



INTERSTATE TECHNOLOGY & REGULATORY COUNCIL

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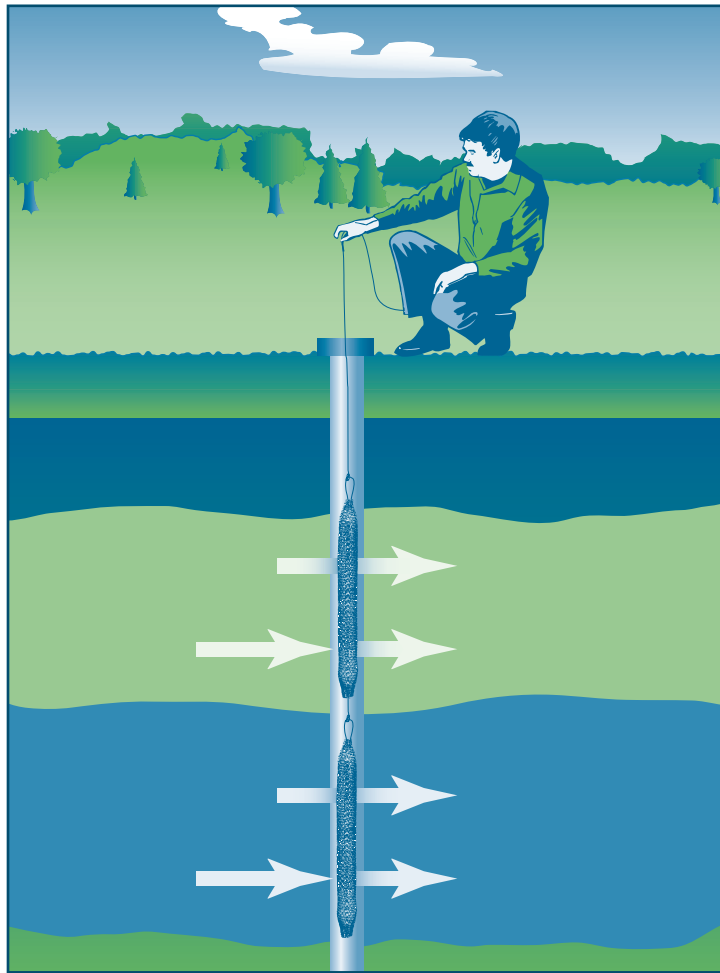


INTERSTATE TECHNOLOGY & REGULATORY COUNCIL



Technology Overview

Technology Overview of Passive Sampler Technologies



March 2006

Prepared by
The Interstate Technology & Regulatory Council
Diffusion Sampler Team

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Established in 1995, the Interstate Technology & Regulatory Council (ITRC) is a state-led, national coalition of personnel from the environmental regulatory agencies of some 40 states and the District of Columbia, three federal agencies, tribes, and public and industry stakeholders. The organization is devoted to reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers. More information about ITRC and its available products and services can be found on the Internet at www.itrcweb.org.

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EXECUTIVE SUMMARY

This document presents technical overviews of 12 passive sampling technologies. It describes each technology's basis of operation, intended applications, advantages, limitations, and development status. Contacts for additional information are provided. This overview is an outgrowth of interest and information generated in preparation of the *ITRC Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor VOCs in Groundwater* in February 2004. While the initial focus was on passive sampling of groundwater monitor wells, many of the technologies are applicable to surface water and/or vapor as well. Although not a comprehensive overview of all passive sampling technologies, it is of interest to those concerned with the development and use of passive sampling devices. A summary table highlighting the important attributes of each technology, including appropriate analytes, availability, and cost information, follows the 12 individual text descriptions.

The authors define a "passive" sampler as one that is able to acquire a sample from a discrete location without the active media transport induced by pumping or purge techniques. All of these passive technologies rely on the sampling device being exposed to media in ambient equilibrium during the sampler deployment period. For example, in wells, the well water is expected to be in natural exchange with the formation water. All of the devices provide a sample from a specific location (i.e., point samples). Spatial integration, if any, is a result of natural ambient flow of the sampled medium.

The passive samplers in this document are classified on the basis of sampler mechanism and nature of the collected sample, as follows:

1. *Devices that recover a grab well water sample.* Samples are an instantaneous representation of conditions at the sampling point at the moment of sample collection.
 - HydraSleeve™ Samplers
 - Snap Sampler™
2. *Devices that rely on diffusion of the analytes for the sampler to reach and maintain equilibrium with the sampled medium.* Samples are time-weighted toward conditions at the sampling point during the latter portion of the deployment period. The degree of weighting depends on analyte and device-specific diffusion rates. Typically, conditions during the last few days of sampler deployment are represented.
 - Regenerated-Cellulose Dialysis Membrane Samplers
 - Nylon-Screen Passive Diffusion Samplers (NSPDS)
 - Passive Vapor Diffusion Samplers (PVDs)
 - Peeper Samplers
 - Polyethylene Diffusion Bag Samplers (PDBs)
 - Rigid Porous Polyethylene Samplers (RPPS)
3. *Devices that rely on diffusion and sorption to accumulate analytes in the sampler.* Samples are a time-integrated representation of conditions at the sampling point over the

entire deployment period. The accumulated mass and duration of deployment are used to calculate analyte concentrations in the sampled medium.

- Semi-Permeable Membrane Devices (SPMDs)
- GORE™ Sorber Module
- Polar Organic Chemical Integrative Samplers (POCIS)
- Passive In-Situ Concentration Extraction Sampler (PISCES)

Some of these sampling technologies are relatively mature and accepted for appropriate applications by regulators in some regions and states. Nonetheless, they are still considered to be innovative technologies and few if any specific policies governing their use have been written into official regulations.

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APPENDICES

- Appendix A. Acronyms
- Appendix B. Glossary
- Appendix C. ITRC Team Contacts, Fact Sheet, and Product List

TECHNICAL OVERVIEW OF PASSIVE SAMPLER TECHNOLOGIES

1. INTRODUCTION

In 2001 the Interstate Technology Regulatory Council (ITRC) organized a Diffusion Sampler Workgroup to elucidate a passive sampling technology involving polyethylene diffusion bags (PDBs). The scientific validity and cost effectiveness of using this technology to sample volatile organic compounds (VOCs) in groundwater had been documented earlier. However, lack of awareness and misconceptions were hindering the use of this technology for monitoring groundwater quality at remediation sites around the country. A major goal of the workgroup was to educate the regulatory community on PDB technology, including its advantages, and limitations. This was accomplished by developing guidance documents, designing a central website for information, developing a cost model, assembling a database of sites where the technology has been employed, and encouraging exchange among regulators, investigators, and practitioners. As a result of these efforts there is now a much greater awareness and appreciation of PDB technology throughout the country, and its use has markedly increased.

In the course of developing guidance for the evaluation and comparison of PDB data with data from other sampling methods, the workgroup found it essential to have an in-depth understanding of the fundamental nature of samples obtained by each particular method. Temporal and spatial characteristics inherent to each method often produce equally valid, sometimes different representations of a given hydrologic setting. For example, groundwater sampling by conventional volume-based purge or low-flow purge sampling methods produces samples that are spatially integrated to varying degrees, but weighted toward zones of higher hydraulic conductivity. Differences between results from location-specific passive samples and integrated purge samples are sometimes a complication in regulatory acceptance of passive sampling data.

The present document is an extension of information obtained during the comparative evaluation of PDB data. The purpose is to provide a technical overview of some of these technologies, including their applications, advantages, limitations, and development status. Although not an extensive treatment, it is a starting point for those who are interested in innovative sampling devices.

Selection of a sampling technique should be based on a detailed and explicit formulation of the data quality objectives and end use of the data, together with a thorough understanding of the characteristics inherent to each sampling technology. Sampling methods best able to meet the specific objectives at the lowest cost can then be identified. The general statement “to obtain a representative sample” is often too broad. It should be further refined to tailor the sampling approach and obtain the highest quality and most informative data.

1.1 Passive Sampling Technologies

In the course of investigating and discussing PDB sampling the ITRC workgroup encountered other passive sampling techniques. Some of these techniques are applicable to surface waters, vapor, as well as groundwater. The workgroup received presentations on a number of devices

that did not require the costly process of pumping groundwater to the surface. We define a “passive” sampler as one that is able to acquire a sample from a discrete location or interval in a well, without the active transport associated with a pump or purge technique. In wells, all of these passive methods rely on the well water being in equilibrium with the formation water. Some of the diffusion based samplers are limited to certain suites of analytes.

The passive samplers included in this document can be classified into three categories:

1. *Devices that recover a grab sample.* Samples are an instantaneous representation of conditions at the sampling point at the moment of sample collection.
 - HydraSleeve™ Samplers
 - Snap Sampler™
2. *Devices that rely on diffusion of the analytes to reach equilibrium between the sampler and the well water.* Samples are time-weighted toward conditions at the sampling point during the latter portion of the deployment period. The degree of weighting depends on analyte and device-specific diffusion rates. Typically, conditions during only the last few days of sampler deployment are represented.
 - Regenerated-Cellulose Dialysis Membrane Samplers
 - Nylon-Screen Passive Diffusion Samplers (NSPDS)
 - Passive Vapor Diffusion Samplers (PVDs)
 - Peeper Samplers
 - Polyethylene Diffusion Bag Samplers (PDBs)
 - Rigid Porous Polyethylene Samplers (RPPS)
3. *Devices that rely on diffusion and sorption to accumulate analytes in the sampler.* Samples are a time-integrated representation of conditions at the sampling point over the entire deployment period. The accumulated mass and duration of deployment are used to calculate analyte concentrations in the sampled medium.
 - Semi-Permeable Membrane Devices (SPMDs)
 - GORE™ Sorber Module
 - Polar Organic Chemical Integrative Samplers (POCIS)
 - Passive In-Situ Concentration Extraction Sampler (PISCES)

These technologies are discussed in the following sections. The common treatment is to describe the technology and its applications, evaluate the current “state of the art,” and provide details on the features and limitations of the technology (including costs and deployment considerations). References and contact information are provided for each technology. A summary table comparing the properties of these devices is at the end of this document.

1.2 Diffusion Sampler Information Center (DSIC)

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), U.S. Geological Survey, U.S. Army Corps of Engineers, private industry, and multiple state agencies. 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 information and news on a variety of passive sampler technologies.

1.3 Passive Samplers Discussion Group

The Passive Samplers discussion group is a global forum for discussing passive (non-purge) sampling devices for groundwater and surface water environments. The intent is to provide information on innovative sampling technologies and encourage active interchange between researchers, practitioners, and regulators who deal with environmental sampling. The success of this discussion group relies on member participation, so we welcome anyone with experience or interest in this topic. Please pass an invitation along to your colleagues.

To join the list, send an email to LISTSERV@LISTSERV.WPI.ORG with a blank subject line and the following information in the message area: subscribe PASSIVE_SAMPLERS. You may choose to no longer participate on the listserve at any time by following the directions you will receive after joining the list.

2. HYDRASLEEVE™ SAMPLERS

2.1 Description and Application

The HydraSleeve™ groundwater sampler was developed in 1999 and is designed to recover groundwater samples from monitoring wells without purging. It can be used to sample a wide spectrum of analytes (e.g., VOCs, semi-volatile organics, metals) and can also be used to sample low-yielding wells. The HydraSleeve™ allows one to recover a discrete sample from the screened zone where the sampler is activated, with no drawdown and minimal agitation of the water column. The reed valve design keeps the device closed except during sample collection, thereby assuring that the sample is collected from the desired interval within the screened zone.

2.1.1 Physical Characteristics

HydraSleeve™ samplers consist of three basic components: a reusable weight; a long, flexible, lay-flat sample sleeve (usually made of polyethylene); and a self-sealing valve. The bottom of the flexible tube is sealed and the weight is attached to it. The valve is located at the top of the lay-flat sample sleeve and includes an attachment point for the suspension line.

Collecting a sample with the HydraSleeve™ is a simple, one-person operation. The sampler is deployed attaching a suspension cord to the top and a weight to the bottom and lowering the empty sampler into the well. During installation, hydrostatic pressure causes the sampler to retain its flat and empty profile for an indefinite period prior to sample collection. After lowering the sampler to the desired sample depth, the water column is allowed to equilibrate. Its slim cross section minimizes the disturbance to the water column during placement, reducing the time needed for the well to return to equilibrium. To initiate sample collection the HydraSleeve™ is pulled upward through the sample zone at one foot per second or faster. As it moves upward, the valve at the top opens and the sleeve is pulled over a “core” of water. As the fluid is captured, the sleeve expands to contain the sample, similar to pulling on a sock. Because there is no pumping or water withdrawal there is no drawdown and only minimal agitation of the water column. Once the sample sleeve is full, the self-sealing valve closes, preventing loss of the sample or the entry of extraneous fluid as the HydraSleeve™ is recovered. At the surface, the HydraSleeve™ is punctured with the pointed discharge straw and the sample transferred to suitable containers for transport to the laboratory. The HydraSleeve™ can be made different lengths and diameters to accommodate various well diameters and volume requirements. To save time waiting for equilibrium during repetitive sampling events, a sealed HydraSleeve™ can be left in the well between sampling events. To test for vertical stratification within a well, multiple HydraSleeve™ samplers can be suspended on the same cable and deployed simultaneously. Additional instructions on the use of the HydraSleeve™ are presented in the *HydraSleeve™ Field Manual*, available through the vendors.

2.1.2 Target Media

The HydraSleeve™ sampler can sample most liquid media but was specifically designed to collect groundwater samples from a discrete interval in monitoring or water wells. By collecting a discrete interval water sample, the HydraSleeve™ can sample all groundwater analytes as long as an adequate volume of sample is recovered for analysis.



Figure 2-1. 1.5-inch HydraSleeve™ and stainless steel weight (1-liter capacity)

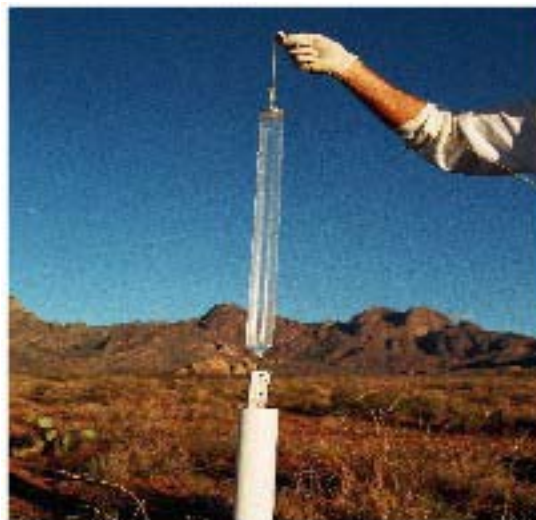


Figure 2-2. Full 1.5-inch HydraSleeve™ (1 liter capacity)

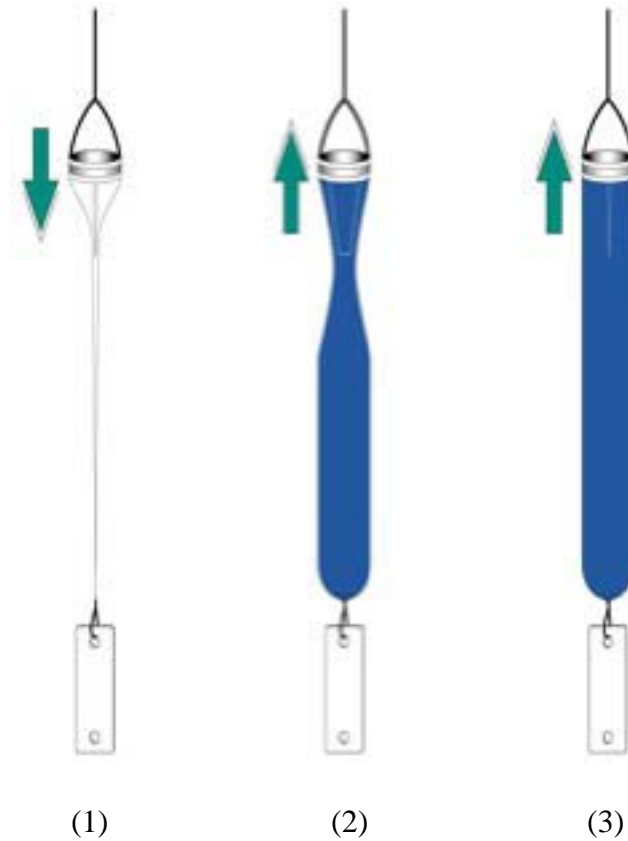


Figure 2-3. Deployment and retrieval

(1) Sampler placement

Reusable weight is attached and the HydraSleeve™ is lowered and placed at the desired position in the well screen. In-situ water pressure keeps the reed valve closed, preventing water from entering the sampler. Well is allowed to return to equilibrium.

(2) Sample collection

The reed valve opens to allow filling when the sampler is moved upward faster than 1 foot per second, either in one continuous upward pull or by cycling the sampler up and down to sample a shorter interval. There is no change in water level, and only minimal agitation during collection.

(3) Sample retrieval

When the flexible sleeve is full, the reed valve closes and the sampler can be recovered without entry of extraneous overlying fluids. Samples are removed by puncturing the sleeve with the pointed discharge tube and draining the contents into sample containers or field filtration equipment.

2.1.3 Potential Analyte Capabilities

As mentioned above, the HydraSleeve™ can sample all groundwater analytes as long as an adequate volume of sample is recovered for analysis. The HydraSleeve™ can be used to sample a wide spectrum of analytes including but not limited to the following: VOCs, semi-volatile organics, metals, major cations and anions, dissolved trace metals, dissolved sulfide, dissolved gases (methane/ethene/carbon dioxide), total dissolved solids, dissolved organic carbon, dissolved silica, explosive compounds, and perchlorate.

2.1.4 Sample Volume

Volume varies with the diameter and length of the HydraSleeve™. Standard HydraSleeve™ samplers are sized to fit in 2-inch wells—1.5-inch outside diameter (OD) by 36-inches long—and 4-inch wells (2.5-inch OD by 24-inches long). The standard 1.5-inch sampler holds 1-liter and the 2.5-inch sampler holds 2-liters of sample. HydraSleeve™ samplers can be custom fabricated in varying lengths and diameters for specific volume requirements. Overall, the HydraSleeve™ samplers have been made to obtain sample volume ranging from 80 milliliters to more than 4 liters.

2.2 State of the Art

2.2.1 Lab Testing

Laboratory testing for chemical parameters has shown excellent correlation with control samples for those compounds tested. Additional project sites are needed for testing additional parameters. The U.S. Army Core of Engineers Cold Regions Research and Engineering Laboratory (CRREL) conducted a detailed performance study comparing the results of the HydraSleeve™ and other sampling devices to control samples collected out of a standpipe with spiked concentrations of various contaminants (Parker and Clark, 2002). Parameters included volatile organic compounds, explosives, pesticides, and inorganic compounds. The HydraSleeve™ samples varied less than 5 percent from the control samples for all parameters, showing no adverse impact in the standpipe from the sample collection method.

2.2.2 Field Testing

The most comprehensive field test to date is a comparison demonstration project conducted at the former McClellan Air Force Base in Sacramento, California. The final McClellan report, (Parsons, 2005), describes the results of a field demonstration of six “no-purge” groundwater sampling devices. Analyses of VOCs, metals, anions, and 1,4 dioxane concentrations were compared to those collected from low-flow and conventional three-well-volume purge samples from the same well. From a performance perspective the report concluded that the HydraSleeve™ typically produced results most similar to the more conservative (i.e. higher concentration) results obtained from the conventional and low-flow sampling methods. The HydraSleeve™ was also the least expensive sampler tested. It was simpler to deploy and retrieve, and permitted a larger volume of water to be collected. Of the six no-purge devices tested, the HydraSleeve™ was also the only one that delivered viable samples for all of the

analytes tested. The report concluded that the HydraSleeve™ appears to be a technically viable method for monitoring all of the compounds included in the demonstration.

A “Point Source Bailer Demonstration” at the former Mather Air Force Base (AFB) was conducted in eight monitoring wells using the HydraSleeve™ (Montgomery Watson Harza, 2002). The samples were analyzed for volatile organic compounds and metals. The results were compared with historical analytical data from the eight monitoring wells. The results of the HydraSleeve™ sampling compared favorably with historical data; however, the statistical comparison was based on a limited data set containing a number of variables. The report concluded that the HydraSleeve™ shows promise as a reliable alternative sampling tool.

Two small-scale tests have been conducted by Jacques Whitford Consultants (Fernandes and Roberts, 2001; Sladky and Roberts, 2002). The studies compared samples collected with the HydraSleeve™ to samples collected using low-flow methods and analyzed for VOCs and semi-volatile organic compounds (SVOCs). The studies concluded the HydraSleeve™ provided a technically sound alternative to conventional low-flow methods for collecting samples for VOCs and SVOCs.

2.2.3 Examples of Acceptance and Use

See above for examples.

2.2.4 Current State of Research

Most recent research has focused on improving valve design to permit more rapid filling while reducing turbulent flow and to provide a better seal when the sampler is full. Modifications now enable the HydraSleeve™ to fill when pulled the length of the sampler. The exterior of the HydraSleeve™ has also been modified to minimize disturbance of the water column during placement, reducing the time required for the well to return to equilibrium.

2.2.5 Availability

The HydraSleeve™ is commercially available and is covered under U.S. Patents 6,481,300 and 6,837,120.

2.3 Features and Limitations

2.3.1 Cost

Reusable Weight: ~ \$25.00

1.5-inch OD HydraSleeve™: ~ \$20.00

2.5-inch OD HydraSleeve™: ~ \$25.00

2.3.2 Deployment Considerations including Advantages and/or Limitations

HydraSleeve™ samplers have been manufactured to sample wells as small as one-inch inside diameter. There is no upper limit to the well diameter that can be sampled, nor does there appear to be a depth limit. Samples have been successfully collected at depths more than 700 feet below ground surface.

Sample volume and sample interval length are the primary considerations when deploying the HydraSleeve™. Volume is determined by the diameter and length of the HydraSleeve™. When using the continuous pull technique, the length of the sampler determines the length of the sampled interval. Increasing the diameter and/or the length of the HydraSleeve™ increases the sample volume collected. The maximum diameter of the HydraSleeve™ is dictated by the inside diameter of the well to be sampled. The length of the well screen controls the maximum sampler length. The HydraSleeve™ should not be longer than the screened interval of the well. Typically, to assure that the sampler is completely filled by the time it exits the top of the well screen most HydraSleeve™ samplers are not more than half the length of the well screen. The larger the diameter and the longer the screen interval of the well being sampled the larger the diameter and length of the HydraSleeve™ that can be used to collect a greater sample volume of fluids. Practically, the limiting factor, assuming you have a large diameter and long screen interval well, is the weight of the full sampler and the means to retrieve it.

