and PDB samplers are not recommended for natural attenuation monitoring.

- PDB samplers rely on the free movement of water through the well screen. If the well screen is occluded or if the aquifer or the sandpack surrounding the well screen is more transmissive than the well screen, then VOC concentrations in the well might not represent concentrations in the adjacent aquifer.

- VOC concentrations in PDB samplers usually represent concentrations found at the elevation of the sampler within the well screen or open interval. This is often not a limitation, but might be in a situation where the groundwater contamination is above or below the screen, or not in the interrogated sample interval.

- In well screens transecting zones of different hydraulic head, VOC concentrations in water from PDB samplers could represent concentrations in a part of the aquifer not adjacent to the PDB sampler. However, multiple PDB samplers may be used in conjunction with borehole flow meter testing to gain insight on the movement of contaminants into and out of the well screen.

- In well screens transecting zones of different chemical concentrations or constituents, the use of a single PDB sampler may not adequately target nor provide accurate concentration values for the most contaminated zone. However, multiple PDB samplers can be used to locate the zone of highest concentration in the screen. Multiple PDB samplers may be needed in wells where flow patterns through the screen change as a result of groundwater pumping or seasonal fluctuations. Analytical costs when using multiple PDB samplers can be reduced by selecting a limited number of the samplers for laboratory analysis based on field screening using gas chromatography at the time of sample collection.

Independent Verification and Use in the Northeast:

PDB sampling technology was developed by the United States Geological Survey (USGS) for long-term groundwater monitoring use. The technology has not been evaluated in the EPA's Environmental Technology Verification (ETV) Program. However, the USGS, in cooperation with the U.S. EPA, the Interstate Technology and Regulatory Cooperation (ITRC) Workgroup, the U.S. Army Corps of Engineers, the U.S. Air Force, the U.S. Naval Facilities Engineering Command, the Federal Remediation Technologies Roundtable, and the Defense Logistics Agency, published the *Users Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells* in March 2001. The users guide can be obtained at http://diffusionsampler.itrcweb.org and http://www.frtr.gov. The guidance includes case studies on the use of PDB samplers at six sites, including one in the Northeast, Hanscom Air Force Base in Bedford, Massachusetts. The case studies evaluate the results of PDB samplers in comparison to conventional high volume purging and/or low-flow sampling methods.

PDB samplers have been used successfully at numerous other army and navy sites throughout the country, including the Naval Air Station in Brunswick, Maine. In addition to these military sites, PDB sampling technology has been successfully tested during site characterization and/or for long-term monitoring at Superfund and/or state level sites in several Northeast states, including New Hampshire and Vermont. PDB samplers have been approved for monitoring on a site-by-site basis in New Jersey and New York.

Recommendations:

The TRC has determined that, if used in appropriate situations, passive diffusion bag sampling technology can provide useful data that should lower the cost of long-term groundwater monitoring. Potential users of PDB sampling technology are strongly urged to consult the *Users Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells* (March 2001) prior to planning the field effort. The TRC recommends the following items to improve or insure product performance; however, users should recognize that there might be additional requirements for use at a particular site.

1. PDB samplers are appropriate for use at well-characterized sites where the target chemicals are known and have been determined appropriate for PDB samplers.
2. Before PDB samplers replace low flow or purge groundwater sampling techniques, a side by side comparison should be completed.
3. PDB samplers should equilibrate for a minimum of 2-weeks in monitoring wells constructed in sandy soils. The user must demonstrate that the chosen equilibrium time used is appropriate when applying PDB samplers in less permeable formations; in waters colder than have been previously well tested (10^{o}C); or for target chemicals without sufficient corroborating data from prior studies.
4. For the initial sampling event, multiple PDBs should be deployed in all monitoring wells with screens greater than 5 feet in length, as discussed previously. Once contaminant stratification, or other complicating factors are determined NOT to be present, then a single PDB sampler in a well might be appropriate.
5. Replicate samples should be collected from a single PDB sampler at a rate of 1 set of replicates from 1 in every 10 PDB samplers deployed (10 percent).
6. For PDB samplers that are not purchased pre-filled, a sample of the water used to fill the PDB samplers should be collected when the bags are being filled and analyzed to detect any possible introduction of VOCs by the water used.
7. For pre-filled PDB samplers, water from an extra sampler that is not deployed should be collected as a trip blank to determine whether contaminants have affected the samplers prior to deployment. This

type of trip blank should be collected at the time of deployment.

8. A traditional trip blank should also be used to assess whether external VOCs contaminate the sample due to the sample handling and/or analytical processes. These trip blanks are water filled VOA vials that are transported with the sample collection equipment and are collected at the time of sample collection.
9. Users must accurately measure the sampler's position within the well. "As-built" well diagrams are important.
10. PDB samplers should not contact non-aqueous phase liquid (NAPL) during deployment or retrieval to prevent cross contamination.
11. When PDB samplers are retrieved, they should be visually inspected and observations recorded in the field book, including deposits or coatings. Any irregularities noted should be reported to the project manager. Samplers that have a heavy build-up of organic coating or a tear in the membrane should be rejected.

The NEWMOA Technology Review Committee has issued this Advisory Opinion on this 31st day of January, 2002.

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[1] Gas-filled diffusion samplers have been successfully used to measure contaminant concentrations in ambient air, surface water, and also to measure the movement of VOCs from groundwater into surface water. However, at this time, written guidance procedures to implement these methods have not been issued by the EPA or USGS or other environmental government agency. Therefore, this advisory opinion focuses only on the diffusion sampler use for which guidance has been issued by a government agency. Check http://DiffusionSampler.itrcweb.org for the most up-to-date information on all uses of PDB samplers.

[2] In this document, the Northeast states are: Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Rhode Island and Vermont.

[3] Vroblesky, Don A., *User's Guide for Polyethylene-based Passive Diffusion Bag Samplers to Obtain Volatile Organic*

Compound Concentrations in Wells, USGS, March 2001.
[4] Vroblesky, Don and George Nicholas, Presenters, ITRC internet training on passive diffusion bag samplers, first presented in June 2001 and archived at: http://clu-in.org/studio/seminar.cfm.
[5] Vroblesky, D.A. and Campbell, T.R., "Equilibrium Times, Stability, and Compound Selectivity of Diffusion Samplers for Collection of Groundwater VOC Concentrations", *Advances in Environmental Research*, 2001, v. 5, no. 1, p. 1-12.
[6] A current list of vendors can be obtained from the USGS Technology Transfer Enterprise Office, Mail Stop 211, Reston, VA 20192, or 703-648-4344, or on the Internet at: http://sc.water.usgs.gov/publications/difsamplers.html.
[7] Samplers can be purchased pre-filled or unfilled. Unfilled samplers are equipped with a plug and funnel to allow users can add the laboratory-grade dionized water themselves.
[8] Vroblesky, D.A. and Campbell, T.R., "Equilibrium Times, Stability, and Compound Selectivity of Diffusion Samplers for Collection of Groundwater VOC Concentrations", *Advances in Environmental Research*, 2001, v. 5, no. 1, p. 1-12.
[9] ITRC Fact Sheet, *Passive Diffusion Bag (PDB) Samplers, Frequently Asked Questions (FAQs*), November 2001.