Advantages of the HydraSleeve™ include the following:

- does not purge water
- provides samples for all analytical parameters
- effective in low yield wells
- allows rapid installation and sample collection
- easy to use, one-person operation
- inexpensive to purchase and use
- samples discrete interval in well
- multiple samplers deployed to provide a vertical contaminant profile
- other uses could include sampling of surface water and tanks

2.3.3 Nature of Sample

The HydraSleeve™ collects an instantaneous discrete interval sample as it is recovered.

2.3.4 Decontamination Requirements

The HydraSleeve™ is a disposable groundwater sampler. Only the reusable stainless steel weight needs to be decontaminated if moved from well to well. Suspension lines may be reused if dedicated to a particular well.

2.3.5 Sample Handling and Shipping

Prompt transfer from the HydraSleeve™ to sample containers is required.

2.4 Unanswered Questions

Questions that remain unanswered for the HydraSleeve™ are as follows:

- How does the HydraSleeve™ compare with other accepted groundwater sampling methods? Initial test results indicate good correlation with lab or conventional results for compounds tested including: volatile organic compounds, explosive compounds, hexavalent chromium, and mercury.
- Will HydraSleeve™ samplers be accepted by the regulatory community and users?

2.5 Selected References

Cordry, K. E. 2004. *HydraSleeve™ Field Manual*. GeoInsight Inc., 680 Hickory Loop Suite B, Las Cruces NM 88005. October

Fernandes, A. C., and Roberts, J. 2001. *Zero-Purge Groundwater Sampling at a Spent Purifier Media Disposal Site*, in paper presented at the 14th International Symposium on Site Remediation and Environmental Management in the Utility Industry, Orlando, Fla., December.

Montgomery Watson Harza, Inc. 2002. *Point Source Bailer Demonstration Report, Former Mather Air Force Base, Mather, California*. August.

Sladky, B., and Roberts, J. 2002. *Zero-Purge Groundwater Sampling for Semivolatile Organic Compounds*, in paper presented at the Gas Technology Institute Conference, Orlando, Fla., September.

Parker, L. V., and Clark, C. H. 2002. *Study of Five Discrete Interval-Type Groundwater Sampling Device*. ERDC/CRREL TR-02-12. Cold Regions Research and Engineering Laboratory, U. S. Army Corps of Engineers, Engineer Research and Development Center, http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR02-12.pdf

Parsons, 2005, *Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California*. Prepared for the U.S. Army Corp of Engineers, Air Force Center for Environmental Excellence and Air Force Real Property Agency, Contract F44650-9900005, October 2005.

2.6 Contact Information

Vendors:

GeoInsight Inc.
1680 Hickory Loop Suite B
Las Cruces, NM 88005
Phone: (800) 996-2225
www.geoinsightonline.com
www.hydrasleeve.com

EON Products, Inc
3230 Industrial Way SW
Suite B
Snellville GA, 30039
Phone: 800-474-2490
Web: www.eonpro.com
Email: no-purge@eonpro.com

3. SNAP SAMPLER™

3.1 Description and Application

The Snap Sampler™ is a new patent-pending groundwater sampler designed to collect representative groundwater samples in situ without purging. The Snap Sampler™ utilizes specialty double-ended bottles close while submerged in the well. The in-well closure feature eliminates transferring sample to laboratory-prepared containers at the well head.

3.1.1 Physical Characteristics

The Snap Sampler™ volatile organic analysis (VOA) vial is similar to standard-sized 40 mL glass VOA vials but has double end-openings. A 125 mL polyethylene bottle is also available for larger sample volume. Both bottle types have two Snap Caps™ made of perfluoroalkoxy (PFA) Teflon® that seal water within the Snap Sampler™ VOA vial with an internal closure spring. The closure spring is made of stainless steel coated with PFA Teflon®.

To deploy the sampling device, a Snap Sampler™ is placed inside the Snap Sampler™ and the Snap Caps™ are attached in an open position to the sampler's trigger mechanism. Up to four Snap Samplers™ can be attached in series to collect up to four sample bottles with one trigger. The Snap Sampler™ is lowered into its deployment position by the trigger, which consists of high density polyethylene (HDPE) tubing with an internal stainless steel trigger cable coated with fluorinated ethylene propylene (FEP) Teflon®. The trigger tubing is fixed at the surface at a specialized well head docking station. The docking station does not affect water level measuring devices and can be configured to avoid interfering with commonly-used well locks.

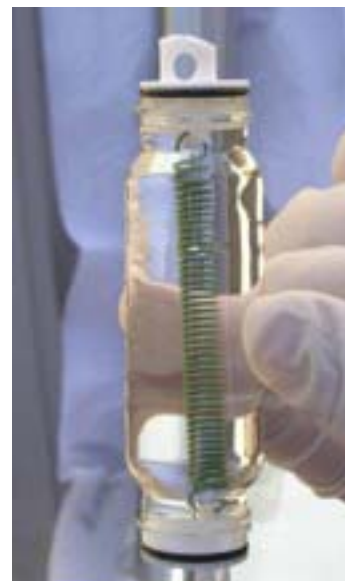


Figure 3-1. Snap Sampler™ volatile organic analysis (VOA) vial



Figure 3-2. Snap Sampler™

3.1.2 Target Media

Deployment of any type of sampling device into a well will disturb the natural flow-through conditions of resident groundwater. As a result, a well re-equilibration period is recommended for the Snap Sampler™ for passive deployments. The equilibration period for passive sampling may be as little as 24 hours, depending on well flow-through conditions and data objectives. Longer deployments of 90 days or more are also possible, allowing the user to conduct once-per-sampling-event mobilizations. Deployments for simple grab samples may only be minutes, as the Snap Sampler™ is open during deployment and water at the final deployment position can be captured immediately.

When ready to collect samples, the trigger cable is manually pulled at the well head to activate the sampler release mechanism. The mechanism releases the Snap Caps™, which close on the Snap Sampler™ bottle. The sampler is then retrieved from the well with the closed bottles. Acid preservative can be added to a specially-sized cavity in one of the Snap Caps™, and standard septa screw caps are placed on each end of the bottle. The Snap Sampler™ VOA vial can be used directly in common laboratory auto sampler equipment, so samples are not exposed to ambient air during retrieval, field preparation, or analysis at the lab unless manual dilutions or reanalyses are required.

Snap Sampler™ VOA vials are designed to collect VOC contaminants without the analyte limitations of other passive samplers currently available. The VOA vial is open to the well environment during the deployment period, so there is no membrane to selectively prevent or slow equilibration with water in the well. All VOCs, including acetone, MEK, trimethylbenzenes, MTBE and 1,4-dioxane can be sampled with the Snap Sampler™. Also, because Snap Sampler™ bottles are open to the well environment, the samples collected with the Snap Sampler™ are not limited to VOCs. Utilizing minimum sample volume requirements, this sampler can be used for analyzing many different physical and/or chemical water quality parameters, including metals. The 125 mL polyethylene bottle is available to increase sample volume capacity.

The diameter of the sampler is 1.65 inches. The length of the 40-ml device is approximately 8 inches with a single sampler and the length of the 125-ml device is approximately 10.5 inches with a single sampler. Up to four samplers can be placed in series with each trigger line.

3.1.3 Potential Analyte Capabilities

The Snap Sampler™ VOA vial is primarily designed to collect samples for any VOCs; however, virtually any analyte can be sampled with the Snap Sampler™ using 40 mL VOA or 120 mL of POLY. Analytical constraint on sample volume is the only practical limitation. All plastic samplers are available for metals analyses.

3.1.4 Sample Volume

Four 125 mL Snap Samplers™ can be used for analyses requiring sample volumes as much as about 500 mL. Multiple triggers with multiple bottles can be used to increase volume; however, long analyte lists requiring large volumes of water may not be practical candidates for the Snap Sampler™ until analytical capability further improves sample volume requirements.

3.2 State of the Art

3.2.1 Lab Testing

The Snap Sampler™ has undergone laboratory testing to demonstrate that its components and VOA bottles do not contribute VOCs to blank deionized water. Ongoing periodic quality assurance testing is designed to assure continued availability of “clean” samplers and bottles. Side-by-side comparisons conducted by the U.S. Army Corps of Engineers show very good correlation between the Snap Sampler™ and control samples for explosives and VOCs. Additional testing by the Army Corps of Engineers for metals is scheduled.

3.2.2 Field Testing

Field testing has been conducted at several sites.

Recent deployments of the Snap Sampler™ include:

- A 90-sampler deployment (26 samples) was completed at the former McClellan AFB in Sacramento, California (Parsons, 2005). Constituents of Concern (COCs), VOCs, and 1,4-dioxane, anions.
- A two-round, 26-sampler deployment (13 samples) at a private site in Santa Fe Springs, California (www.snapsampler.com). COCs, VOCs, MtBE, 1,4 dioxane.
- A 14-sampler deployment (7 samples) at a private site near Fort Wayne, Indiana (www.snapsampler.com). COCs, VOCs.
- A complex multi-test comparison deployment of 26 samplers (45 samples) for the University of Waterloo at a private site in Guelph, Ontario, Canada (Britt, et al, 2005). (www.snapsampler.com). COCs, VOCs.
- A 78-sampler deployment (26 samples) at the U.S. Navy facility and Port Hueneme, California (www.snapsampler.com). COCs, VOCs, MtBE.
- A two-round, 66-sampler deployment (11 samples) at a private site near Albany, New York. COCs, VOCs, Natural Attenuation Parameters.
- A two-round, 39-sampler, 21-sampler deployment (11/10 samples) at a private site in Trenton, New Jersey. COCs, VOCs, pharmaceuticals.

3.2.3 Examples of Acceptance and Use

See above for examples.

3.2.4 Current State of Research

Results from laboratory and field deployments conducted to date show good correlations with controls and comparison methods (Parsons 2005, Britt, et al, 2005; Parker/ERDC-CRREL, in prep). Results appear to show slightly, but consistently, higher VOC results compared to other comparison methods. The avoidance of surface pouring is the likely explanation for this difference. Non-VOC comparisons show consistency. The Snap Sampler™ has been deployed for up to 90 days with results consistent with shorter deployments. Research by the vendor and institutions such as the U.S. Air Force, U.S. Army Corps of Engineers, and the University of Waterloo is ongoing.

3.2.5 Availability

The Snap Sampler™ is commercially available and can be purchased or leased from the vendor. Please contact vendor for additional information.

3.3 Features and Limitations

3.3.1 Cost

The Snap Sampler™ is available for sale and through a lease program. Samplers can be leased for \$1 to \$2 per day, for quarterly and monthly rentals, respectively. Samplers for purchase are available in acetal copolymer (plastic) for \$165 each. One sampler is required for each bottle to be collected in a passive sampling mode (i.e., deployed for an equilibration period). Depending on the laboratory requirements, two or three samplers would be required to monitor each targeted

depth interval in a well. In grab sampling mode (i.e., deployment and immediate retrieval), the same Snap Sampler™ can be used repeatedly to collect multiple bottles.

Each well must be outfitted with a dedicated Snap Sampler™ trigger line. The sampler trigger line consists of a polyethylene tube with internal cable, with fittings at both ends to connect to the sampler and the surface docking station. Trigger tubing is \$1.25 per foot for light duty applications (less than 40 feet) and \$1.75 per foot for deeper applications. Custom trigger construction is \$30 per trigger. Triggers are made to a well-specific length and are not generally reusable at different wells. Well docking stations for 2-inch or 4-inch SCH40 PVC wells are \$35. VOA and POLY bottles are currently \$16 each, but are expected to drop in price as production increases.

3.3.2 Deployment Considerations including Advantages and/or Limitations

The Snap Sampler™ triggers are specifically made for each well. The Snap Sampler™ can be deployed in 2-inch or larger diameter wells. The length of the trigger is fixed once constructed, so generally, the triggers can not be used in other wells of different depths. Information about screen interval, and depth from top-of-casing to the screen interval is critical for selecting trigger lengths. This information must be gathered in advance and provided to the Snap Sampler™ vendor for construction of well-specific triggers. Long triggers are available on a disposable reel. During retrievals and redeployments, a mechanical reel is recommended.

Since deployment of any type of sampling device into a well will disturb the natural conditions of resident groundwater, a well re-equilibration period is recommended between deployment of any sampling device into a well and sample collection using that device. Depending on the hydrogeology surrounding well, this period may vary.

3.3.3 Nature of Sample

When it is triggered, the Snap Sampler™ collects water residing at the well interval corresponding to the sampler's current level. The method relies on flow-through and ambient mixing within the well to transfer formation water into the well and into the sample bottles at the time of collection. Like other passive methods, "live" formation water in the well screen is required for effective use of this method.

3.3.4 Decontamination Requirements

The Snap Sampler™ is intended for redeployment in the same well from which it came, so extensive decontamination is not required for redeployment. When deployed and redeployed in the same well from sampling event to sampling event, the Snap Sampler™ needs only to be cleaned to the extent that objects, sediment, or other debris is removed from the sampler trigger mechanism to operate properly.

In the event that the Snap Sampler™ is to be moved between wells for sampling, decontamination is accomplished by disassembling the sampler and washing the individual parts. The trigger tube and wire are not intended to be used between wells.

3.3.5 Sample Handling and Shipping

Snap Sampler™ samples are retrieved from the well in the same sample container that is transported to the laboratory. Field personnel are required to remove the bottles from the Snap Sampler™, and without opening the vials, trim the Snap Caps™ and place septa caps on the bottles. If field preservation is needed, preservative is added through a cavity in one of the Snap Caps™ before securing the septa cap. The vial can then be labeled and transported to the laboratory in the same fashion as standard VOA vials. The sample is not exposed to the atmosphere at the well head or at the lab if automated sampling equipment is used; however, if manual dilutions or reanalyses are required by the laboratory, the sample may be exposed to the atmosphere briefly during sample preparation.

3.4 Unanswered Questions

Laboratory and field testing has been conducted for VOCs, 1,4-dioxane, anions, some natural attenuation parameters, explosives, and a few pharmaceutical compounds. While there do not appear to be analyte limitations, additional testing for other constituents is needed to validate the method for other analytes.

3.5 Selected References

Britt, S.L., B.L. Parker, J.A. Cherry, 2005, *Field Testing the Snap Sampler™, a Comparison with Low-Flow and Polyethylene Diffusion Bag Samplers*. Battelle In Situ and On Site Bioremediation Symposium, June 2005, Baltimore MD.

Britt, S.L., B.L. Parker, J.A. Cherry, In Prep, *Field Testing the Snap Sampler™—a Comparison with Low Flow, Volume Purging and the Polyethylene Diffusion Bag Sampler*. For submittal to Ground Water Monitoring and Remediation

Parker, L.V. (ERDC/CRREL), In. Preparation, Laboratory testing underway

Parsons, 2005, *Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California*. Prepared for the U.S. Army Corp of Engineers, Air Force Center for Environmental Excellence and Air Force Real Property Agency, Contract F44650-9900005, October 2005.

3.6 Contact Information

Vendor:

Sandy Britt

ProHydro, Inc.

1011 Fairport Road

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Sandy.Britt@ProHydroInc.com

www.SnapSampler.com

4. REGENERATED-CELLULOSE DIALYSIS MEMBRANE SAMPLERS

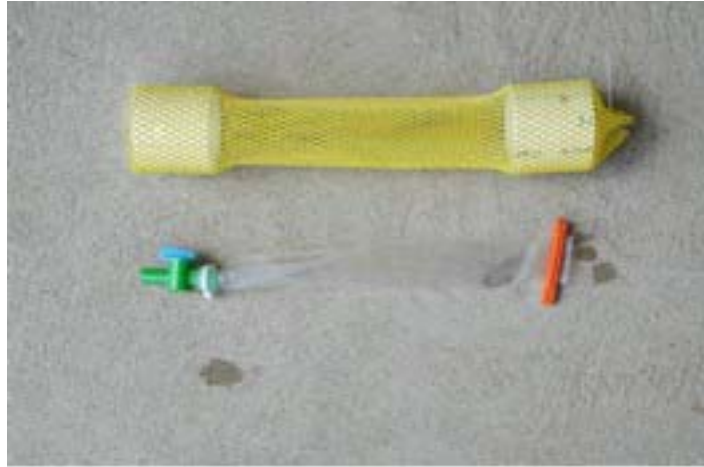
4.1 Description and Application

Regenerated-cellulose dialysis membrane samplers were developed to sample wells for inorganic ionic constituents as well as organic constituents using a diffusion-type sampler. Prior to their development, diffusion samplers (constructed with polyethylene membrane) could only sample for VOCs (Vroblesky, 2001a, 2001b). Dialysis membrane samplers have been successfully tested in the lab (Ehlke and others, 2004; Leblanc, 2003; Imbrigiotta, 2004, unpublished data; Harter and Talozzi, 2004) and in the field (Tunks and others, 2000; Vroblesky and others, 2002; Vroblesky and Pravecek, 2002; Imbrigiotta and others, 2002; Vroblesky and others, 2003; Harter and Talozzi, 2004) for a variety of water-quality parameters, including VOCs, major cations and anions, nutrients, trace metals, specific conductance, total dissolved solids, dissolved organic carbon, dissolved gases, sulfide, and explosive compounds. Other advantages to using dialysis membrane samplers include decreased groundwater monitoring costs and field time compared to purging methods (Puls and Barcelona, 1996); elimination of virtually all purge water and the cost of its disposal; exclusion of turbidity from samples, elimination of cleaning and cross-contamination because of its disposability, and quick equilibration for most constituents.

4.1.1 Physical Characteristics

The dialysis sampler consists of a deionized water-filled tube of high-grade regenerated-cellulose dialysis membrane inside an outer protective layer of low density polyethylene (LDPE) mesh. The sampler may have PVC pipes external to the dialysis membrane in low-ionic strength waters or an internal perforated PVC pipe to support the membrane in high ionic strength waters. The sampler may have a stopcock at one end to facilitate sample transfer. Each dialysis sampler has an attached weight to overcome its buoyancy and is suspended in a well by means of a dedicated or disposable wire or polyethylene rope. The regenerated cellulose diffusion membrane has a pore size of 18 Angstroms and a molecular weight cut-off (MWCO) of 8000 Daltons. The sampler may be constructed using either 31.8 mm (1.25 inches) or 63.7 mm (2.5 inches) diameter membranes.

Figures 4-1 through 4-3 depict aspects of the dialysis sampler.



**Figure 4-1. Parts of a dialysis sampler before filling
(~ 2.5 inches in diameter by 24 inches long)**



**Figure 4-2. Fully constructed dialysis sampler
(~ 2.5 inches in diameter by 48 inches long)**



Figure 4-3. Dialysis sampler with internal PVC support shown (~ 1.25 inches in diameter by 14 inches long)

4.1.2 Target Media

This sampler has mainly been used for sampling groundwater. The sampler also has been used in sediment pore water, but with mixed results because some investigations have noted physical breakdown of cellulose-based membranes in sediment/water deployments (Hopner, 1981; Martens and Klump, 1980).

4.1.3 Potential Analyte Capabilities

Dialysis samplers have been found to collect samples in laboratory and field tests for 59 VOCs on the EPA 8260b analytical schedule (EPA, 2003) including MTBE, major cations and anions, dissolved trace metals, dissolved gases (methane/ethene/carbon dioxide), total dissolved solids, dissolved organic carbon, dissolved silica, and explosive compounds. Dialysis samplers have not been tested for but are anticipated to collect samples for SVOCs (polychlorinated biphenyls, pesticides), perchlorate, field parameters, and radionuclides. The parameters tested in the laboratory and in field comparisons are shown in Tables 4-1 and 4-2.

Table 4-1. Water-quality parameters tested in the laboratory

Favorable laboratory diffusion testing results		
VOCs		
1,1,1,2-Tetrachloroethane	2,2-Dichloropropane	Isopropylbenzene
1,1,1-Trichloroethane	2-Chlorotoluene	m-Xylene
1,1,2,2-Tetrachloroethane	4-Chlorotoluene	Methyl tert-butyl ether
1,1,2-Trichloroethane	Benzene	Methylene chloride
1,1-Dichloroethane	Bromobenzene	n-Butylbenzene
1,1-Dichloroethene	Bromochloromethane	n-Propylbenzene
1,1-Dichloropropene	Bromodichloromethane	Naphthalene
1,2,3-Trichlorobenzene	Bromoform	o-Xylene
1,2,3-Trichloropropane	Bromomethane	p-Isopropyltoluene

Favorable laboratory diffusion testing results		
1,2,4-Trichlorobenzene	Carbon tetrachloride	p-Xylene
1,2,4-Trimethylbenzene	Chlorobenzene	sec-Butylbenzene
1,2-Dibromo-3-chloropropane	Chloroethane	Styrene
1,2-Dibromoethane	Chloroform	tert-Butylbenzene
1,2-Dichlorobenzene	Chloromethane	Tetrachloroethene
1,2-Dichloroethane	cis-1,2-Dichloroethene	Toluene
1,2-Dichloropropane	Dibromochloromethane	trans-1,2-Dichloroethene
1,3,5-Trimethylbenzene	Dibromomethane	Trichloroethene
1,3-Dichlorobenzene	Dichlorodifluoromethane	Trichlorofluoromethane
1,3-Dichloropropane	Ethylbenzene	Vinyl chloride
1,4-Dichlorobenzene	Hexachlorobutadiene	
<i>Cations and Trace Metals</i>		
Calcium	Barium	Molybdenum
Magnesium	Cadmium	Nickel
Potassium	Chromium	Selenium
Sodium	Copper	Vanadium
Aluminum	Iron	Zinc
Arsenic	Lead	
Antimony	Manganese	
<i>Anions</i>		
Bicarbonate/Alkalinity	Chloride	Sulfate
Carbonate/Alkalinity	Fluoride	
Bromide	Nitrate	
<i>Explosives</i>		
HMX	TNT	1,3-TNB
RDX	TNB	Nitrobenzene
2,4-DNT		
<i>Other Parameters</i>		
Silica	Methane	Specific conductance
Dissolved organic carbon	Methane	
Unfavorable laboratory diffusion testing results		
Mercury	Silver	Tin
Sulfide		

Table 4-2. Water-quality parameters sampled in the field comparison testing

Parameters with favorable field comparison results for dialysis samplers vs. purging		
<i>VOCs</i>		
1,1,1-Trichloroethane	Dichlorodifluoromethane	p-Isopropyltoluene
1,1-Dichloroethane	Ethylbenzene	p-Xylene
1,1-Dichloroethene	Isopropylbenzene	sec-Butylbenzene
1,2,4-Trimethylbenzene	m-Xylene	Styrene
1,2-Dibromoethane	Methyl tert-butyl ether	tert-Butylbenzene
1,3,5-Trimethylbenzene	Methylene chloride	Tetrachloroethene
Benzene	n-Butylbenzene	Toluene
Chloroform	n-Propylbenzene	trans-1,2-Dichloroethene
Chloromethane	Naphthalene	Trichloroethene
Cis-1,2-Dichloroethene	o-Xylene	Vinyl chloride
<i>Cations and Trace Metals</i>		
Calcium	Barium	Molybdenum
Magnesium	Cadmium	Nickel
Potassium	Chromium	Selenium
Sodium	Copper	Vanadium
Aluminum	Iron	Zinc
Arsenic	Lead	
Antimony	Manganese	
<i>Anions</i>		
Bicarbonate/Alkalinity	Chloride	Nitrate
Bromide	Fluoride	Sulfate
<i>Other Parameters</i>		
Silica	Sulfide	Total dissolved solids
Methane	Dissolved organic carbon	Specific conductance
Carbon dioxide	Ethene	

4.1.4 Sample Volume

The sampler volume depends on the diameter and length of the dialysis bag. The 31.8-mm (1.25-inches) diameter dialysis membrane contains a volume of 5.1 mL/cm. The 63.7-mm (2.5-inches) diameter membrane contains 31.8 mL/cm. So, for example, dialysis bags 30.5 cm (12 inches) long will contain volumes of 155 mL and 969 mL for the narrow-diameter and wide-diameter membranes, respectively. Larger sample volumes can be collected using longer bags. The ITRC (2004) recommends that no diffusion sampler represent more than 5-feet of a well's open interval, so 5-foot long bags should be considered the upper limit for length.

4.2 State of the Art

4.2.1 Lab Testing

Ehlke and others (2004) tested the permeability of the regenerated cellulose sampler for iron, bromide, and chlorinated VOCs, and determined equilibration times for these same constituents. Imbrigiotta (2004 unpublished data) tested the permeability of dialysis membrane for 59 VOCs on the Method 8260b list, including MTBE, major cations and anions, trace metals, dissolved organic carbon, methane, and sulfide, and determined equilibration times for these constituents. Leblanc (2003) tested the permeability of the dialysis sampler for explosives compounds and determined equilibration times for these compounds also. Vrobley and others (2002) lab tested the permeability and equilibration times for arsenic, chloride, chromium, iron, lead, manganese, selenium, and sulfate. Harter and Talozzi (2004) tested the equilibration times for nitrate and specific conductance in dialysis samplers.

For groundwater with temperatures of 10°C to 20°C, equilibration times range from one to three days for all VOCs, one to seven days for major cations and anions, most trace metals, total dissolved solids, dissolved organic carbon, dissolved sulfide, and other dissolved gases (Imbrigiotta, 2005, unpublished data). Explosives equilibration times range from seven to 14 days (L. Parker, U.S. Army Core of Engineers, CRREL, Hanover, NH, written communication, November 2005). Concentration and temperature have been found to slightly effect equilibration times for some chemicals. Groundwater with higher concentrations of some elements or compounds tends to equilibrate faster than groundwater with lower concentrations of these same chemicals. Also, groundwater with higher temperatures tends to allow some elements or compounds to equilibrate slightly faster than groundwater with lower temperatures.

4.2.2 Field Testing

Imbrigiotta and others (2002) compared the recovery of chlorinated VOCs, alkalinity, iron, and chloride in dialysis samplers vs. low-flow purge samples and modified conventional purge samples. Vrobley and others (2002) compared the recovery of arsenic, chloride, iron, manganese, and sulfate vs. low-flow purging. Vrobley and Pravecek (2002) compared alkalinity, arsenic, chloride, iron, lead, methane, sulfate, sulfide, zinc, and aromatic VOCs recovery in dialysis samplers vs. low-flow purge samples. Vrobley and others (2003) compared chloride and chlorinated VOCs vs. low-flow purging. Tunks and others (2000) and Parsons (2005) performed two different field demonstrations at McClellan AFB in California where various passive groundwater sampling devices, including dialysis membrane samplers, were compared to one another and to traditional sampling methods (i.e., low-flow purge/sample and three-well-volume purge/sample) on the basis of analytical results and costs. Harter and Talozzi (2004) compared nitrate and specific conductance results from water samples obtained by dialysis samplers and a five to 10 volume purge technique.

4.2.3 Examples of Acceptance and Use

The New Jersey Department of Environmental Protection (NJDEP) has allowed dialysis diffusion sampler deployment as the sole means of sampling 25 wells at the Naval Air Warfare

Center (NAWC) West Trenton, NJ, site after comparison testing showed less than +/- 25 percent relative percent differences in concentration of chlorinated VOCs recovered by the dialysis sampler and low-flow purging.

Dialysis samplers have been tested at the following sites: Naval Air Warfare Center, West Trenton, NJ (39 wells); Naval Industrial Ordnance Plant, Fridley, MN (3 wells); Andersen AFB, Guam, (5 wells); Hickam AFB, Hawaii (13 wells); and McClellan AFB (Parsons, 2005), California (10 wells). As stated above the only site where dialysis membrane diffusion samplers have been approved as the sole means of collecting groundwater samples is the NAWC, West Trenton, NJ (25 wells).

4.2.4 Current State of Research

An Environmental Securities Technology Certification Program (ESTCP) funded project (Imbrigiotta, 2005, unpublished data) tested the ability of dialysis membranes to allow selected chemicals to diffuse through and to determine how long it will take these chemicals to reach equilibrium. The second part of the project involved field comparisons at three DOD sites for many of the same contaminants tested in the lab and determined how the dialysis samplers compared to low-flow purging. Results from these studies indicated that most VOCs and major cations and anions, trace metals, dissolved gases, silica, total dissolved solids, and dissolved organic carbon were recovered in concentrations that were not significantly different from those recovered by low-flow purging. This study will be available by early 2006. A large field comparison was conducted by Parsons (2005) at McClellan AFB comparing six different types of passive groundwater sampling devices, including the dialysis membrane sampler, with low-flow purging and conventional purging for a variety of target compounds. Results for this study indicated that regenerated cellulose dialysis membrane samplers recovered concentrations of VOCs, anions, 1,4-dioxane, and hexavalent chromium as well or better than low-flow purging. They noted that dialysis samplers generally recovered lower concentrations of trace metals than low-flow purging in their tests. Overall, the dialysis sampler was rated equal to low-flow purging in this study.

4.2.5 Availability

Fully constructed dialysis membrane samplers are not currently available from any commercial vendor. Regenerated-cellulose dialysis membrane is available from Membrane Filtration Products, Inc (Sequin, TX) and Spectrum Laboratories Inc. (Laguna Hills, CA).

4.3 Features and Limitations

4.3.1 Cost

Cost of pre-cleaned 50-mm and 100-mm diameter regenerated-cellulose membranes = \$187/10 m (\$5.70/foot). The cost of construction materials for a 2-foot sampler (including membrane, protective mesh, weights, suspension line, stopcock, and clamps) ~ \$32. The cost of a fully constructed 2-foot sampler (including labor to construct) ~ \$40. If or when these samplers are commercially available the unit cost is expected to decrease dramatically.

4.3.2 Deployment Considerations including Advantages and/or Limitations

Regenerated cellulose dialysis membrane can be used to sample wells 2-inches or greater in diameter. Dialysis samplers have been used in wells to depths of 240 feet but should be useable at greater depths.

Vertical chemical profiling and vertical flow profiling should be done prior to deployment of any groundwater sampling device, including dialysis membrane diffusion samplers. Vertical profiling is done to determine the depth of highest contamination and greatest influx of water to the well. Depending on data quality objectives, the dialysis sampler should be positioned in each well at the ideal depth interval (e.g., the depth of greatest mass influx). Dialysis samplers must be constructed within a week of deployment and must be kept wet during this time to preserve the permeability, flexibility, and strength of the membrane. Dialysis samplers must be allowed to equilibrate for at least the length of time determined in laboratory equilibration tests for the contaminants of concern at a site. The line suspending a dialysis sampler in a well must be secured at the surface.

A limitation of this sampler is that over time it may begin to biodegrade in some pore-water and groundwater systems; however, the ability of the samplers to produce chemical concentrations comparable to other methods in previous investigations indicates that during short-term deployment, such factors may not significantly affect the sampler usefulness. Although it may not happen in every instance, if biodegradation of the membrane occurs, it is likely to take varying lengths of time (e.g., four to six weeks) depending on ambient conditions (e.g., temperature, bacterial populations).

4.3.3 Nature of Sample

Dialysis membrane diffusion samplers collect samples that represent the chemical concentration at the sample point during the last one to three days prior to collection.

4.3.4 Decontamination Requirements

The dialysis sampler is a disposable groundwater sampler. Only the reusable stainless-steel weight needs to be decontaminated if moved from well to well. Suspension lines may be reused if dedicated to a particular well.

4.3.5 Sample Handling and Shipping

Prompt transfer of the sample from the dialysis sampler to sample containers is required prior to shipment to a laboratory. Stopcocks make the transfer of sample easier and quicker.

4.4 Unanswered Questions

Questions that remain unanswered for the dialysis sampler are as follows:

- Do SVOCs, PCBs, or pesticides diffuse through dialysis membranes, and how long do these compounds take to equilibrate?

- What type of bacteria or fungi biologically attacks the regenerated cellulose membrane, and how long does it take for the bacteria or fungi to affect the performance of membrane?

4.5 Selected References

- Ehlke, T.A., Imbrigiotta, T.E., and Dale, J.M. 2004. *Laboratory Comparison of Polyethylene and Dialysis Membrane Diffusion Samplers*. Ground Water Monitoring and Remediation. 34 (1): 53-59.
- Harter, T, and Talozzi, S. 2004. *Evaluation of a Simple Inexpensive Dialysis Sampler for Small Diameter Monitoring Wells*. Ground Water Monitoring and Remediation. 24 (4): 97-105.
- Hopner, T. 1981. *Design and Use of a Diffusion Sampler for Interstitial Water from Fine-Grained Sediments*. Environmental Technology Letters. 2:187-196.
- Imbrigiotta, T.E., Ehlke, T.A., Lacombe, P.J., and Dale, J.M. 2002. *Comparison of Dialysis Membrane Diffusion Samplers and Two Purging Methods in Bedrock Wells*. In A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA. May 2002.
- Interstate Technology and Regulatory Council. 2004. *Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Ground Water*. ITRC Technical/Regulatory Guidelines Report. February 2004. 24 p.
- LeBlanc, D.R. 2003. *Diffusion and Drive-Point Sampling to Detect Ordnance-Related Compounds in Shallow Ground Water Beneath Snake Pond, Cape Cod, Massachusetts, 2001-2002*. U.S. Geological Survey Water Resources Investigations Report 03-4133. 20 p.
- Magaritz, M., Wells, M., Amiel, A.J., and Ronen, D. 1989. *Application of a Multi-Layer Sampler Based on the Dialysis Cell Technique for the Study of Trace Metals in Ground Water*. Applied Geochemistry. 4: 617-624.
- Martens, C.S., and Klump, J.V. 1980. *Biogeochemical Cycling in an Organic-Rich Coastal Marine Basin. I. Methane Sediment-Water Exchange Processes*. Geochimica et Cosmochimica Acta. 44: 471-490.
- Parsons, 2005, *Final Results Report For the Demonstration of No-Purge Groundwater Sampling Devices At Former McClellan Air Force Base, California*. Contract F44650-9900005, October 2005.
- Puls, R.W., and Barcelona, M.J. 1996. *Ground Water Issue: Low-Flow (Minimal Draw-Down) Ground-Water Sampling Procedures*. U.S. Environmental Protection Agency Report EPA/540/S-95/504, R.S. Kerr Environmental Research Center, Ada, OK.

- Ronen, D., Magaritz, M., and Levy, I. 1987. *An In Situ Multilevel Sampler for Preventive Monitoring and Study of Hydrochemical Profiles in Aquifers*. Ground Water Monitoring Review. 7(4): 69-74.
- Tunks, J.P., P.R. Guest, J. Santillan, and M. Faile. 2000. *Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater*. Proceedings of the Remediation of Chlorinated and Recalcitrant Compounds Second International Conference, Monterey, California, May 22-25, 2000.
- U.S. Environmental Protection Agency. 2003. *SW-846 Online, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*.
<http://www.epa.gov/epaoswer/hazwaste/test/main.htm>.
- Vroblesky, D.A. 2001a. *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. 120 p.
- Vroblesky, D.A. 2001b. *Users 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. 18 p.
- Vroblesky, D.A., Manish, Joshi, Morrell, Jeffrey, and Peterson, J.E. 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. 29 p.
- Vroblesky, D.A., Petkewich, M.D., and Campbell, T.R. 2002. *Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone*. U.S. Geological Survey Water Resources Investigations Report 02-4031. 24 p.
- Vroblesky, D.A., and Pravecek, T. 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. 28 p.

4.6 Contact Information

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Vendors:

No commercial vendors currently sell fully constructed dialysis membrane diffusion samplers.

The following vendor sells the regenerated dialysis membrane:

Membrane Filtration Products, Inc.
314 N. River Street
Seguin, TX 78155

5. NYLON-SCREEN PASSIVE DIFFUSION SAMPLERS

5.1 Description and Application

NSPDS are diffusion based samplers developed to sample for a broader range of analytes than can be collected by the PDB sampler.

5.1.1 Physical Characteristics

A NSPDS typically consists of a 175 mL polypropylene wide mouth bottle (diameter of 62 mm at top, 58 mm at bottom and a height of 58 mm) filled with analyte-free water, with a 125 μ -mesh nylon screen placed across opening and covered with a cap that has an opening of about 58 mm in diameter (Figure 5-1). The resulting bottle volume to diffusion area (V/A —see Webster et al, 1998) is about 60 or the height of the bottle.



Figure 5-1. Nylon-screen passive diffusion sampler

5.1.2 Target Media

The target media for NSPDS is groundwater.

5.1.3 Sample Volume

The NSPDS sample volume is 175 ml per bottle with a diameter of approximately 3 inches. Results to date show good comparisons with other sampling techniques. Larger volumes can be obtained by using a stack of bottles in the same mesh sleeve. It should be noted that the minimum required sample volume to conduct most standard analyses may be much less than the typically requested volume, depending on the choice of analytical methods and desired detections. Prior coordination with the laboratory could eliminate this minimum volume limitation as a concern.

5.2 State of the Art

5.2.1 Lab Testing

NSPDS of a smaller volume initially were tested in field studies in 2002 by Vrobley, Petkewich and Campbell. They looked at an arsenic-contaminated groundwater-discharge zone beneath a stream and collected samples for arsenic, calcium, chloride, iron, manganese, sulfate, and dissolved oxygen. Data indicated that, in general, NSPDS are capable of obtaining concentrations of inorganic solutes in groundwater that correspond to concentrations obtained by low-flow sampling and that NSPDS in stream-bed sediment can be used to locate contaminant-discharge zones of groundwater inorganic solutes.

In January 2003 Columbia Analytical Services, in cooperation with criteria developed by Vrobley of the USGS, conducted equilibration studies for NSPDS and included VOCs (Benzene; Tetrachloroethene, or PCE; Trichloroethene, or TCE; and 1,4 dioxane) as well as inorganic constituents, perchlorate, chloride, arsenic, and iron. All contaminants exhibited excellent diffusion from the test jars into the sampler water and equilibration was generally achieved in 24 hours. Further studies were conducted by Columbia Analytical Services in April of 2003 (Vrobley, Scheible, and Teall, 2003) on a suite of metals, and again, with the exception of silver, the NSPDS showed good transfer from test jars into sampler water. Subsequent studies by Columbia in August 2003 with samplers more suitable for 2-inch diameter wells (30 and 60 mL bottles with heights of about 60 mm and V/As of up to 175) showed poor comparisons with water in test jars.

5.2.2 Field Testing

More recent field trials (Environmental Alliance, August 2004, for perchlorates and BBL, October 2004, for 1,4- dioxane) are utilizing samplers with bottles in the 50-75 V/A range, results were very good for both perchlorate and 1,4 dioxane. However, that same size showed inconsistent results when used for metals. Additional field studies are planned in 2005 (contact Columbia Analytical Services, Inc. – see vendor section).

5.2.3 Examples of Acceptance and Use

See above for examples.

5.2.4 Current State of Research

Additional field studies are taking place.

5.2.5 Availability

These samplers have not been fully commercialized and are available in limited amounts through Columbia Analytical Services, Inc. (see vendor contact information). A patent application is being considered by the USGS.

5.3 Features and Limitations

5.3.1 Cost

Estimated commercial cost is approximately \$40 to \$50 each.

5.3.2 Deployment Considerations including Advantages and/or Limitations

NSPDS were originally designed to fit in 2-inch diameter wells; however, inconsistent results from the smaller volume NSPDS, as currently designed, suggests the use of these devices is better suited to larger wells, where the larger volume samplers may be used. The diameter of the well will affect the sample volume of each individual sampler. This volume limitation can be addressed by deploying the samplers in stacks. So far, no depth limitation has been recognized.

For deployment in wells, the NSPDS samplers are placed inside a mesh liner, which is attached to the hanging line with zip ties. The samplers can be arranged in stacks depending on the volume of water needed for analyses. The nylon screen is faced downward to minimize mixing of water in the samplers with shallower well water during recovery. The sampler retains the water, when not submerged, by a combination of surface tension between the water and the screen, and the vacuum that develops in the inverted bottle. Over time, chemicals diffuse across the nylon screen and equilibrate with the water inside the sampler. Upon retrieval, the contents of the sampler are transferred to laboratory sample containers or blank caps are used to replace the cutout cap holding the screen and the sampler bottles are themselves sent to the laboratory for analysis.

Sampling for reduction-oxidation (redox)-sensitive metals, such as lead, iron, and manganese, in an open borehole with NSPDS (or other passive in-well methods) is subject to a number of uncertainties and should be approached with caution. The main reason is that water in a well screened in an anaerobic aquifer can become oxygenated when oxygenated water from near the air-water interface is distributed throughout the well. This can happen when lateral transport of anaerobic groundwater through the screened interval is insufficient to outpace oxygen circulation through the well by diffusive, convective, or advective water movement in the well. When the well bore is oxygenated, but the adjacent aquifer is anaerobic, redox-sensitive solutes in the well

bore should not be expected to be the same concentrations as in the aquifer. When using water-filled diffusion samplers to sample redox-sensitive parameters in a well that maintains anaerobic water in the well bore, one approach to avoid oxidation and precipitation of redox-sensitive metals is to use anaerobic water as the sampler filling solution. When deployed in anaerobic water, however, the fill solution in the diffusion sampler becomes anaerobic by diffusion. Insufficient work has been done to determine whether prefilling with anaerobic water is necessary.

A limitation of this sampler is that the sample volume may be a concern if using these devices to test for a wide range of analytes. Prior coordination with the laboratory could eliminate volume limitation as a concern. Additional testing is necessary to delineate possible analyte limitations and the relationship to sampler orientation for these samplers.

5.3.3 Nature of Samples

NSPDS collects a time-weighted discrete interval sample.

5.3.4 Decontamination Requirements

Decontamination of the sampler is expected to be minimal, particularly once it becomes available commercially. A disposable device is common for similar types of other passive diffusion samplers.

5.3.5 Sample Handling and Shipping

Prompt transfer of sample from the NSPDS to sample containers is required.

5.4 Unanswered Questions

Additional laboratory and field testing is expected to be required prior to regulatory acceptance of the technology. For example, there is some uncertainty regarding whether sampler orientation has an influence on detected concentrations and equilibration time. Although not a problem in a 4-inch-diameter well, in 2-inch-diameter wells the samplers must be oriented up or down. Webster et al. (1998) examined the influence of orientation on bottles having similar design factors (however, he used a polysulfone membrane) and found that when deployed in saline pore water, bottles oriented with the opening toward the side equilibrated significantly quicker than bottles oriented with the opening up or down.

5.5 Selected References

Vroblecky, D.A., Petkewich, M., and Campbell, T., 2002. *Field Tests of diffusion Samplers for Inorganic Constituents in Wells and at a Ground Water Discharge Zone*. USGS Water Resources Investigations Report 02-0431

Vroblecky D. (USGS), Scheible W. and Teall G (Columbia Analytical Services (CAS)), 2003. *Laboratory Equilibration Study of Nylon-Screen Passive Diffusion Samplers for VOCs, and Select Inorganics*. Presented at ITRC Spring Meeting, March 2003, Annapolis MD.

Webster I.T., Teasdale, P.R., and Grigg, N., 1998, *Theoretical and Experimental Analysis of Peeper Equilibration Dynamics*: Environmental Science and Technology, v. 32, no. 11, p. 1727-1733.

5.6 Contact Information

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6. PASSIVE VAPOR DIFFUSION (PVD) SAMPLERS

6.1 Description and Application

Passive-vapor-diffusion (PVD) samplers were developed by the United States Geological Survey (Vroblesky and others, 1992; Vroblesky and others, 1996) and have been used successfully as reconnaissance tools at many hazardous waste sites. The primary use of PVD samplers is to identify locations where VOC contaminated groundwater is discharging into surface water (Vroblesky and others, 1996; Vroblesky and Robertson, 1996; Vroblesky and Hyde, 1997; Church and others, 2002). PVD samplers also have been used as passive-soil-gas samplers in the unsaturated zone (Vroblesky and others, 1992). USGS Water-Resources Investigations Report 02-4186 (Church and others, 2002) provides detailed guidance for construction and use of PVD samplers.

6.1.1 Physical Characteristics

PVD samplers (Figure 6-1) consist of an uncapped, empty 20 or 40 mL glass crimp-top or VOA vial enclosed in two layers of low-density polyethylene (LDPE) tubing or two zip lock bags. The crimp-top vials are preferred because of the thicker septum and better seal. Typically, samplers

are attached to wire surveyor flags and buried 0.5 to 1.5 feet deep in bottom sediments of areas where groundwater is discharging to streams, rivers, or lakes. VOCs dissolved in pore water will diffuse through the LDPE until air concentrations in the vial equilibrate with dissolved concentrations outside the LDPE membrane. In general, Vroblesky (2002a) estimates that it takes one to three weeks for a PVD sampler to equilibrate with pore water. If the samplers are being used to locate a plume, it may not be necessary for the samplers to reach equilibrium with pore water. However, the samplers do have to remain in place long enough for detectable concentrations of VOCs to diffuse across the LDPE membrane into the sampler.

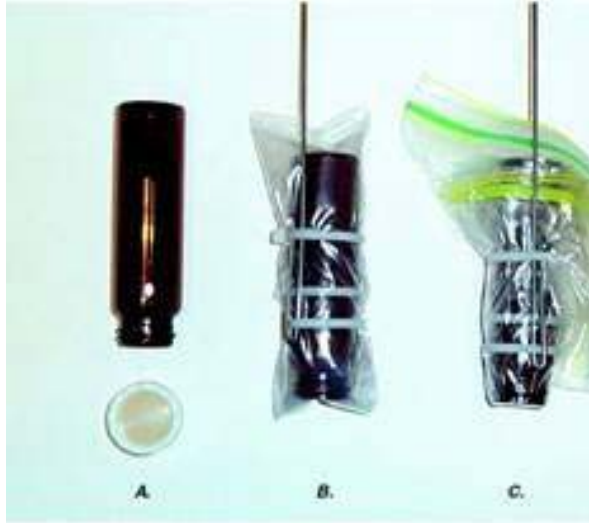


Figure 6-1. Passive vapor diffusion samplers constructed from VOA vials (A) and LDPE tubing (B) or zip-lock



Figure 6-2. Commercially available samplers with VOA vial sealed inside two layers of LDPE membrane (Photo from EON, 2005)



Figure 6-3. PVD to scale in hand (Photo from Church and others, 2002)

6.1.2 Target Media

PVD samplers are most commonly installed in sediments beneath rivers or streams, wetlands, lakes, or coastal zones to determine if and where VOC contaminated groundwater is discharging to surface water (Church and others, 2002). PVD samplers also have been used to measure VOCs in soil gas (Vroblesky and others, 1992). In both cases results are reported as vapor phase concentrations.

6.1.3 Potential Analyte Capabilities

A variety of VOCs are capable of diffusing through LDPE (Table 8.1). Of these, the constituents, those with a relatively high vapor pressure are detectable in PVD samplers. Laboratory experiments have not yet been done to determine the specific vapor pressures suitable for detection by PVD samplers; however, the method has been successfully used for chlorinated ethenes, such as PCE (vapor pressure is 14 mm at 20C), TCE (60 mm at 20C), and c-dichloroethylene (cDCE) (500 mm at 20C) as well as petroleum hydrocarbons, such as benzene (76 mm at 20C), ethylbenzene (7 mm at 20C), xylenes (5 to 6.5 mm at 20C), and toluene (22 mm at 20C) (Savoie and Taylor, 2002).

6.1.4 Sample Volume

The sample volume is 20 or 40 mL of air.

6.2 State of the Art

6.2.1 Lab Testing

PVD samplers have been tested in the laboratory. Vroblesky (2002) summarizes laboratory and field-testing data.

6.2.2 Field Testing

PVD samplers also have been deployed at numerous hazardous waste sites. Vroblesky (2002) summarizes laboratory and field-testing data.

6.2.3 Examples of Acceptance and Use

Church and others (2002) describe the use of PVD samplers at nine superfund sites in New England. The nine sites include river, stream, wetland, lake, and coastal shoreline discharge areas. PVD samplers also have been used at state hazardous waste sites and for site discovery purposes in Massachusetts. The ITRC Diffusion Sampler Information Center web site (<http://diffusionsampler.itrcweb.org/common/default.asp>) provides information about additional sites where PVD samplers have been deployed.

6.2.4 Current State of Research

The USGS developed and began using PVD samplers in the 1990s (Vroblesky and others, 1992; Vroblesky and others, 1996). Vroblesky (2002) summarizes laboratory testing and field study data. Use of PVD samplers for detecting VOCs in pore water in sediment is well established. Vroblesky and others (1992) installed PVD samplers in the vadose zone at a petroleum tank farm and compared results to passive soil-gas samplers containing activated carbon and to the distribution of toluene in groundwater. Based on this study, Vroblesky and others (1992) concluded that PVD samplers could effectively locate areas of toluene-contaminated groundwater. There are no other published studies describing use of PVD samplers in the vadose zone.

6.2.5 Availability

The samplers are not patented and are easy to construct using VOA vials, polyethylene bags, or lay flat polyethylene tubing and a heat sealer. Church and others (2002) provide instructions for constructing and deploying PVD samplers. Vapor diffusion samplers also can be purchased from Eon Products, Inc.

6.3 Features and Limitations

6.3.1 Cost

PVD samplers can be purchased for less than \$10.00.

6.3.2 Deployment Considerations including Advantages and/or Limitations

PVD samplers are most easily deployed in shallow water. Scuba divers may be needed to install samplers at depths greater than 4 feet. Typical installation procedures involve using either an auger or shovel, or drive point assemblies to place the samplers in sediment (Church and others, 2002). At two state hazardous waste sites in Massachusetts, samplers were attached to 5-foot by one-inch by one-inch wooden stakes (tomato stakes) for installation in soft sediment. At both sites approximately one- to two-feet of soft sediment overlies sand and gravel. Samplers were pushed through the soft sediment to the sand and gravel layer without use of a shovel, auger, or drive point assembly. This allowed quick installation of the sampler with minimal introduction of surface water to the sampler location.

Samplers are removed by pulling the surveyor flag or wooden stake. The outer bag or tubing is removed and a cap with a Teflon or Teflon lined septum is screwed or crimped on the VOA vial over the inner bag or tubing.

Samplers are only useful in areas where groundwater is discharging to the surface water body. This may require an independent evaluation of relative water level (head) differences between surface water and shallow groundwater in the area where the PVD samplers are being installed.

The recommended deployment time for PVD samplers in sandy sediment is two weeks (Church and others, 2002; Vroblesky, 2002). Depending on temperature, contaminant properties,

sediment characteristics, and hydrologic conditions, there can be significant differences in equilibrium concentrations and equilibration times. For example, VOC concentrations in PVD samplers deployed during September in South Carolina in high hydraulic conductivity sediments (21-65 ft/day) in an area with strong upward hydraulic gradients (0.3 ft/ft) stabilized after 12 to 24 hours (Vroblesky, 2002). In contrast, Lyford and others (2000) concluded that it might take three weeks or more for PVD samplers to equilibrate in fine-grained sediment during January and February at a site in Massachusetts; however, samplers recovered eight days after deployment at the Massachusetts site contained measurable concentrations of VOCs and an eight-day deployment would have been sufficient to locate areas where VOC contaminated groundwater is discharging to surface water (Vroblesky, 2002).

6.3.3 Nature of Sample

Vapor concentrations within a PVD sampler approach equilibrium with dissolved VOC concentrations in contaminated groundwater moving past the sampler. Samplers may or may not reach full equilibrium with the discharging groundwater within the deployment period. If the samplers are used for reconnaissance purposes, consideration of whether the sampler has reached full equilibrium with groundwater is not particularly important. Samplers provide useful information as long as they accumulate measurable concentrations of VOCs.

While it is theoretically possible to calculate equilibrium groundwater concentrations using vapor concentrations and Henry's Law, there are numerous uncertainties in these calculations and calculated values should be viewed as estimates (Church and others, 2002). Other sampling methods should be used if quantitative determination of VOC concentrations in groundwater is necessary.

6.3.4 Decontamination Requirements

PVD samplers are disposable and there are no decontamination requirements.

6.3.5 Sample Handling and Shipping

Care must be taken during sample retrieval and handling to insure that the inner LDPE tubing or bag remains clean. A clean inner bag is necessary to insure that the septum cap can be screwed on tightly, form a good seal with the VOA vial, prevent loss of VOCs, and prevent sediment or water from being trapped between the septum cap and the inner bag. Capping over the inner bag should be done as quickly as possible after sampler retrieval to minimize VOC loss.

Air samples from PVD samplers are commonly analyzed in the field with a portable gas chromatograph or in a mobile laboratory; however, samples can be shipped to a fixed laboratory for gas chromatograph (GC) analysis. Vroblesky (2002) states that capped samples are stable for up to 121 hours. Large temperature changes, including transporting on ice, should be avoided when handling VOC vapor samples; the resulting pressure gradients may accelerate VOC transfer across any imperfect seals.

6.4 Unanswered Questions

Based on a single study conducted by Vroblesky and others (1992), PVD samplers are effective sampling devices in the vadose zone. Additional studies and/or field demonstrations using PVD samplers for soil-gas surveys should be conducted to fully evaluate this application of the technology.

6.5 Selected References

- Church, P.E., Vroblesky, D.A., Lyford, F.P., and Willey, R.E., 2002, Guidance on the Use of Passive-Vapor-Diffusion Samplers to Detect Volatile Organic Compounds in Ground Water-Discharge Areas, and Example Applications in New England: United States Geological Survey Water-Resources Investigations Report 02-4186.
<http://water.usgs.gov/pubs/wri/wrir024186/>
- ITRC, 2004, Technical and Regulatory Guidance for using Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Groundwater: Interstate Technology and Regulatory Council. <http://diffusionsampler.itrcweb.org/common/default.asp>
- Lyford, F. P.; Willey, R. E.; Clifford, S., 2000, Field tests of polyethylene-membrane diffusion sampler for characterizing volatile organic compounds in stream-bottom sediments, Nyanza chemical waste dump superfund site, Ashland, Massachusetts: U.S. Geological Survey, Water-Resources Investigations Report 00-4108.
<http://water.usgs.gov/pubs/wri/wri004108/>
- Savoie, J.G., and Taylor, M.G., 2002, Baird & McGuire Superfund Site, Holbrook, Massachusetts: in Guidance on the use of passive vapor-diffusion samplers to detect volatile organic compounds in ground-water-discharge areas, and example applications in New England, edited by Church, P.E., Vroblesky, D.A., Lyford, F.P., and Willey, R.E., U.S. Geological Survey Water Resources Investigations Report 02-4186, p. 34-36.
- Vroblesky, D.A., 2001, User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells: United States Geological Survey Water-Resources Investigations Report 01-4060.
<http://sc.water.usgs.gov/publications/difsamplers.html>
- Vroblesky, D.A., 2002, Appendix 1: Laboratory and Field Testing of Passive-Vapor-Diffusion Sampler Equilibration Times, Temperature Effects, and Sample Stability; in Church, P.E., Vroblesky, D.A., Lyford, F.P., and Willey, R.E., 2002, Guidance on the Use of Passive-Vapor-Diffusion Samplers to Detect Volatile Organic Compounds in Ground Water-Discharge Areas, and Example Applications in New England: United States Geological Survey Water-Resources Investigations Report 02-4186.
<http://water.usgs.gov/pubs/wri/wrir024186/>
- Vroblesky, D.A., Robertson, J.F., Fernandez, Mario, and Aelion, C.M., 1992, The permeable membrane method of passive soil-gas collection; in Proceedings of the Sixth National

Outdoor Action Conference: Las Vegas, Nev., National Water Well Association, May 5–13, 1992, p. 3–26.

Vroblesky, D.A., Rhodes, L.C., Robertson, J.F., and Harrigan, J.A., 1996, Locating VOC Contamination In A Fractured-Rock Aquifer At The Ground-Water/Surface-Water Interface Using Passive Vapor Collectors: *Ground Water*, v. 34, no. 2, p. 223–230.

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Vendor:

Samplers can be constructed using VOA vials and LDPE tubing or bags or purchased from various supply houses or purchase prefabricated samplers from:

EON Products, Inc.
3230 Industrial Way SW
Suite B
Snellville GA, 30039
Phone: 800-474-2490
Web: www.eonpro.com
Email: no-purge@eonpro.com

7. PEEPER SAMPLERS

7.1 Description and Application

Peeper samplers (a.k.a. Hesslein In-situ Pore Water Sampler) are rigid structures, which can hold volumes of water separated from the environment by porous membranes to monitor constituents in saturated environments. Peepers rely on diffusion of the analytes to reach equilibrium between the sampler and the pore water. Peepers (i.e., dialysis cells) have been used for in situ monitoring of dissolved constituents in saturated sediments (Hesslein, 1976). The efficiency of peeper samplers depends on equilibration time of the analyte, the analyte's diffusion coefficient, its adsorption–desorption properties, the surrounding ambient-solution temperatures, and sediment porosity; however, peeper samplers have several advantages over older centrifugation methods including in situ monitoring of trace elements, quick and efficient sampling times, increased depth resolution, and minimal temperature and O₂ (g) diffusion effects. The main advantage of the peeper sampler is that it measures an exact pore water concentration, which can be compared to Risk-Based standards (i.e., RBCA) or Federal/State Cleanup Criteria.

Before deployment they are filled with an appropriate grade of water as discussed in the diffusion bag section. There are several different types of peeper samplers, which are described in more detail in section 7.1.1. Peeper samplers can be stacked in a specially designed corer so that they sample discrete depths, direct driven for near surface (1 to 3 meters) evaluation, or they can be placed in a shallow rectangular array for near surface area distribution determinations. A polysulfone membrane sampler (PsMS) is a modification of the traditional peeper sampler and was first implemented as part of a field demonstration of passive groundwater sampling devices performed at McClellan AFB, near Sacramento, California (Parsons 2004). The samplers constructed for use in the McClellan AFB study were comprised of a rigid 2-inch long section of 2-inch OD PVC pipe that was covered on both ends with the flexible polysulfone membrane.

7.1.1 Physical Characteristics

Typical peeper samplers employ a rigid body with an opening or openings that are covered with a permeable membrane or mesh (Jackson, 2003). Acrylic cylindrical chambers are a common type that contain holes in their sides that are fitted with the membrane or mesh material (see Figure 7-1). Another peeper design resembles a box corer with individual cells inside that can obtain a small transect with depth (see Figure 7-2).

Peeper samplers can be constructed of lexan, acrylic, teflon, stainless steel or any millable material. Material selection is a function of required depth and analytes of interest. Sizes can vary from the “Plates” that are 5 to 100 cm in length and approximately 1 to 3 cm in depth. Peeper samplers can also be constructed as “Cylinders” that have outer diameters ranging from 1 cm to 7 cm and range in length up to 4 meters.

Typical PsMS are constructed of a polysulfone membrane fitted around the ends of a 2-inch PVC pipe. The pore size of the polysulfone membrane is about 0.2 microns. The volume of each sampler canister is approximately 108 mL. Two canisters are typically deployed at each sample depth to provide adequate sample volume for subsequent analysis.

The groundwater sample is transferred from the sampler to the appropriate sample container upon retrieval by puncturing the membrane with a straw and pouring the contents from the sampler into the bottle through the straw. Considerations regarding the orientation of peeper samplers (Webster et. al., 1998) led to the deployment of the PsMSs in an orientation where the membrane was positioned horizontally (see Figure 7-3).

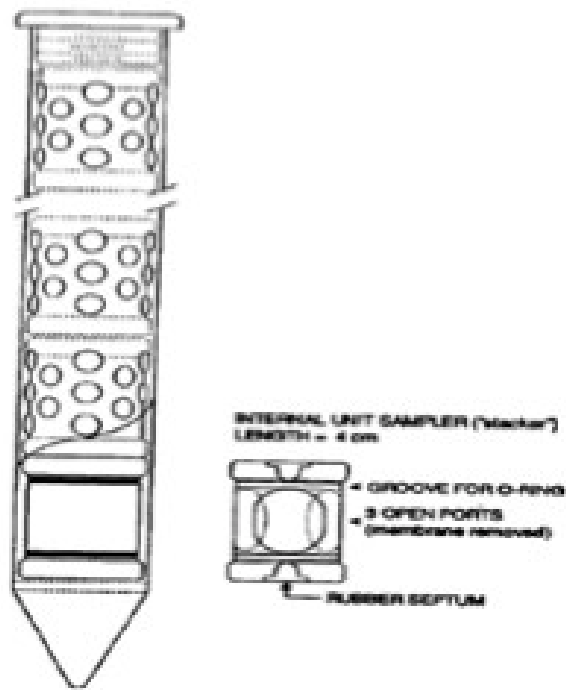
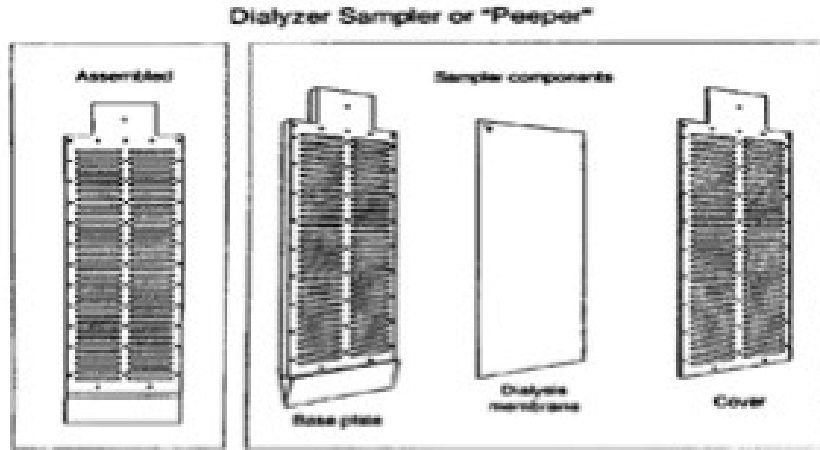


Figure 7-1. Acrylic cylindrical peeper sampler



Figure 7-2. Box corer peeper sampler

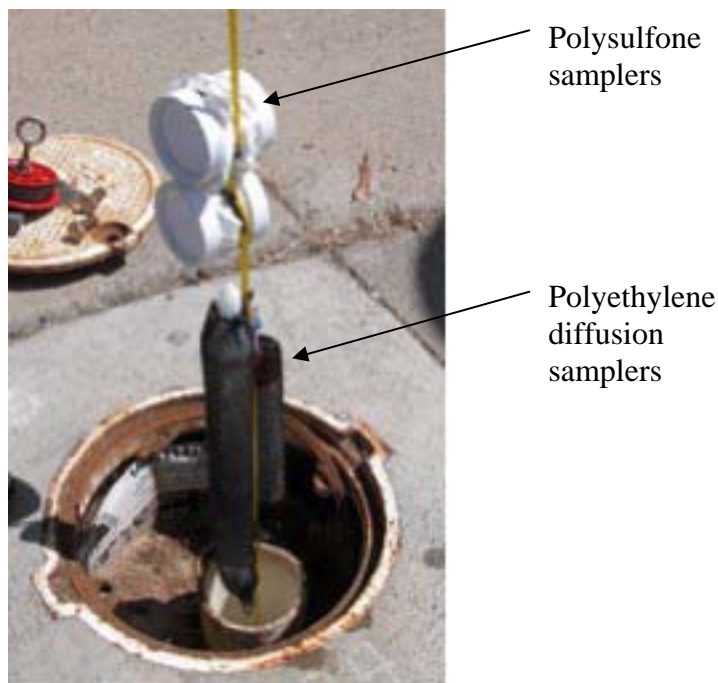


Figure 7-3. Polysulfone membrane samplers (PsMSs), orientation of samplers in well during deployment. Two PsMSs indicated by arrow, with other types of passive samplers attached below.

7.1.2 Target Media

Peeper samplers were designed to collect pore water samples from the groundwater/surface water interface associated with streams, lakes, near surface groundwater, and wetlands. The PsMS devices are designed to sample groundwater in wells.

7.1.3 Potential Analyte Capabilities

Theoretically, these samplers should be capable of monitoring most compounds (inorganic and organic) present in dissolved phases. Monitored analytes (see citation for details of methods and results) include volatile organic compounds, organic acids, gases, perchlorate, and phytodegradation products that are listed in Table 7-1 (e.g., Jackson et al, 2004, 2005, Jackson and Pardue 1997). Selection of membrane type and sampler material is a function of the analytes of interest.

Table 7-1. Analytes studied using peeper samplers

Volatile Organic Compounds	Other Porewater Constituents	Gases
1,1,1,2-Tetrachloroethane 1,1,2,2-Tetrachloroethane 1,1,2-Trichloroethane 1,1-Dichloroethane Chloroethane Tetrachloroethene Trichloroethene cis-1,2-Dichloroethene trans-1,2-Dichloroethene Vinyl chloride	Organic acids Fe ²⁺ , Mn ²⁺ , SO ₄ ²⁻ , pH, NO ₃ ⁻ , NO ₂ ⁻ , P	Methane Ethane Ethylene Carbon dioxide

7.1.4 Sample Volume

A typical peeper plate design provides smaller sample volumes depending on the width of the sampler. Sample size typically ranges from 1 to 20 mL per cell with cell width generally ~ 1cm. PsMS devices range in size but typically have a larger sample volume compared to peeper samplers.

7.2 State of the Art

7.2.1 Lab Testing

Peeper samplers and PsMSs have been lab tested in the United States. Please refer to case studies in the section below titled “Examples of Acceptance and Use.” Theoretical and experimental analysis of peeper sampler equilibration dynamics can be found in the publication Environ. Sci. Technol. 32: 1727-1733.

7.2.2 Field Testing

Peeper samplers have been field tested at numerous sites in the United States. The PsMSs have been field tested at McClellan AFB (Parsons, 2005). Refer to the case studies in the section below titled “Examples of Acceptance and Use.”

7.2.3 Examples of Acceptance and Use

Past Studies of peeper samplers include the following:

- Seasonal Changes in Marsh Sediment (DOC, NH₄⁺, Fe) conducted by Jackson and Pardue, (1997)
- Nitrogen Discharge from GW to Rivers conducted by Doussan et al., 1998
- Phytoremediation of Chlorinated Solvents in Groundwater conducted by Jackson, Pardue, and Martino, (Jackson et al, 2005)
- Perchlorate Transport in Stream Sediments conducted by Tan, Anderson, and Jackson Tan et al, 2004

7.2.4 Current State of Research

Case studies of peeper samplers include the following:

- Perchlorate Fate and Transport in Stream Sediments (NWIRP) and Lake Sediments (Lake Waco and Belton)
- Monitoring Phytoremediation Processes (J-Field Aberdeen Proving Grounds)
- Monitoring Solvent Discharge in Stream Sediments (Marvin Jonas Transfer Station, NJ)
- McClellan Air Force Base (AFB) (Parsons, 2005)

7.2.5 Availability

Peeper samplers are available commercially and are also fabricated by researchers. PsMSs are fabricated by specialized consulting firms.

7.3 Features and Limitations

7.3.1 Cost

A commercially available peeper plate sampler is approximately \$312.00 per sampler, which consists of both the skeleton and membrane.

The PsMS is not commercially available. The sampler cost is estimated at \$91 per sampler per well, based on work associated with the former McClellan AFB demonstration study.

7.3.2 Deployment Considerations including Advantages and/or Limitations

The equilibration time for peeper samplers and PsMSs can range from hours to a month depending upon the contaminant of interest, sediment type, peeper sampler volume, and membrane pore size. A week to 14 days is the most common time period to allow for analytes to equilibrate within peeper samplers, which is based on some unpublished lab testing and results from the field. Theoretical and experimental analysis of peeper sampler equilibration dynamics can be found in the publication *Environ. Science & Technology* 32: 1727-1733.

PsMS samplers were typically designed to fit into wells with a minimum inside diameter of 4 inches. There is no limit to the depth at which they could be deployed. As described earlier, the membrane orientation was only demonstrated in one direction (perpendicular to horizontal flow). The samplers should be constructed under water to ensure that the capsule is completely filled with purified water prior to deployment.

One drawback of a typical peeper plate design is that they provide small sample volumes at high depth resolution (cm intervals) although cells can be pooled to produce 100-300 ml per foot. PsMS devices range in size but typically have a larger sample volume compared to peeper samplers.

7.3.3 Nature of Sample

The peeper sampler and PsMSs devices rely on diffusion of the analytes to reach equilibrium between the sampler and the pore water or groundwater. Due to the lack of field- or bench-scale testing of PsMSs, potential advantages or disadvantages of this sampler have not been quantified.

7.3.4 Decontamination Requirements

The inner membrane cannot be reused. The “skeleton” of these samplers are reusable if properly decontaminated with a series of methanol/acetone and deionized water rinses.

7.3.5 Sample Handling and Shipping

Proper sample transport to the laboratory is essential for minimizing sample alteration. Samples removed from wetlands or lacustrine environments, through piston or other coring devices, may be anoxic. Consequently, samples must be kept anaerobic during transport to the laboratory. Otherwise, normal shipping procedures specified by your laboratory should be followed.

7.4 Unanswered Questions

[None]

7.5 Selected References

- Hesslein, R.H. 1976. An in situ Sampler For Close Interval Pore Water Studies. *Limnol. Oceanogr.* 21:912-914.
- US Army, Aberdeen Proving Ground, December 1999. Appendix J Standard Operating Procedures Work Plan for CERCLA Remedial Investigation/Feasibility Study (Generic Work Plan).
- Grigg, N.J., Webster, I.T., and P.W. Ford. 1999 Porewater Convection Induced by Peeper Emplacement in Saline Sediment, *Limnol. Oceanogr.* 44(2): 425-430
- Jackson, A., 2003. Peeper Samplers. Presentation to the Diffusion Sampling Workgroup at the 2003 ITRC Fall Membership Meeting. Monterey, CA. October 1.
- Tan, K., Todd A. Anderson, and W. Andrew Jackson. (2005) Temporal and Spatial Variation of Perchlorate in Streambed Sediments: Results From In-Situ Dialysis Samplers. *Environmental Pollution.* 136/2:283-291.
- Jackson, W.A., L. Martino, S. Hirsh, J. Wrobel, and J. Pardue. (2005) Application of a Dialysis Sampler to Monitor Phytoremediation Processes. *Environmental Monitoring and Assessment.* 107(1-3)155-171
- Jackson, A. and J. Pardue. (1999) Potential for Intrinsic and Enhanced Crude Oil Degradation in Louisiana’s Fresh Marshes. *Wetlands* 19(1):28-34.

- Parsons, 2004. Final Work Plan for the Demonstration of Passive Groundwater Sampling Devices at Former McClellan Air Force Base, California. May.
- Parsons, 2005, Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California. Prepared for the U.S. Army Corp of Engineers, Air Force Center for Environmental Excellence and Air Force Real Property Agency, Contract F44650-9900005, October 2005.
- Webster, I., Teasdale, P., and Grigg, N., 1998. Theoretical and Experimental Analysis of Peepers Equilibration Dynamics. Environmental Science and Technology, Vol. 32, pgs. 1727-1733.
- Vroblesky D. (USGS), Scheible W. and Teall G (Columbia Analytical Services (CAS)), 2003. Laboratory Equilibration Study of Nylon-Screen Passive Diffusion Samplers for VOCs, and Select Inorganics. Presented at ITRC Spring Meeting, March 2003, Annapolis MD.

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8. POLYETHYLENE DIFFUSION BAG (PDB) SAMPLERS

8.1 Description and Application

The Polyethylene Diffusion Bag (PDB) sampler was developed in the late 1990's and has become a widely accepted technique for determining concentrations of VOCs in groundwater monitoring wells. PDBs are installed in groundwater monitoring wells, at one or more intervals below the water surface in the well screen, and left in place under natural flow conditions. After sufficient residence-time the PDBs are removed and the contents discharged directly into analysis vials for standard volatile analysis. Because pumping and purging field time are eliminated and waste water disposal is reduced to a few milliliters, the technique results in significant cost savings over purge and pump techniques. The technique also provides depth specific profiling for compound and concentrations. PDBs are also used in saturated sediments in and around surface water to approximate VOC discharge to the surface.

The PDBs' ability to reflect dissolved VOC concentrations in the adjacent aquifer allows determination of stratification and vertical concentration gradients of VOC contaminants. Generally, each two-foot-long PDB sampler represents not more than five feet of the well screen. Interval VOC concentrations may be measured at specific well screen depths by hanging PDB samplers in series (Figure 8-1). In addition to gaining information about the well's hydrogeological attributes, correct positioning of a future single PDB sampler may be determined.



Figure 8-1. Deployment of PDB samplers to vertically profile well

8.1.1 Physical Characteristics

PDB samplers are made of low density polyethylene (typically 4mils thick) film which serves as a semi-permeable membrane. The membrane is formed into the shape of a tube to create a sample chamber which is filled with de-ionized water and sealed. Various configurations are commercially available either pre-filled and sealed at both ends at the factory, or with a fill port and plug for filling at the factory, in the field, or at the user's lab. PDB samplers are typically 18 to 24 inches long and 1.25 to 1.75 inches in diameter to fit into a 2-inch diameter and larger monitoring wells (Figure 8-2). These dimensions provide 200 to 350 ml of sample for multiple VOA samples and duplicates. Other diameters and lengths are available to fit smaller diameter wells or to provide specific sample volumes. PDBs are available with an exterior polyethylene mesh that protects against abrasion (Figure 8-3). Figure 8-4 displays a protective canister available for deployment of PDBs in sediments.

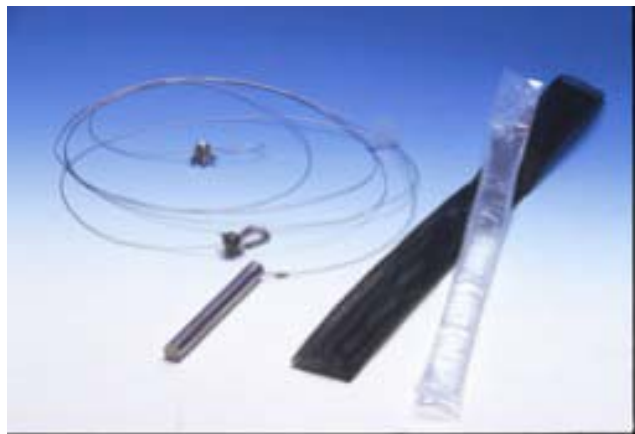


Figure 8-2. Typical passive diffusion bag sampler with protective mesh sleeve, weight, and deployment supplies



Figure 8-3. EON diffusion bag sampler and supplies



Figure 8-4. Protective screen canister for PDB deployment in sediments

PDBs operate using the principles of molecular diffusion across the semi-permeable polyethylene membrane. VOCs in the aquifer are transported into the well through the screen by natural flow and by diffusion. The deionized water in the PDB contains no organic compounds when installed and therefore a concentration gradient exists between the compounds in the well and the interior of the membrane.

VOCs in the groundwater are driven to diffuse into the sampler until the concentration gradient equilibrates between the water in the well and the water in the sampler. The PDB maintains dynamic equilibrium so that if analyte concentrations in the well change, the concentrations in the sampler will change accordingly. Diffusion rates vary by compound so the sample in the PDB typically represents the concentrations of the last several days prior to removal.

During sampler installation water in the well can become stratigraphically mixed. It is therefore necessary to allow enough time for the analyte concentrations in the well to re-stratify and for flow to resume according to natural conditions. It is generally recommended that the samplers are left in place a minimum of two weeks to allow the well to resume normal flow and stratification and for equilibration. Samplers can be left in from one sampling event to another then removed and replaced with a new sampler to minimize mobilization and maximize efficiency.

Using a PDB is a simple operation. Deployment consists of attaching the PDB sampler to a carefully measured, weighted suspension cord and lowering the PDB to the exact predetermined location within the screened interval of the well (Figure 8-5). Recovery is a simple matter of pulling the sampler out of the well and transferring the contents to VOA vials (Figure 8-6). Transfer should be made within minutes of removal from submersion to prevent loss of volatiles to the air.



Figure 8-5. PDB deployment



Figure 8-6. Transferring sample to VOA vials. Discharge of PDB sampler using a discharge straw in the right photo.

8.1.2 Target Media

PDBs were initially designed to collect representative concentrations of VOCs from specific intervals in groundwater monitoring wells. In the years since they were commercially introduced studies have successfully used PDBs to collect representative VOC concentrations from water laden sediments and to collect soil gas samples for VOC analysis. Since polyethylene based PDBs are semi-permeable, certain compounds are restricted from diffusing through the membrane. This feature has been put to effective use to provide an indicator of the effectiveness in certain remediation projects where a strong oxidizing agent is pumped into a well to reduce compounds such as PCE. The PDB will effectively screen out the oxidizing agent and allow measurement of residual PCE.

8.1.3 Potential Analyte Capabilities

PDB samplers cannot be used for all contaminants; metals and other inorganic compounds will not diffuse through the membrane. The general target is non-polar VOCs with a molecule size of less than 10 angstroms. A partial list of VOC compounds test in the laboratory and field are shown in tables 8-1 and 8-2.

Table 8-1. PDB samplers: 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

Favorable laboratory diffusion testing results		
Carbon tetrachloride	1,1-Dichloroethene	1,1,1-Trichloroethane
Chloroethane	<i>cis</i> -1,2-Dichloroethene	1,1,2-Trichloroethane
Chloroform	<i>trans</i> -1,2-Dichloroethene	Trichloroethene (TCE)
Chloromethane	1,2-Dichloropropane	Trichlorofluoromethane
2-Chlorovinylether	<i>cis</i> -Dichloropropene	1,2,3-Trichloropropane
Dibromochloromethane	1,2-Dibromoethane	Vinyl chloride
Dibromomethane	<i>trans</i> -1,3-Dichloropropene	Xylenes (total)
1,2-Dichlorobenzene	Ethyl benzene	
Unfavorable laboratory diffusion testing results		
Acetone	Methyl <i>tert</i> -butyl ether	
Methyl <i>iso</i> -butyl ketone	Styrene	

**Table 8-2. Field experience sampling VOCs with PDBs
(Parsons 2004)**

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
<i>n</i> -Butylbenzene	Dichlorodifluoromethane	1,2,3-Trichlorobenzene*
<i>sec</i> -Butylbenzene	1,1-Dichloroethane	1,2,4-Trichlorobenzene*
<i>tert</i> -Butylbenzene	1,2-Dichloroethane	1,1,1-Trichloroethane
Carbon disulfide	1,1-Dichloroethene	1,1,2-Trichloroethane
Carbon tetrachloride	<i>cis</i> -1,2-Dichloroethene	Trichloroethene
Chlorobenzene	<i>trans</i> -1,2-Dichloroethene	Trichlorofluoromethane
Chloroethane	1,2-Dichloropropane	1,1,2-Trichloro-1,2,2-trifluoroethane
Chloromethane	Ethylbenzene	Vinyl chloride
Dibromochloromethane	Hexachlorobutadiene*	<i>m,p</i> -Xylene
1,2-Dibromoethane*	<i>p</i> -Isopropyltoluene	<i>o</i> -Xylene
Dibromomethane*	1-Methylethylbenzene	Xylenes, total
Data suggest that PDB sampling may be problematic for these target compounds (see reference)		
<i>tert</i> -Amyl methyl ether*	Naphthalene	1,2,4-Trimethylbenzene
Bromoform*	<i>n</i> -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.

8.1.4 Sample Volume

Volume varies with the diameter and length of the PDB. Standard PDBs are sized to fit in 2-inch wells (1.25-inch OD by 18-24-inches long). The standard PDB sampler holds 220-350 mL of water. PDB samplers can be custom fabricated in varying lengths and diameters for specific volume requirements. Generally, PDBs have been made to obtain a sample volume of 250 to 350 mL.

8.2 State of the Art

8.2.1 Lab Testing

Laboratory testing for chemical parameters has shown excellent correlation for those compounds tested.

8.2.2 Field Testing

Numerous studies have been performed to demonstrate the appropriateness of the use of PDB and allowed it to be recognized as a valid groundwater sampling technique. The Air Force Center for Environmental Excellence funded a nationwide study of PDB use within 17 bases.

8.2.3 Examples of Acceptance and Use

Multiple sites nationwide are currently using PDB for VOC long-term monitoring (LTM), site characterization, and remedial process optimization (RPO). Two sites in Cape Canaveral Air Force Space Florida obtained regulatory closure using the PDB sampling technique. The PDB have been accepted in several states as a valid sampling technique and the ITRC guidance document is currently going through a state concurrence process to obtain regulatory acceptance of this technique. The NJDEP published in August 2005 their Field Sampling Procedures Manual which has specific guidance on using the PDBs for sampling groundwater and surface water sediments.

8.2.4 Current State of Research

The USGS developed in the late 1990's and has become a widely accepted technique for determining concentrations of VOCs in groundwater monitoring wells.

8.2.5 Availability

PDB samplers are commercially available (see vendor contact information). Patent 5,804,743 covers the PDB sampling methodology and is available for non-exclusive licensing through the U.S. Geological Survey Technology Enterprise Office.

8.3 Features and Limitations

8.3.1 Cost

PDB sampler: ~ \$25.00

Customized deployment equipment: ~ \$60 per well with multiple PDBs deployed

(Includes: weight, poly tether material, connections to sampler, ID tag, well cap, and miscellaneous expenses.)

8.3.2 Deployment Considerations including Advantages and/or Limitations

Target analyte, contaminant stratification, and horizontal flow are the primary considerations when deploying the PDB. PDBs should be deployed only at well characterized sites where the contaminants of concerns have been identified as VOC compounds (see Tables 7-1 and 7-2).

PDB samplers have been manufactured to sample wells as small as 1-inch inside diameter. Samples have been successfully collected at depths over 700 feet below ground surface.

Advantages of PDB samplers include the following:

- do not purge water
- only sample for VOC compounds
- effective in low yield wells
- allow for rapid installation and sample collection
- easy to use
- inexpensive to purchase and use
- samples discrete interval or can integrate sample over longer vertical interval.
- multiple, stacked samplers provide vertical contaminant profile
- collect samples from discrete intervals in surface water bodies and tank

8.3.3 Nature of Sample

PDBs collect a time-weighted discrete interval sample.

8.3.4 Decontamination Requirements

The PDB is a disposable groundwater sampler. Only the reusable stainless steel weight and suspension cord need to be decontaminated if moved from well to well.

8.3.5 Sample Handling and Shipping

Transfer of water from the PDB to sample containers is required before shipping samples to the laboratory.

8.4 Unanswered Questions

[None]

8.5 Selected References

ITRC, 2004. Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Groundwater.

Parsons. 2004. Final Comprehensive Results Report for the Passive Diffusion Bag Sampler Demonstration.

Vroblesky, D. A. 2001. User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compounds Concentrations in Wells, Part 1 and 2. US Geological Survey Water Resources Investigation Reports 01-4060 and 01-4061.

ITRC, Diffusion Sampler Information Center (DSIC),
<http://diffusionsampler.itrcweb.org/common/default.asp>

NJDEP, August 2005, Field Sampling Procedures Manual, Chapters 5 and 6.
<http://www.state.nj.us/dep/srp/guidance/fspm/>

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9. RIGID POROUS POLYETHYLENE SAMPLERS (RPPS)

9.1 Description and Application

Rigid porous polyethylene samplers (RPPSs) are diffusion based samplers developed to sample for a broader range of analytes than can be collected by the PDB sampler.

9.1.1 Physical Characteristics

The RPPS consists of a 1.5-inch OD, six to seven-inch-long, rigid polyethylene tube with caps on both ends. The tube is constructed from thin sheets of foam-like porous polyethylene with pore sizes of 6 to 15 microns. The sampler is filled with water free of the target analytes, capped at both ends, and placed inside a mesh liner, which is subsequently attached to a deployment rope using cable-ties and deployed in a well. Over time, chemicals diffuse across the porous polyethylene and equilibrate with the water inside the sampler. Upon retrieval, the contents of the sampler are transferred to laboratory sample containers via stopcocks.



Figure 9-1. RPPS with mesh covering used to secure sampler to deployment rope



Figure 9-2. Two RPPSs attached side-by-side along other passive sampling devices on a deployment rope



Figure 9-3. Transferring sampler contents into sample containers*

*Note: plastic wrap tightly wrapped around this RPPS, which was used to prevent water leaking from the sampler through the membrane pores during bottle filling. Subsequent changes in RPPS design to address leakage have eliminated the need for the plastic wrap. A plug is placed in one end and a cap, without a stopcock, on the other. The RPPS is deployed plug-down in the well. When the RPPS is retrieved it is inverted, the plug is removed, and the contents poured into the sample bottles immediately. Leakage is minimized and sample transfer into the bottles is much quicker.

9.1.2 Target Media

The RPPS were specifically designed to collect groundwater samples from a discrete interval in monitoring or water wells.

9.1.3 Potential Analyte Capabilities

Theoretically, these samplers should be capable of monitoring most compounds (inorganic and organic, both volatile and semi-volatile) present in dissolved phases in the groundwater.

9.1.4 Sample Volume

Tests performed to date indicate that the maximum feasible sampler length is approximately 7.5 inches. Use of a longer sampler would result in leakage of sampled water out of the sampler walls due to the higher head pressure present in the sampler (Vroblesky, 2004). For a sampler having a diameter of 1.5 inches OD, the resultant sample volume is about 175 mL. Larger volumes can be obtained by using a larger-diameter sampler, when the well diameter allows, or by using multiple samplers attached end-to-end or side-by-side. It should be noted that the minimum required sample volume to conduct most standard analyses may be much less than the typically requested volume, depending on the choice of analytical methods and desired detections. Prior coordination with the laboratory could eliminate this minimum volume limitation as a concern.

9.2 State of the Art

9.2.1 Lab Testing

Bench-scale test results indicated that this type of sampler can yield accurate results for VOCs (including MTBE), chromium, and chloride (Vroblesky, 2004). The equilibration time for VOCs and chloride is eight days or less. Solutes in the samplers had achieved equilibrium with the solutes in the test solution by the first sampling time, eight days after deployment. The equilibration time for chromium was less certain because reliable samples for chromium were not collected until day 22, at which time chromium concentrations in the sampler had fully equilibrated with the test water.

9.2.2 Field Testing

RPPS devices were included in a field demonstration of multiple passive groundwater sampling devices at the former McClellan AFB (Sacramento, California) in 2004 (Demonstration of Alternative Groundwater Sampling Technologies at McClellan AFB, Parsons 2005). According to the preliminary data, the RPPS seemed to perform well at monitoring for anions, metals, and hexavalent chromium. While performing similarly to the low-flow purge method, the RPPS did not work as well as the other passive devices in this study for organics such as VOCs and 1,4-dioxane.

9.2.3 Examples of Acceptance and Use

Refer to above lab and field testing.

9.2.4 Current State of Research

The RPPS are undergoing continued laboratory testing and field testing. The additional laboratory and field tests will further determine the applicability of these devices to the full range of analytes that are of interest in groundwater. In one recent laboratory study the RPPS worked well for many of the semivolatiles, except for the very insoluble ones like the poly aromatic hydrocarbons (PAHs). One possible reason is they may be sorbing to the polyethylene material. In a second laboratory study, the RPPS worked quite well for anions, most metals, hexavalent chromium, and 1,4-dioxane (Columbia Analytical Services, Inc. unpublished data, 2005). These devices are currently deployed at a site in New Jersey for metals (Roux & Associates) and at a site in Florida for 1,4-dioxane (Kubal-Furr Associates). Additional field and laboratory testing is needed to ascertain the effectiveness of these devices.

9.2.5 Availability

These samplers have not been fully commercialized and are available in limited amounts through Columbia Analytical Services, Inc. (see vendor contact information). A patent application is being considered by the USGS.

9.3 Features and Limitations

9.3.1 Cost

The RPPS has limited commercial availability at this time. Initial commercial cost is approximately \$40.00 to \$50.00.

9.3.2 Deployment Considerations including Advantages and/or Limitations

As designed, the samplers could fit into wells with a minimum inside diameter of 2.0 inches. There is no limit to the depth at which they could be deployed.

The porous polyethylene sampler pores tend to retain air even when submerged. Therefore, the air entrained in the pore space must be removed by flushing with water prior to deployment if the sampler is to be used for nonvolatile solutes. This step is not needed when sampling for VOCs only.

Sampling for reduction-oxidation (redox)-sensitive metals, such as lead, iron, and manganese, in an open borehole with RPPSs (or other passive in-well method) is subject to a number of uncertainties and should be approached with caution. The main reason is that water in a well screened in an anaerobic aquifer can become oxygenated when oxygenated water from near the air-water interface is distributed throughout the well. This can happen when lateral transport of anaerobic groundwater through the screened interval is insufficient to outpace oxygen circulation through the well by diffusive, convective, or advective water movement in the well. When the well bore is oxygenated, but the adjacent aquifer is anaerobic, redox-sensitive solutes in the well bore should not be expected to be the same concentrations as in the aquifer. When using water-filled diffusion samplers to sample redox-sensitive parameters in a well that maintains anaerobic water in the well bore, one approach to avoid oxidation and precipitation of redox-sensitive metals is to use anaerobic water as the sampler filling solution. When deployed in anaerobic water, however, the fill solution in the diffusion sampler becomes anaerobic by diffusion, and not enough work has been done yet to determine whether prefilling with anaerobic water is necessary or if there will be any affect on equilibration time.

A limitation for this sampler is that sample volume may be a concern if using these devices to test for a wide range of analytes. Prior coordination with the laboratory could eliminate volume limitation as a concern. Additional testing is necessary to delineate possible analyte limitations for these samplers.

9.3.3 Nature of Sample

The RPPS collects a time-weighted discrete interval sample.

9.3.4 Decontamination Requirements

Decontamination of the sampler is expected to be minimal, particularly once it becomes available commercially. A disposable device is common for similar types of other passive diffusion samplers.

9.3.5 Sample Handling and Shipping

Prompt transfer of sample from the RPPS to sample containers is required.

9.4 Unanswered Questions

Additional laboratory and field testing is expected to be required prior to regulatory acceptance of the technology.

9.5 Selected References

Parsons, 2005, Final Results Report For the Demonstration of No-Purge Groundwater Sampling Devices At Former McClellan Air Force Base, California. Contract F44650-9900005, October 2005.

9.6 Contact Information

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10. SEMI-PERMEABLE MEMBRANE DEVICES (SPMDS)

10.1 Description and Application

Semi-permeable Membrane Devices (SPMDs) are designed to sample chemicals dissolved in surface water, mimicking the bioconcentration of organic contaminants into the fatty tissues of organisms. The SPMD enables concentration of trace organic contaminant mixtures for analysis, toxicity assessments, and toxicity identification evaluation. The SPMD has also been used to sample chemicals in groundwater and air. It is designed to sample lipid or fat-soluble (nonpolar or hydrophobic) semi-volatile organic chemicals from water and air. The SPMD is an integrative sampler which accumulates analyte mass over a deployment period ranging from days to months. SPMDs provide a highly reproducible means for monitoring contaminant levels, and are largely unaffected by many environmental stressors that affect biomonitoring organisms.

10.1.1 Physical Characteristics

The SPMD consists of a neutral, high molecular weight lipid (> 600 daltons) such as triolein which is encased in a thin-walled (50-100 µm) lay flat polyethylene membrane tube. The

nonporous membrane allows the nonpolar chemicals to pass through to the lipid where the chemicals are concentrated. Larger molecules (> 600 daltons) and materials such as particulate matter and microorganisms are excluded. A standard SPMD is 2.5 cm wide by 91.4 cm long containing 1 mL of triolein. SPMDs of different sizes can be made by maintaining the ≈ 100 cm²/g SPMD ratio.

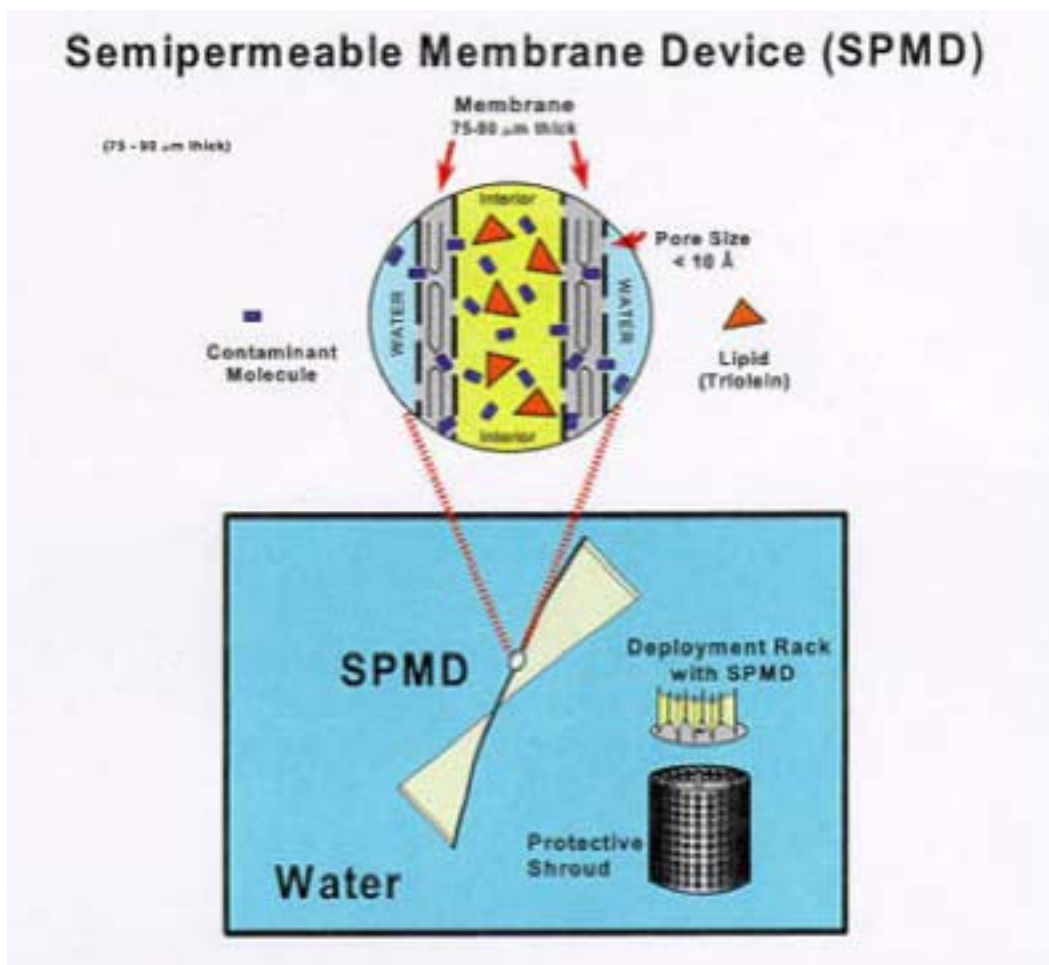


Figure 10-1. Lipid containing semipermeable membrane device (SPMD) and typical deployment apparatus

SPMD deployments typically are for one month, however, depending on the study design, deployment times can range from days to months. SPMDs are transported to and from the sampling site in gas-tight metal cans. Following receipt of a field deployed SPMD, the device is stored frozen until processing. Chemical residues in the SPMD are recovered by using an organic solvent dialysis step. SPMDs are submersed in an organic solvent such as hexane and analytes diffuse out into the hexane while lipids remain inside the tubing. Following dialysis, all targeted chemicals are in the hexane and the used SPMD can be discarded. At this point, the sample is ready for further processing (cleanup and/or fractionation), analysis, toxicity screening, etc.



Figure 10-2. SPMD (left) and a surface water deployment canister containing 5 SPMDs (right). Deployment canisters are commercially available for groundwater monitoring wells as well.

SPMDs use the Performance Reference Compound (PRC) approach to account for site-specific environmental factors (flow/turbulence, temperature, biofouling, etc.). PRCs are compounds which are added to the SPMD during construction, and during the exposure a percentage of each PRC is lost to the surrounding water or air. Determination of the amount of PRC lost provides an exposure adjustment factor to adjust laboratory-derived sampling rates to site specific conditions.

10.1.2 Target Media

SPMDs can sample hydrophobic organic contaminants from water or air under nearly any environmental conditions.

10.1.3 Potential Analytes

Chemicals sampled by SPMDs include hydrophobic, bioavailable organic chemicals such as polychlorinated biphenyls (PCBs), PAHs, organochlorine pesticides, dioxins and furans, selected organophosphate and pyrethroid pesticides, and many other nonpolar organic chemicals.

10.1.4 Sample Volume

The volume of water sampled during a SPMD deployment is a function of the sampling rate for a particular chemical and the sampling duration. For example, a SPMD deployed for 30 days, sampling a chemical with a sampling rate of 5 L per day, will result in an equivalent of 150 L of water sampled. These sampling rates can vary with changes in the water flow/turbulence, temperature, and buildup of a biofilm on the sampler's surface. To satisfy certain detection limit requirements, the extracts from multiple devices can be combined thereby increasing the total volume of water sampled.

10.2 State of the Art

10.2.1 Lab Testing

Characterization of the SPMD for sampling various classes of nonpolar organic chemicals in water and air have been performed in the laboratory. This includes calibration of the SPMD to determine sampling rates for select chemicals under different flow/turbulence and temperature regimes. This approach has allowed for the development of theoretical models to describe sampler performance. Optimization of processing techniques, instrumental analysis methods, and application of bioassay/toxicity testing have also been performed for the SPMD matrix.

10.2.2 Field Testing

SPMDs have been used in numerous field deployments across the U.S. and internationally since the early 1990s. These deployments have ranged from stagnant pools to major river systems, clear natural springs and other groundwater to biologically-active wastewater streams, and freshwater to marine systems. SPMDs have been used for sampling indoor and outdoor air contamination as part of human health assessments. Comparison of water and air concentrations of select targeted chemicals derived from SPMD data to that from traditional sampling methods (grab samples, HiVol samples, biomonitoring organisms) have validated the SPMD's ability to determine the in situ concentrations of nonpolar organic chemicals.

10.2.3 Examples of Acceptance and Use

SPMDs have been used by many U.S. federal agencies (e.g., USGS, EPA, National Park Service and the U.S. Fish and Wildlife Service) and internationally for the monitoring of water-soluble organic contaminants in numerous studies across the globe. The Virginia Department of Environmental Quality is currently using SPMDs in a statewide probabilistic study and is examining the use of SPMDs for their Total Maximum Daily Limit (TMDL) determinations of PCBs. The EPA has been instrumental in developing the SPMD as an airborne contamination monitor. The Environment Agency of England and Wales has adopted the SPMD as part of their monitoring programs.

10.2.4 Current State of Research

The UK Environment Agency has nearly completed an accreditation process for the SPMD. The Institute of Public Health in the Czech Republic is also performing an accreditation of the SPMD as a standard method and currently the SPMD is being considered by the European Union as a standard method for dissolved phase chemicals. A book will be published by Springer, New York, NY (available in spring of 2006) which summarizes the state and breadth of SPMD technology.

10.2.5 Availability

The SPMD is covered by U.S. Patents 5,098,573 and 5,395,426. SPMDs are available commercially and are also fabricated by some researchers.

10.3 Features and Limitations

10.3.1 Cost

The SPMD is commercially available. Cost associated with purchasing a typical 91.4 cm length SPMD consist of the membrane-triolein device (\$50); and the SPMD holders, which contains the devices, and canister (\$250; holders and canister). For ultra-trace level analysis, the lipid needs to be extracted prior to use which is an extra cost (\$5). There are various methods that can be used to recover and fractionate analytes which vary in costs. The SPMD holders and canisters can also be leased for a monthly rate.

10.3.2 Deployment Considerations including Advantages and/or Limitations

Careful selection of the study site is important for a successful deployment. When sampling water, it is critical that the samplers be deployed where they will remain submerged, but not buried in the sediment, during the exposure period. It is important to keep the samplers shaded to prevent degradation of some light-sensitive chemicals. When possible, avoid deployments in the extremely turbulent flow to prevent damage. The biggest danger to the sampler is vandalism. Keeping the samplers securely tethered, hidden, and out of areas frequented by people can help prevent vandalism.

10.3.3 Nature of Sample

Following processing of SPMDs in the laboratory, the sample is an enriched extract in an organic solvent such as hexane. Depending on the desired use of the sample, additional processing (i.e., cleanup and/or fractionation) may be necessary.

10.3.4 Decontamination Requirements

Prior to SPMD use, the lipid, membrane, and deployment hardware undergo a thorough cleaning to remove any potential interferences. Before analysis of exposed SPMDs, it is necessary to do surficial cleaning to remove sediments, biofouling, etc., which may adhere to the membrane surface. At a minimum, this cleaning involves gentle scrubbing of the SPMD surface with a soft brush.

10.3.5 Sample Handling and Shipping

SPMDs should be shipped between the laboratory and sampling site in air-tight containers to prevent potential contamination from airborne chemicals. Shipping the SPMDs frozen or at least cold, helps to prevent loss of chemical or additional sampling from the surrounding air.

10.4 Unanswered Questions

Questions that remain unanswered for SPMDs are as follows:

- Are all sampling rates available for all contaminants? Sampling rates are necessary to estimate the ambient concentrations of targeted chemicals. Sampling rate data are available

for hundreds of major environmental contaminants in water but are often unavailable for contaminants less frequently detected. To date, a limited number of chemical sampling rates have been determined in air.

- How can the potential for biofouling of the membrane surface be reduced or eliminated? Biofouling is generally not observed in groundwater monitoring.

10.5 Selected References

Huckins, J.N., Petty, J.D., Prest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., Johnson, B.T. *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants*; Report for the American Petroleum Institute (API); API publication number 4690; API: Washington, DC, 2002.

Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, K., Alvarez, D.A., Cranor, W.L., Clark, R.C., Mogensen, B.B. *Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices*. *Environ. Sci. Technol.* 2002, 26, 85-91.

Huckins, J.N., Prest, H.F., Petty, J.D., Lebo, J.A., Hodgins, M.M., Clark, R.C., Alvarez, D.A., Gala, W.R., Steen, A., Gale, R., Ingersoll, C.G. *Overview and Comparison of Lipid-Containing Semipermeable Membrane Devices and Oysters (*Crassostrea gigas*) for Assessing Organic Chemical Exposure*. *Environ. Tox. Chem.* 2004, 23, 1617-1628.

Gustavson, K.E. and Harkin, J.M. *Comparison of Sampling Techniques and Evaluation of Semipermeable Membrane Devices (SPMDs) for Monitoring Polynuclear Aromatic Hydrocarbons (PAHs) in Groundwater*. *Environ. Sci. Technol.* 2000, 34, 4445-4451.
SPMD web site: <http://www.waux.cerc.cr.usgs.gov/SPMD/>

10.6 Contact Information

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Information on vendors can be obtained from the USGS Technology Transfer office.
<http://www.usgs.gov/tech-transfer/patent.html>

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11. GORE™ SORBER MODULE

11.1 Description and Application

The GORE™ Sorber Module (Figure 11-1) is a device that relies on diffusion and sorption to accumulate analytes in the sampler. These modules yield a total mass of analytes that can be correlated with analyte concentrations in water or air. This device can be utilized to sample soil gas in the vadose zone and dissolved organic analytes in water saturated soils or in groundwater monitoring wells. This device has been used in both fresh and saltwater environments, including sampling sediments in marshes, streams, river embankments, and coastal settings. In addition, these devices have been used in vapor intrusion studies and indoor and outdoor air monitoring investigations.



**Figure 11-1. Gore™
Module**

11.1.1 Physical Characteristics

Each module is approximately ¼ inches in diameter and 13 inches in length and consists of a tube of GORE-TEX® membrane that contains four Sorber packets, in series, that contain sorbent material (Figure 11-2). The Gore-Tex membrane is microporous expanded Polytetrafluoroethylene (ePTFE) and is relatively chemically inert. The hydrophobic nature of the membrane allows vapor migration to the sorbent but prevents water and sediments from reaching the inner sorbent material. A typical Sorber packet is about 25 mm in length, 3 mm in diameter, and contains a granular adsorbent material that is selected on the basis of the specific compounds to be detected. For VOCs and SVOCs, hydrophobic carbonaceous and polymeric resins are used although the Sorber packets can be custom designed for specific analytes. Organic compounds dissolved in water partition to the vapor phase (Henry's Law) and move across the membrane to the sorbent. The end of the module has a loop with a unique serial number label. For groundwater monitoring applications, the module is suspended in a monitoring well on a length of line with a stainless steel weight attached to the bottom. The narrow diameter of the module facilitates deployment in piezometers and small diameter wells (1/2 inch ID and larger).

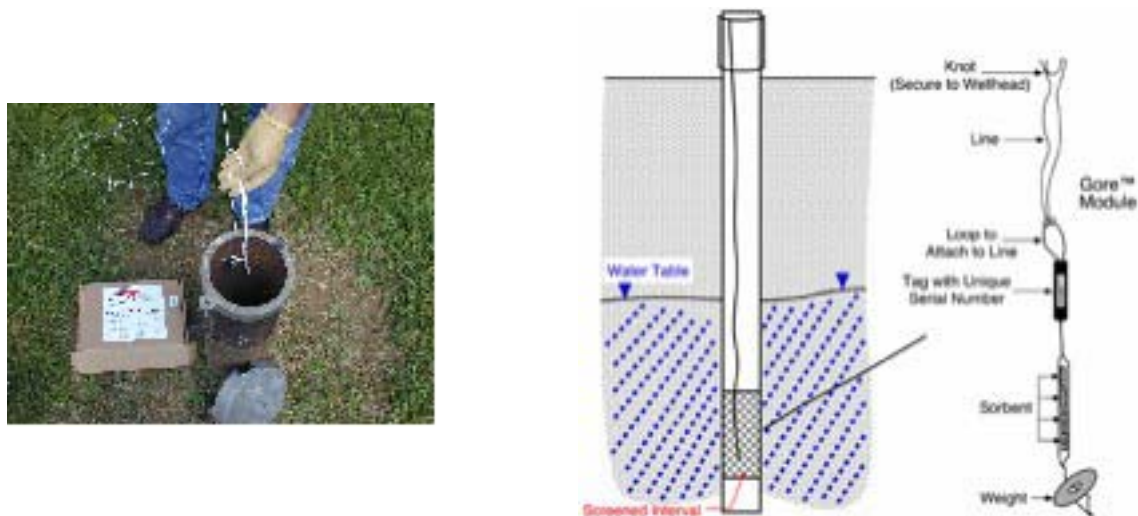


Figure 11-2. Installation of a GORE™ Module in a monitoring well.

Each module is clean when it comes from the manufacturer and is contained in a sealed glass vial. After removing the module from the vial, it is placed at the desired depth in the screened interval (Figure 11-2), or several modules can be placed at multiple depths within the screened interval. After the exposure period of 15 minutes to four hours, the module is retrieved, and returned to its glass vial and shipping container. The glass vials containing the exposed modules, along with trip blanks and Chain-of-Custody (COC) forms, are shipped to Gore's dedicated laboratory in Elkton, MD, usually via overnight courier. Experiments conducted by Gore have determined that the modules do not have to be kept cold for shipment and will keep in the glass vials (without refrigeration) until they are analyzed, usually within four to seven days.

11.1.2 Target Media

The module can be deployed in virtually any geological setting (from low permeability clays to high permeability sands) with any moisture level (from dry to saturated soils).

11.1.3 Potential Analyte Capabilities

These devices have been used to detect VOCs and SVOCS including halogenated solvents, aliphatic and aromatic hydrocarbons, ethers, alcohols, ketones, PAHs, nitroaromatic explosives, chemical agent breakdown products, pesticides, herbicides, and polychlorinated biphenyls (PCBs).

11.1.4 Sample Volume

The volume of water sampled during a GORE™ Sorber Module deployment is a function of the sampling rate for a particular chemical and the sampling duration.

11.2 State of the Art

Currently, there are no peer reviewed journal publications that include data on the capabilities of the GORE™ Module. However, the USEPA Environmental Technology Verification (ETV) program (Einfeld and Koglin 2000) conducted a study with known concentrations of VOCs in a standpipe and a field study at a site contaminated with TCE. In addition, Gore has also conducted numerous surveys, including ones with the DOD and USGS. Data from these investigations have been presented at several professional conferences (Hodny and Brown 2000; Hodny et al. 2001a, 2001b; Brown et al. 2001).

11.2.1 Lab Testing

In the ETV study, Einfeld and Koglin (2000) tested the utility of this device for sampling VOC contaminated water. The test was conducted in a 100-foot standpipe. The test solution contained six VOCs at concentrations that were approximately 15 µg/L. The exposure time was 48 hours. All six of the target analytes were collected by the modules. However, the authors did not report the mass of analytes desorbed from the modules or correlate the desorbed masses with the concentrations found in the standpipe. They did report on the precision of the devices and noted that one of the four replicate samples had to be discarded because water had penetrated through the membrane. They concluded that this precision was comparable to their reference method for the various analytes in the control samples.

11.2.2 Field Testing

The EPA's ETV program also conducted a field test in five two-inch diameter PVC monitoring wells to determine the ability of the modules to recover representative values of TCE (Einfeld and Koglin 2000). Concentrations in the wells varied from five to 2000 µg/L; and the exposure time was 48 hours. Reference samples were collected with a co-located submersible (Fultz) pump at 12-hour intervals throughout the 48-hour exposure period to give a time-integrated concentration for these wells. The researchers concluded that there was a strong correlation between the mass of TCE desorbed by the modules and the concentration of TCE in the wells.

They noted that log-log plots yielded good linearity over three orders of magnitude with correlation coefficients of greater than 0.99; however, they noted that the precision with these devices was considerably poorer in this study than it was in the standpipe study. They also noted that they had what they believed to be outliers in their data set. They felt that these outliers were indicative of a membrane defect and recommended separate modules be deployed for additional quality control.

They felt that because these devices can be used for a wide range of VOCs and SVOCs that they would be useful for screening applications where there are multiple contaminants and precision requirements are modest; however, they felt this device would be of limited use in monitoring compliance. They also noted that because this device is designed for trend analysis, it would be well suited in plume edge monitoring for gross changes in groundwater concentrations.

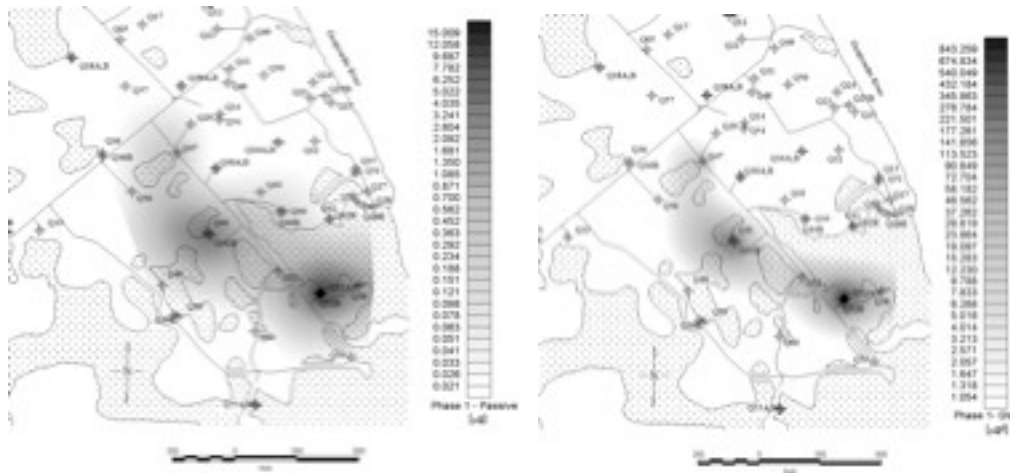
Data from several field investigations conducted by Gore have been given at several technical conferences (Hodny and Brown 2000; Hodny et al. 2001a, 2001b; Brown et al. 2001). These data have shown that VOC and SVOC values from the modules correlate strongly (positive linear relationships) with groundwater data collected by conventional methods, including low-flow sampling and passive sampling methods.

11.2.3 Examples of Acceptance and Use

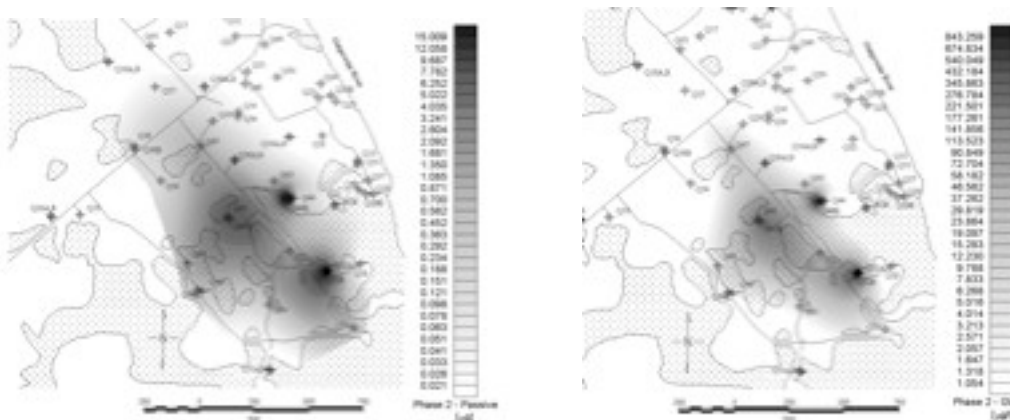
The following case study is provided by the manufacturer and illustrates the enhanced sensitivity in plume delineation that can be obtained using this device. The site is a military facility located in the mid-Atlantic region of the U.S., where 30 or more years of munitions testing has occurred and a large network of monitoring wells exists. The water table is approximately 30 feet deep, and the soils are unconsolidated alluvial deposits. Groundwater concentrations of the organic contaminants as high as 2,000 ug/L have been reported.

GORE™ Modules were deployed in wells during two sampling events. The modules were placed in the screened intervals and exposed for 48 hours. Conventional groundwater sampling followed each passive sampling event. The first event included 28 wells and a total of 33 wells (including the first 28) were sampled during the second event.

Correlation between the mass detected using the modules and the groundwater concentrations were excellent. Figures 11-3 and 11-4 illustrate the excellent comparability of the two data sets spatially for each sampling event. The plumes generated using the module results were more widespread indicative of lower detection limits and greater sensitivity.



**Figure 11-3. Comparison of GORE™ Module data and conventional groundwater sampling data
(First phase of sampling, for 1,1,2,2-tetrachloroethane, for the first sampling event)**



**Figure 11-4. Comparison of GORE™ Module data and conventional groundwater sampling data
(second phase of sampling, for 1,1,2,2-tetrachloroethane, for the second sampling event)**

For this site a comparative analysis of actual sampling costs for the GORE™ module method and conventional groundwater sampling revealed a 70% decrease in costs, or a savings of approximately \$600,000, over the estimated 20-year life of the monitoring project.

11.2.4 Current State of Research

Gore is currently conducting both laboratory and field sampling to study uptake rates and system factors that reflect the efficiency of adsorption and desorption as a function of the sorbent, compound, and analytical methods.

11.2.5 Availability

The GORE™ Modules are commercially available from W. L. Gore & Associates, Inc., and are covered by USA and foreign patents.

11.3 Features and Limitations

11.3.1 Cost

The GORE™ Sampler pricing included the sampler, trip blank, deployment supplies, lab analysis, and reporting. Costs are \$185 to \$285 per sample depending upon analytes tested.

11.3.2 Deployment Considerations including Advantages and/or Limitations

Some advantages of the GORE™ Sampler include the following:

- simple to install and retrieve thereby decreasing field labor costs
- no purge water is generated
- applicable to a wide range VOC and SVOC compounds
- sensitive to parts per trillion levels
- minimal handling is required reducing possible field sampling errors
- single use, no material decontamination needed
- can be used in monitoring wells, sediments, surface water, springs, and other aqueous settings, regardless of their flow or turbidity
- can be used in small-diameter monitoring wells and piezometers
- simple shipping requirements (no ice or coolers needed) and lower shipping costs
- short residence period
- modules contain duplicate samples

Some limitations of the GORE™ Sampler include the following:

- gives total mass desorbed, therefore requiring calibration with measured concentration in wells.
- single source supplier and laboratory
- no field parameters or inorganics can be measured
- compound detection is limited by vapor pressure
- cannot be used when LNAPLs are present
- cannot be used when DNAPLs are present that extend into the screened interval

11.3.3 Nature of Sample

Each module is clean when it comes from the manufacturer and is contained in a sealed glass vial.

In the laboratory, the modules are transferred to thermal desorption tubes for analysis. They are then analyzed by thermal desorption gas chromatograph/mass spectrometer (GC/MS) using modified EPA 8260 and 8270 methods for VOCs and SVOCs, respectively.

11.3.4 Decontamination Requirements

No decontamination is required for the modules, since they are designed for one time use.

11.3.5 Sampling Handling and Shipping

The glass vials containing the exposed modules, along with trip blanks and COC forms, are shipped to Gore's dedicated laboratory in Elkton, MD, usually via overnight courier. Experiments conducted by Gore have determined that the modules do not have to be kept cold for shipment and will keep in the glass vials (without refrigeration) until they are analyzed, usually within four to seven days.

11.4 Unanswered Questions

Additional studies correlating the mass desorbed with aqueous concentrations are needed. Although a wide range of VOC and SVOC compounds have been examined, the exact compound applicability has yet to be defined. Studies are now underway at Gore to address this issue.

11.5 Selected References

- Brown, A., J. W. Hodny, G. Shaw, and D.J. Green (2001) *Estimating Groundwater Contamination Using Passive Sampling*, paper presented at the USACE Environmental Development Workshop, Portland, Oregon.
- Einfeld, W. and E. N. Koglin, (2000), *GORE-SORBER® Water Quality Monitoring*, Environmental Technology Verification Report, Groundwater Sampling Technologies, US EPA document EPA/600/R-00/091, October 2000.
http://www.epa.gov/etv/pdfs/vrvs/01_vr_gore.pdf
- Hodny, J.W., and A. Brown, (2000), *Passive Collectors as a Groundwater Monitoring Tool*, presented at the Small Drinking Water and Wastewater Systems Conference, January 12-15, 2000 Phoenix, AZ
- Hodny, J.W., G. Shaw, and D.J. Green, (2001a), *Estimating Ground Water Contamination Using Passive Sampling*, paper presented at the 13th Annual South Dakota Department of Environmental and Natural Resources Ground Water Quality Monitoring Conference, Aberdeen, South Dakota.
- Hodny, J.W., G. Shaw and D.J. Green (2001b) *Passive Sampling and Groundwater Contamination*” paper presented at the Third NSF International Symposium on Small Drinking Water and Wastewater Systems Conference, April 22-25, 2001 Washington, DC, USA

US EPA (1996) *Test Methods of Evaluating Solid Wastes: Physical Chemical Methods; Third Edition; Final Update III*, Report number EPA SW-846-3.3, Government Printing Office Order # 955-001-00000-1, Office of Solid Waste and Emergency Response, Washington D.C.

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12. POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS)

12.1 Description and Application

The Polar Organic Chemical Integrative Sampler (POCIS) is designed to sample water-soluble (polar or hydrophilic) organic chemicals from aqueous environments. This device relies on diffusion and sorption to accumulate a total mass of analytes. The residence period ranges from weeks to months. This device has no mechanical or moving parts. The POCIS samples chemicals from the dissolved phase, mimicking the respiratory exposure of aquatic organisms. The POCIS provides a reproducible means for monitoring contaminant levels, and is unaffected by many environmental stressors that affect biomonitoring organisms. The POCIS also concentrates trace organic contaminants for toxicity assessments and toxicity identification evaluation (TIE) approaches.

12.1.1 Physical Characteristics

The POCIS consists of a solid material (sorbent) contained between two microporous polyethersulfone membranes. The membranes allow water and dissolved chemicals to pass through to the sorbent where the chemicals are trapped. Larger materials such as sediment and particulate matter are excluded. The membrane resists biofouling which can significantly reduce the amount of the chemical sampled. The type of sorbent used can be changed to specifically target certain chemicals or chemical classes. A standard POCIS consists of a sampling surface area (surface area of exposed membrane) to sorbent mass ratio of $\cong 180 \text{ cm}^2/\text{g}$. A typical field deployed POCIS has an effective sampling surface area of 41 cm^2 . Figure 12-1 depicts an exploded view of a single POCIS disk. The polyethersulfone membranes are not amenable to standard sealing techniques (i.e., heat sealing) and therefore must be secured with a compression ring system to prevent loss of sorbent. The compression rings are typically made from stainless steel or other rigid inert materials. Individual POCIS can be secured on a support rod or on a rack system for insertion in a protective deployment canister. The protective canister, usually made of stainless steel or PVC, deflects debris that may displace the POCIS array.

Two configurations of the POCIS are commonly used, each containing different sorbents. A “Generic” configuration contains a mixture of three sorbent materials and is used for most pesticides, natural and synthetic hormones, many wastewater-related chemicals, and other water-soluble organic chemicals. The “Pharmaceutical” configuration contains a single sorbent designed for sampling most pharmaceutical classes. It is common to deploy POCIS of several different configurations together to maximize the types of chemicals sampled.

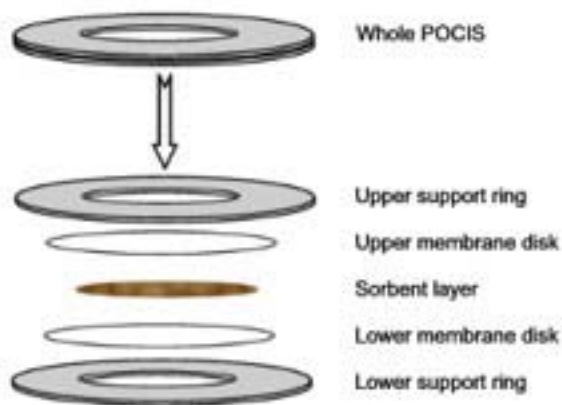


Figure 12-1. Exploded view of a single POCIS



Figure 12-2. Array of POCIS on support rod ready for deployment in a protective canister

POCIS deployments typically are for one month; however, depending on the study design, deployment times can range from weeks to months. Following receipt of an environmentally exposed POCIS from the field the sorbent is transferred into a chromatography column where the sampled chemicals are recovered using an organic solvent. The types of solvents used are optimized for the sorbent and the targeted chemicals.

POCIS extracts have been analyzed by various instrumental techniques, including high performance liquid chromatography (HPLC), GC, GC/MS, and liquid chromatograph/mass spectrometer (LC/MS). Extracts have also been tested with various bio-indicator tests such as Microtox[®] and the Yeast Estrogen Screen (YES) to determine the toxicological significance of the complex mixture of chemicals sampled by the POCIS.

12.1.2 Target Media

The POCIS can sample polar organic contaminants from water under nearly any environmental conditions. The samplers have been successfully used in fresh, estuarine, and marine waters.

12.1.3 Potential Analyte Capabilities

Chemicals sampled by the POCIS can include complex mixtures of pesticides, prescription and nonprescription drugs, personal care and common consumer products, industrial and domestic-

use materials, and degradation products of these compounds. A listing of some of the chemicals identified in POCIS extracts is shown in Table 12-1.

Table 12-1. Representative contaminants identified in POCIS extracts

<i>23 pharmaceuticals including</i>	<i>Various polar pesticides including</i>
Acetaminophen	Alachlor
Azithromycin	Chlorpyrifos
Carbamazepine	Diazinon
Dextropropoxyphene	Dichlorvos
Diphenhydramine	Diuron
Erythromycin	Isoproturon
Propranolol	Metolachlor
Sulfa drugs (antibiotics)	
Tetracycline antibiotics	<i>Various household and industrial products and degradation products including</i>
Thiabendazole	Alkyl phenols (nonyl phenol)
Trimethoprim	Benzophenone
<i>Illicit drugs</i>	Caffeine
Methamphetamine	DEET
MDMA (Ecstasy)	PFOS/PFOA
	Tonalide
<i>Natural and synthetic hormones</i>	Triclosan
17 β -estradiol	
17 α -ethynylestradiol	<i>Fire Retardants</i>
Estrone	Fryol CEF
Estriol	Fryol FR2
	Tri(2-butoxyethyl)phosphate
<i>12 Triazine herbicides including</i>	
Atrazine	
Cyanazine	
Hydroxyatrazine	
Terbutylazine	

Approximately 120 individual chemicals have been identified in POCIS samples. Essentially, nearly all compounds with $\log K_{ow} < 3.0$.

12.1.4 Sample Volume

Each POCIS disk will sample a certain volume of water per day. The volume of water sampled varies from chemical to chemical and is dependent on the physico-chemical properties of the compound and the sampling duration. These sampling rates can vary with changes in the water flow/turbulence, temperature, and buildup of suspended solids on the sampler's surface. To satisfy certain detection limit requirements, the extracts from multiple disks can be combined thereby increasing the total volume of water sampled.

12.2 State of the Art

12.2.1 Lab Testing

Optimization of the POCIS for the sampling of various classes of pesticides and pharmaceuticals has been performed in the laboratory. Characterization of various membrane materials and

sorbent compositions resulted in the current configurations. Calibration of the POCIS to determine sampling rates for selected chemicals under different turbulence regimes has allowed for the development of theoretical models to describe sampler performance.

12.2.2 Field Testing

The POCIS have been used in numerous field deployments across the United States and internationally. These deployments range from stagnant pools to major river systems; deep, clear natural springs to biologically-active wastewater streams; and freshwater to marine systems. Although the POCIS has not been used for groundwater, it is applicable for this type of monitoring. Due to lower sampling rates in stagnant water found in many wells, it will be necessary to deploy multiple samplers and combine the extracts to meet some instrumental detection limitations. Comparison of data derived from POCIS and traditional water sampling methods validate the ability of the POCIS to provide information on dissolved hydrophilic organic chemicals in water.

12.2.3 Examples of Acceptance and Use

The POCIS has been used by federal agencies including USGS, EPA, and the U.S. Fish and Wildlife Service for the monitoring of water-soluble organic contaminants in numerous studies across the U.S. International agencies, such as the United Kingdom Environment Agency, have adopted the POCIS as part of their National Pesticide Monitoring Project. The Environment Agency has also begun an accreditation process for the POCIS.

12.2.4 Current State of Research

The POCIS is continually evaluated for the potential to sample a wide range of hydrophilic organic chemicals. Analyte recovery methods are optimized and new calibration (sampling rate) data is being generated by researchers around the world. Techniques to merge the POCIS with bioindicator tests are under development. The POCIS is currently used in wastewater tracking studies, regulatory effluent monitoring, agricultural chemical runoff and fate determinations, and studies determining biological effects of complex mixtures of chemicals.

12.2.5 Availability

The POCIS was patented in November, 2002 (U.S. Patent 6,478,961). The POCIS is available commercially available from a licensed vendor and is also fabricated and used by the developers.

12.3 Features and Limitations

12.3.1 Cost

Cost associated with a typical POCIS from the vendor consist of:

- POCIS disk (\$60)
- stainless steel canister (\$265)
- POCIS holder which contains three disks (\$40)

- processing and extraction (\$75)

The POCIS stainless steel canister and holder can also be leased for a monthly rate.

12.3.2 Deployment Considerations including Advantages and/or Limitations

Careful selection of the study site is important for a successful deployment. It is critical that the samplers be deployed where they will remain submerged, but not buried in the sediment, during the exposure period. Keeping the samplers shaded may prevent degradation of some light-sensitive chemicals. It is desirable to have the POCIS in areas with water movement to enhance sampling rates, but when possible, avoid deployments in the heaviest flow to prevent damage. The biggest danger to the samplers is vandalism. Keeping the samplers securely tethered, hidden, and out of areas frequented by people can help prevent vandalism.

12.3.3 Nature of Sample

POCIS samples represent an accumulated mass and uptake is essentially irreversible. Following processing of the POCIS in the laboratory, the sample is an enriched extract in an organic solvent such as methanol, dichloromethane, etc. Depending on the desired use of the sample, additional processing (i.e., cleanup and/or fractionation) may be necessary. Applying chemical sampling rates and uptake models, the time-integrated concentration of the chemical over the deployment period can be estimated.

12.3.4 Decontamination Requirements

Prior to initial POCIS construction, the sorbents, membrane, and hardware undergo a thorough cleaning to remove any potential interference. Only minimal cleaning to remove sediments, etc., which may adhere to the surface is necessary following use and during sampler processing. This cleaning generally involves gentle scrubbing of the hardware surface with a soft brush.

Membranes and sorbents are extracted prior to construction of the samplers, and deployment hardware is cleaned by water washing and solvent rinsing. After assembly, samplers are stored frozen in airtight containers to prevent contamination.

12.3.5 Sample Handling and Shipping

The POCIS should be transported to and from the sampling site in airtight containers to prevent potential contamination from airborne chemicals. When possible, the POCIS should be shipped cold to preserve sample integrity.

12.4 Unanswered Questions

Questions that remain unanswered for POCIS are as follows:

- Determination of additional sampling rate data. Sampling rates are necessary to estimate the ambient water concentration of targeted chemicals. To date, a limited number of chemical sampling rates have been determined.

- How to incorporate the Performance Reference Compound (PRC) approach into the POCIS. A PRC is a compound which is added to the POCIS during construction and is lost to the surrounding water during deployment. Determination of the amount of PRC lost provides an environmental adjustment factor to correct laboratory-derived sampling rates for the site-specific environmental factors. Initial studies indicate that surrogate samplers as PRC monitors may be necessary since the POCIS sorbents act as infinite sinks and do not readily release chemicals. This PRC approach has successfully been used with semipermeable membrane devices (SPMDs).

12.5 Selected References

- Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E., 2004. *Development of a Passive, In Situ, Integrative Sampler for Hydrophilic Organic Contaminants in Aquatic Environments*. *Environ. Toxicol. Chem.* 23, 1640-1648.
- Jones-Lepp, T.L., Alvarez, D.A., Petty, J.D., Huckins, J.N., 2004. *Polar Organic Chemical Integrative Sampling (POCIS) and LC-ES/ITMS for Assessing Selected Prescription and Illicit Drugs Treated Sewage Effluent*. *Arch. Environ. Contam. Toxicol.* 47, 427-439.
- Petty, J.D., Huckins, J.N., Alvarez, D.A., Brumbaugh, W.G., Cranor, W.L., Gale, R.W., Rastall, A.C., Jones-Lepp, T.L., Leiker, T.J., Rostad, C.E., Furlong, E.T., 2004. *A Holistic Passive Integrative Sampling Approach for Assessing the Presence and Potential Impacts of Waterborne Environmental Contaminants*. *Chemosphere*, 54, 695-705.
- Alvarez, D.A., Stackelberg, P.E., Petty, J.D., Huckins, J.N., Furlong, E.T., Zaugg, S.D., Meyer, M.T., 2005. *Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream*. *Chemosphere*, 61, 610-622.
- Alvarez, D.A., Jones-Lepp, T.L., Stackelberg, P.E., Petty, J.D., Huckins, J.N., Furlong, E.T., Zaugg, S.D., Meyer, M.T. 2004 *Water Quality Monitoring of Pharmaceuticals and Personal Care Products using Passive Samplers*.
http://www.cerc.usgs.gov/pubs/EChem/PPCP_940AM.mht

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Information on vendors can be obtained from the USGS Technology Transfer office
<http://www.usgs.gov/tech-transfer/patent.html>

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13. PASSIVE IN-SITU CONCENTRATION EXTRACTION SAMPLER (PISCES)

13.1 Description and Application

The Passive In Situ Concentration Extraction Sampler (PISCES) is designed to sample non-polar or hydrophobic organic chemicals in surface water. This device relies on diffusion and sorption to accumulate a total mass of analytes. The residence period ranges from one day to one month.

PISCES consist of a membrane, typically low-density polyethylene (LDPE), forming one end of a metal container filled with an organic solvent, typically hexane or isooctane (2,2,4-trimethylpentane). Analyte uptake is driven by the preferential partitioning of nonionic organic chemicals from water to the solvent. For hydrophobic compounds, partition coefficients are large

(greater than 1,000), and sampling continues at a constant rate for weeks to months without approaching equilibrium between the solvent and the water. Sampling rates do not vary from compound to compound, so relative distribution of compounds in the extract reflect the relative distribution of these compounds dissolved in the water. The solvent is analyzed by conventional analytical methods. The membrane excludes ionic, high molecular-weight natural organic matter, and particulates, thereby simplifying, and in some cases eliminating the need for cleanup of samples before analysis.

13.1.1 Physical Characteristics

PISCES are constructed to be lightweight, rugged, easy to deploy, reusable, and to allow easy addition and retrieval of solvent. The devices consist of a metal (brass) body with a flange at one end to retain the membrane and a screw cap at the other end to allow addition and removal of solvent. The cap is fitted with a PTFE vent filter that keeps water out but allows gases to escape. Two configurations of PISCES are illustrated in Figure 13-1. One has a flange diameter of 7.6 cm (3 inches), a membrane area of 21 cm² and holds 100 mL of solvent. The other has a flange 10 cm (4 inches) square, a membrane area of 50 cm² and holds 200 mL of solvent. Both samplers are approximately 9.5 cm (3.75 inches) long. Caps and flanges are sealed with standard-sized Viton[®] o-rings.

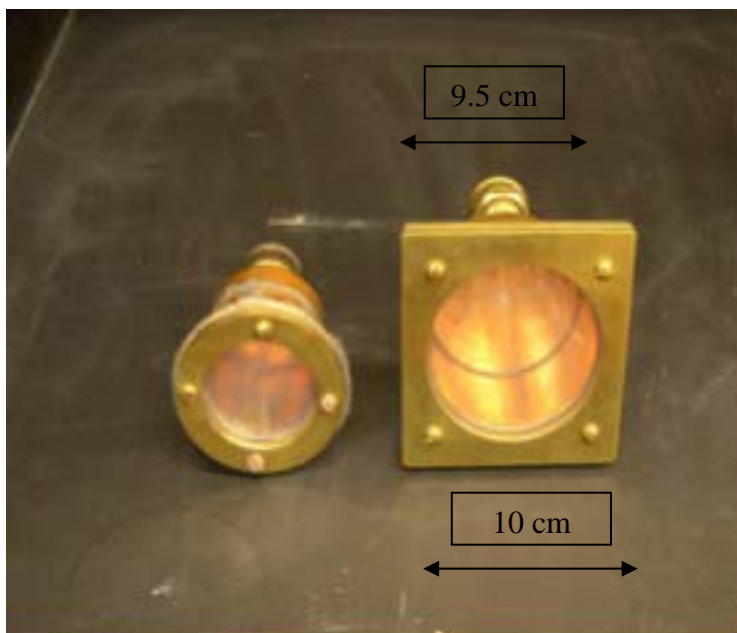


Figure 13-1. Two current versions of PISCES

LDPE membranes typically are 100 μm (0.004 inches) thick. Thinner membranes have been evaluated, but they do not yield higher sampling rates, and they are not as sturdy as the 100 μm membranes.

The solvent used is hexane or isooctane. Neither solvent is lost through the membrane at an appreciable rate as long as the membrane is properly mounted and not damaged. Sampling rate does not differ between these solvents. Hexane extracts are more easily concentrated by evaporation, and more volatile compounds can be separated from hexane and analyzed by gas chromatography; however, hexane is more flammable than isooctane, presenting a greater hazard to field crews and individuals who might tamper with samplers in the field. Isooctane extracts are more difficult to concentrate by evaporation, requiring vacuum distillation if a boiling water bath is used as the heat source. Because of the lower fire hazard, isooctane is the recommended solvent unless volatile analytes such as xylenes are to be analyzed. Alcohols (methanol, ethanol, propanol) are currently being evaluated and show promise as solvents for PISCES.

Samplers are assembled in the laboratory and transported to the sampling site empty. Samplers are filled with solvent immediately before placing in the water to minimize evaporative loss of solvent through the membrane. Usually, samplers are suspended from an anchored float. Samplers have been deployed as deep as 20 m (66 ft) without problems, and can likely be used much deeper. In areas prone to vandalism or other tampering, floats can be anchored below the water surface to make them less visible. In shallow water, samplers can be directly attached to a cinder block and placed on the bottom.

Typical deployment periods are one day to one month. At the end of the deployment, solvent is decanted from the sampler at the sampling site and returned to the laboratory for analysis. If time-series extracts are being collected, the sampler can be refilled with solvent at the sampling site and placed back in the water.

13.1.2 Target Media

PISCES are designed as surface water samplers. They are not suitable for air sampling using hexane or isooctane as solvents because of vaporization of the solvents through the membrane. Quantitative application can typically be achieved in surface water where the water can be considered an infinite source of analyte.

13.1.3 Potential Analyte Capabilities

PISCES will, in principle, sample any nonionic compound that is soluble in the collecting solvent. Laboratory tests have shown successful sampling of alkyl benzenes, chlorinated benzenes, nonylphenols, PCBs and PAHs. Uptake of explosives such as 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX) has not been evaluated but PISCES should sample these nonionic compounds. PISCES only sample truly dissolved compounds. Compounds bound to particles, dissolved organic matter or micelles are not directly sampled.

13.1.4 Sample Volume

Uptake of compounds by PISCES is characterized by the sampling rate. The sampling rate is the volume of water that is cleared of analyte per unit time. Typical sampling rates are 1-4 L/day for

lakes. Rates increase with membrane area, temperature, and water agitation and decrease slightly at salinities up to seawater. Under very turbulent conditions, sampling rates approaching 20 L/day have been observed in the laboratory.

Typically, over 100 L of water is sampled for a one-month exposure. This yields a 100-fold decrease in detection limit relative to the traditional approach of grab-sampling and extraction of a one-liter water sample.

13.2 State of the Art

13.2.1 Lab Testing

PISCES have been tested in the laboratory to determine the effect of membrane properties, solvent properties, analyte properties, temperature, water agitation, salinity, and dissolved organic matter on sampling rate (Rider, 1997; Polito, 2003). These studies demonstrate that uptake is limited by transport of analytes through a boundary layer of water at the water-membrane interface when hydrophobic membranes (polyethylene, polypropylene) are used. Water agitation enhances transport of analytes through this boundary layer and thus increases the sampling rate.

13.2.2 Field Testing

PISCES designs have evolved due to field testing. An important modification was the addition of a vent to release trapped gases. Membranes on early versions without the vent were often found to be severely distended by internal pressure, frequently damaging the membranes by forming pinhole leaks or tears. The internal pressure was due to uptake of dissolved gases (O₂ and N₂) in waters that were slightly oversaturated with O₂ due to photosynthesis. Addition of the vent to release these trapped gases eliminated this problem.

Biofouling is seldom observed on PISCES membranes, even at sites where floats, suspension lines, and anchors become fouled during the exposure period. Presumably, this is because the solvent-saturated membrane is not a hospitable surface for microorganisms.

PISCES have been deployed in surface water investigations from Alaska to New York harbor. State, federal, academic, and private sector scientists as well as volunteers from citizens groups have deployed over 500 samplers.

PISCES have been calibrated in-situ in Onondaga Lake, a 12 km² lake in Syracuse, NY. Sampling rates were consistent with laboratory studies. (Avallone, 2004).

13.2.3 Examples of Acceptance and Use

The most common application of PISCES has been to locate sources of contaminants. The first application identified the major source of PCBs to the Black River, which drains the western Adirondack Mountains in New York (Litten *et al.*, 1993). They have been used by the New York Department of Environmental Conservation to document and track down contaminants in tributaries to the Great Lakes, the Hudson River, and New York Harbor. Target analytes have

included PCBs, PAHs, dichlorodiphenyltrichloroethane (DDT) and mirex. In the laboratory, they have been used to track down sources of contaminants in an urban lake (Hubbard, 1996), and to compare gasoline concentrations in lakes over time (Avallone, 2004). PISCES have also been used by the USGS to track down contaminants in rivers (Colman, 2001; Breault *et al.*, 2004). Other users include the NJDEP and the EPA.

13.2.4 Current State of Research

Laboratory studies are focusing on using alcohols, especially ethanol, as the solvent for PISCES. This solvent is attractive because of much lower fire and toxicity hazard and because volume reduction might be accomplished by extraction rather than evaporation. Samplers are also being evaluated for uptake of more hydrophilic compounds, such as atrazine and organophosphate insecticides. Preliminary lab studies are promising, and preliminary field trials will be carried out in summer, 2005.

13.2.5 Availability

The Research Foundation of SUNY is currently negotiating to license the technology for manufacturing and commercialization. PISCES are subject of U.S. Patent 5,110,473.

13.3 Features and Limitations

13.3.1 Cost

The PISCES is not available commercially; however, fabrication cost is estimated to be \$70-\$100 per unit.

13.3.2 Deployment Considerations including Advantages and/or Limitations

Careful selection of the study site is important for a successful deployment. The vented cap must be at the highest point of the sampler to avoid trapping gases. It is critical that the samplers be deployed where they will remain submerged, but not buried in the sediment, during the exposure period. It is desirable to have the PISCES in areas with water movement to enhance sampling rates, but when possible, avoid deployments in the heaviest flow to prevent damage. Locations prone to vandalism should be avoided, or camouflage should be used to reduce visibility of sampler.

13.3.3 Nature of Sample

PISCES samples represent an accumulated mass and uptake is essentially irreversible. Following processing of the PISCES in the laboratory, the sample is an enriched extract in a solvent such as hexane or isooctane. Depending on the desired use of the sample, additional processing (i.e., cleanup and/or fractionation) may be necessary.

13.3.4 Decontamination Requirements

Membranes and o-rings are soxhlet-extracted before use, and sampler bodies are cleaned by water washing and solvent rinsing (i.e., methanol or acetone). After assembly, samplers are wrapped in aluminum foil to prevent recontamination. No decontamination is required if a sampler is to be redeployed at the same location. If moved to a new location, o-rings should be recleaned and a new, cleaned membrane affixed.

13.3.5 Sample Handling and Shipping

Samplers must not be transported with solvent in them. Solvent is decanted into a suitable container and can be shipped as a flammable material.

13.4 Unanswered Questions

A major impediment to quantitative application of PISCES, especially in streams, is the dependence of sampling rate on water agitation. It would be useful to be able to correct for this effect. However, the effect is not a great problem for source identification studies, because changes in contaminant patterns can often be used to recognize a source. Samplers can be calibrated in-situ in lakes and applied quantitatively.

For all compounds studied so far, the sampling rate is independent of the identity of the compound. Models for diffusion of organic compounds in water predict that a difference in uptake should be detectable among the compounds studied. The lack of an observed effect implies that the models do not accurately describe conditions at the water-membrane interface, or that diffusion coefficients for these compounds in water are not accurately known. While this is a theoretical concern, it is not a practical problem for use of PISCES.

PISCES could be placed in wells. Uptake probably would be limited by transport of analyte into the well rather than by transport of the analyte into the sampler, and this might prove useful for evaluating the flux of low-solubility compounds through a well. Because of the potential for loss of solvent from the sampler, regulatory agencies should be consulted before placing a PISCES in a well.

13.5 Selected References

- Avallone, A. D. (2004) *Temporal and Spatial Dynamics of Gasoline Pollution in New York State Lakes and Rivers and Their Relationship to Motorboat Activity* M.S. Thesis - SUNY College of Environmental Science and Forestry.
- Breault, R. F.; Cooke, M. G.; Merrill, M. (2004) *Sediment Quality and Polychlorinated Biphenyls in the Lower Neponset River, Massachusetts, and Implications for Urban River Restoration* US Geological Survey Scientific Investigations Report 2004-5109.
- Colman, J. A. (2001) *Source Identification and Fish Exposure for Polychlorinated Biphenyls Using Congener Analysis from Passive Water Samplers in the Millers River Basin, Massachusetts* US Geological Survey Water-Resources Investigations Report 00-4250.

Hubbard, S.M. (1996) *Sources of Organic Contaminants to Onondaga Lake*, M.S. Thesis - SUNY College of Environmental Science and Forestry.

Litten, S.; Mead, B.; Hassett, J. (1993) *Application of Passive Samplers (PISCES) to Locating a Source of PCBs on the Black River, New York* Environ. Toxicol. Chem. 12, 639-647.

Polito, J. M. (2003) *Evaluation and Application of Diffusion-Based Passive Samplers for Polycyclic Aromatic Hydrocarbons (PAHs) in Water* Ph.D. Thesis - SUNY College of Environmental Science and Forestry.

Rider, J.C. (1997) *Evaluation of Passive Samplers for Organic Contaminants in Water*, M.S. Thesis - SUNY College of Environmental Science and Forestry.

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14. PASSIVE SAMPLER TECHNOLOGY MATRIX

Table 14-1. Media and common analytes addressed by technology

Document Section	Technology	Media	Common Analytes									
			VOCs	SVOCs	Metals	Anions	Field Parameters	Explosives	Perchlorate	Hex Cr	Oxygenates (MtBE)	
2	HydraSleeve™	Fluid, GW, SW, tanks	All	All	All	All	All	All	All	All	All	All
3	SNAP Sampler™	GW SW	All	All	All	All	All	All	All	All	All	All
4	Dialysis Membrane	GW	All		Most	All	Some	Most				All
5	Nylon-Screen	GW	Most	Most	Most	Most	Most	Most	Most	Most	Most	Most
6	Passive Vapor Diffusion (PVD)	GW, pore water, and soil vapor	Most									
7	Peeper Samplers (membrane dependent)	GW and pore water	Most		Some	Most	Some			Most		
8	Polyethylene Diffusion Bag (PDB)	GW	Most									
9	Rigid Porous Polyethylene	GW	Most	Some	Most	Most				Most	Most	
10	Semi-permeable Membrane Device (SPMD)	GW/SW, soil, sediment, air	Some	Most; hydrophobics				Many		None		
11	GORE™	Water, air,	All	Most					Most			All

Document Section	Technology	Media	Common Analytes									
			VOCs	SVOCs	Metals	Anions	Field Parameters	Explosives	Perchlorate	Hex Cr	Oxygenates (MTBE)	
	Sampler	soil gas, sediment										
12	Polar Organic Chemical Integrative Sampler (POCIS)	GW/SW, sediment	Some	Most; hydrophilics				Many	Many			
13	Passive In-Situ Concentration Extraction Sampler (PISCES)	SW	Some	Most								

Table 14-2. Technology advantages and limitations

Document Section	Technology	Advantages	Limitations	Deployment Considerations	Sample Volume
2	HydraSleeve™	Sample all analytes Inexpensive, disposable No purging Effective in low yield wells Collect samples from discrete intervals in wells and surface water.		Easy to use, one person operation	Typical sampler holds 1 – 2 Liters. Other sizes available
3	SNAP Sampler™	No purging Sample sealed in-situ No sample transfer required All analytes recovered	Small sample volume	Some assembly and disassembly is required Some training required Some decontamination required unless dedicated	40ml and 125ml bottles are available.
4	Dialysis Membrane	Inorganic and organic analytes No purging Excludes turbidity Equilibration time of 1-7 days Disposable	Two trips to the site are needed (deploy/retrieve) Sampler prep required Sampler must be kept wet Limited life (biodegrades)	Some technical training needed to prep samplers. Samplers are easy to deploy and retrieve	1.25-inch diameter membrane by 1 ft long = 155 mLs. 2.5-inch diameter membrane by 1 ft long = 969 mLs.
5	Nylon Screen	Sample most analytes No Purging Disposable	Ratio of membrane area to the volume/height of sampler bottle Wells greater than 4 inches in diameter are optimal	Orientation of membrane is critical.	Vols up to 1 liter possible with stack of 200 ml samplers
6	Passive Vapor	Identifies VOC contaminated	Provides qualitative data, does	Easy to use in water depths	20 or 40 ml gas

Document Section	Technology	Advantages	Limitations	Deployment Considerations	Sample Volume
	Diffusion (PVD)	groundwater discharge areas No purging Rapid screening analysis can be done in the field	not provide actual water concentrations Only for certain VOCs	less than 4 feet.	
7	Peeper Sampler	Measures pore water concentration No purging In-situ monitoring of trace elements	Small sample volume Analytes are specific to the membrane material	Easy and quick installation, Equilibration time minimal	Typically 1-20 mL
8	Polyethylene Diffusion Bag (PDB)	No purging Technical guidance available Saturated sediments, surface and groundwater Permanganate, turbidity and alkalinity are excluded No well diameter limitation	Only selected VOC compounds	Easy to use	Typical sampler holds 220 - 350 mL, Other sizes available
9	Rigid Porous Polyethylene	No purging Organic and inorganic analytes	Small sample volumes. Semivolatiles (hydrophylic) are unconfirmed Additional testing is needed	Easy to use. Sampler pores must be purged of air prior to deployment	~ 175 mL
10	Semipermeable Membrane Device (SPMD)	No purging required Exposure period can be several months, which enables determination of time-integrated ambient chemical concentrations. Mimics bioconcentration of organic contaminants in fatty tissues of organism. Unaffected by many	Exposed SPMDs require processing and cleanup prior to analysis. Biofouling (water) may occur with extended exposures, but corrections for reduction in sampling rates can be made.	Exposure to sunlight should be minimized to prevent photolysis of certain analytes. A typical 1-mL (92 cm long, 5 mL volume) triolein SPMD can be shipped in a 1 pint air-tight can. Potential for vandalism should be assessed at field	A typical 1-mL triolein SPMD (5-mL volume) will extract from as much as 5 to 160 liters (water) or cubic meters (air) after a 30-day exposure.

Document Section	Technology	Advantages	Limitations	Deployment Considerations	Sample Volume
		environmental conditions or stressors that affect biomonitors organisms. Provides semi-quantitative data		sites, especially for long-term exposures.	
11	GORE™ Sampler	VOC, SVOC's, PAH, CWM/ABP's, Explosive breakdown products, Hg No purging Water, soil gas, air, and sediments. Residence time 15 minutes to 4 hours Allows extrapolation for low detection limits (ppb-ppt)	Must correlate total mass with measured concentrations in the groundwater. Not a direct concentration	All material to deploy is supplied. Ten minutes to deploy with non skilled labor.	NA
12	Polar Organic Chemical Integrative Sampler (POCIS)	Easy to deploy and recover Mimics respiratory exposure of aquatic organisms to organic chemicals Unaffected by environmental conditions or stressors that affect biomonitors organisms Sorbent can be changed to target certain chemicals or chemical classes The membrane used is highly resistant to biofouling Qualitative concentration data	Field samples require special processing prior to laboratory analysis.	Exposure to sunlight should be minimized Potential for vandalism should be assessed at field sites, especially for long term exposures A set of four POCIS disks (typical sample size) can be shipped in a 3.85 L container.	A typical set of four POCIS disks (4.7 cm diameter) will extract from 1.5-10 L of water after a 30-day exposure.

Document Section	Technology	Advantages	Limitations	Deployment Considerations	Sample Volume
13	Passive in-situ Concentration Extraction Sampler (PISCES)	Measures dissolved concentrations of organic compounds in surface water Capable of low detection limits Preserves relative concentrations of analytes Time-integrated sample Minimal biofouling Sample from field is in a solvent compatible with trace organic analytical protocols	Semi-quantitative in streams and rivers because of uncertainty in sampling rates Analytical method must be able to separate analytes from solvent (hexane or isooctane)	Must remain submerged in water, but not in sediment.	PISCES contain 200 ml of hexane or isooctane. Samplers deployed in lakes typically will extract analytes from 1-4 liters of water per day.

Table 14-3. Technology availability and cost

Document Section	Technology	Nature of Sample	Decon Required?	Sample Shipping Requirements	Commercial Availability	Commercial Costs	Contact Information/ Vendor
2	HydraSleeve™	Grab	No: disposable	Samples must be transferred to standard sample bottles and shipped per standard practices	Commercially available	Reusable- SS weight \$10-\$25 Expendable- Sample Sleeve \$20-\$25 depending on sampler size	GeoInsight, Inc. 1680 Hickory Loop Ste B Las Cruces, NM 88005 Phone: (800) 996-2225 www. HydraSleeve.com EON Products 3235 Industrial Way SW Snellville, GA 30039 Phone: (800) 474-2490 www.eonpro.com (800) 996-2225
3	SNAP Sampler™	Grab sample	Yes: unless dedicated No: disposable bottles	Samples collected in ready-to-ship bottles. Use standard shipping practices	Commercially available	Reusable Equipment \$400 to \$700 per well. Lease available; Expendable bottles \$16	ProHydro, Inc. 1011 Fairport Road Fairport, NY 14450 (585) 385-0023 ph (585) 385-1774 fax Sandy.Britt@ProHydroInc.com www.SnapSampler.com Sanford Britt

Document Section	Technology	Nature of Sample	Decon Required?	Sample Shipping Requirements	Commercial Availability	Commercial Costs	Contact Information/ Vendor
4	Dialysis Membrane	Equilibrium concentration by diffusion	No: disposable	Samples must be transferred to standard sample bottles and shipped per standard practices	Ready-made samplers are not commercially available. Components are commercially available	Costs uncertain	No commercial vendor currently sells fully constructed sampler. Dialysis membrane vendor: Membrane Filtration Products, Inc. 314 N. River Street Sequin, TX 78155 (800) 647-5758
5	Nylon Screen Sampler	Equilibrium concentration by diffusion	No: disposable	Samples must be transferred to standard sample bottles and shipped per standard practices	Limited Availability	Approximately \$40 - \$50 each	Columbia Analytical Services Inc. 1 Mustard Street, Suite 250 Rochester, NY 14609-6925 Phone: (585) 288-5380 www.caslab.com
6	Passive Vapor Diffusion (PVD)	Equilibrium concentration by diffusion, Vapor sample	No: disposable	Ship to laboratory unchilled for analysis within 5 days, if GC analysis not done in field.	Commercially available	PVD samplers can be purchased for less than \$10.00.	Eon Products, Inc. P.O. Box 390246 Snellville, GA 30039 Phone: (800) 474-2490 diffusion@eonpro.com

Document Section	Technology	Nature of Sample	Decon Required?	Sample Shipping Requirements	Commercial Availability	Commercial Costs	Contact Information/ Vendor
7	Peeper Sampler	Equilibrium concentration by diffusion	No: Unless Dedicated Skeleton No: disposable membrane	Samples must be transferred to small sample bottles and shipped per standard practices	Traditional Peeper is commercially availability Polysulfone Membrane Sampler (PsMS) is not commercially available	Peeper Plate consisting of membrane and skeleton is approx. \$312 pre sampler Cost Uncertain for PsMS	Rickly Hydrological Co 1700 Joyce Avenue Columbus, OH 43219 1-800-561-9677 www.rickly.com John H. Pardue, Ph.D., P.E. Louisiana State University Baton Rouge, LA 70803 225-578-8661
8	Polyethylene Diffusion Bag (PDB)	Equilibrium concentration by diffusion	No: disposable	Samples must be transferred to standard sample bottles and shipped per standard practices	Commercially available	<u>Expendable</u> = \$25 <u>Reusable weight</u> = \$10 - \$25	Columbia Analytical Services Inc. 1 Mustard Street, Suite 250 Rochester, NY 14609-6925 Phone: (585) 288-5380 www.caslab.com EON Products 3235 Industrial Way SW Snellville, GA 30039 Phone: (800) 474-2490 www.eonpro.com
9	Rigid Porous Polyethylene	Equilibrium concentration by diffusion	No: disposable	Samples must be transferred to standard sample bottles and shipped per standard practices	Limited availability	Approximately \$40 - \$50 each.	Columbia Analytical Services Inc. 1 Mustard Street, Suite 250 Rochester, NY 14609-6925 Phone: (585) 288-5380 www.caslab.com

Document Section	Technology	Nature of Sample	Decon Required?	Sample Shipping Requirements	Commercial Availability	Commercial Costs	Contact Information/ Vendor
10	Semipermeable Membrane Device (SPMD)	Accumulated mass by diffusion and sorption	Yes: reusable container No: disposable membrane	Ship frozen in gas-tight metal container. See Huckins et al. Guide for the use of SPMDs; 2002. Published by American Petroleum Institute, Publication No. 4690. Ph: (202) 682-8000	Commercially available	A 92 cm commercially available SPMD is about \$100, includes analyte recovery from the device. Contact Environmental Sampling Technologies (EST). Ph: (816) 232-8860 spmd_estglobal.net	USGS Columbia Environmental Research Center 4200 New Haven Road Columbia, MO 65201 (573) 876-1879 (573) 441-2970 www.cerc.usgs.gov jhuckins@usgs.gov dalvarez@usgs.gov Jim Huckins David Alvarez
11	GORE™ Sampler	Accumulated mass by diffusion and sorption	No: disposable	Ship to lab unchilled	Commercially available	Expendable Equipment \$185-285 each including analysis	WL Gore & Associates Inc. Survey Products 100 Chesapeake Blvd Elkton MD 21922 410-392-7600 environmental@wlgore.com
12	Polar Organic Chemical Integrative Sampler (POCIS)	Accumulated mass by diffusion and sorption	Yes: sampler body No: dedicated membrane disposable	Ship cold in gas-tight metal container. See Alvarez et al. Development of the POCIS; 2004. Published in Environ. Toxicol. Chem., Vol. 23, pp. 1640-1648.	Commercially available	Reusable disk is holder is about \$60. Membrane-sorbent disk for chemical sequestration is disposable.	Environmental Sampling Technologies, Inc. 502 S 5th St. Joseph, MO 64501 www.est-lab.com 816-232-8860 USGS Columbia Environmental Research Center 4200 New Haven Road Columbia, MO 65201

Document Section	Technology	Nature of Sample	Decon Required?	Sample Shipping Requirements	Commercial Availability	Commercial Costs	Contact Information/ Vendor
							(573) 441-2970 www.cerc.usgs.gov dalvarez@usgs.gov jhuckins@usgs.gov David Alvarez Jim Huckins, USGS
13	Passive in-situ Concentration Extraction Sampler (PISCES)	Accumulated mass by diffusion and sorption	Yes: sampler body No: dedicated Membrane disposable	Sample transfer to container is required. Ship as flammable liquid.	Not commercially available	Cost uncertain	Prof. John P. Hassett SUNY College of Environmental Science and Forestry 1 Forestry Drive Syracuse, NY 13210-2726 (315) 470-6827 jphasset@syr.edu

Explanation of Table Categories:

Document Section: Location in the Technology Overview Document, which contains a more complete description of the technology.

Technology: Abbreviated identifier of the technology.

Media: Lists all media that can be sampled by the technology. GW = groundwater, SW = surface water

Common Analytes: Generalized list of common analytes for which the technology is appropriate and has been lab or field tested. Categories are “all,” “most,” “some,” or “unknown”.

Field Parameters: pH, temperature, dissolved oxygen, specific conductance, oxidation – reduction potential (ORP), turbidity.

Advantages: Primary advantages of the technology, specifics listed in document section.

Limitations: Primary limitations of the technology, specifics listed in document section.

Deployment Considerations: Identifies major deployment issues, if any, with the technology and ease of use to deploy, specifics listed in document section.

Sample Volume: Range of sample volumes a typical sampler would collect.

Nature of Sample: Technology grouped as one of the following categories: grab sampler, equilibrium concentration by diffusion, or accumulated mass by diffusion and sorption.

Decon Required: yes (device is reusable if decontaminated or is dedicated to the well), or no (device is disposable)

Shipping Requirements: Lists special considerations for shipment of the sampling device or the collected sample.

Commercial Availability: Lists if the technology is commercially available at the time this document was written. Note – the status of the technology may change and the vender should always be contacted.

Cost: If commercially available then cost is listed to purchase a typical sampler. If the technology is not commercially available then cost is not listed. Costs published in this document can change and the specific vender should be contacted directly for a more accurate quote.

Contact Information / Vendor: Primary contact or vendor of the technology.

Appendix A

Acronyms

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ACRONYMS

ARAR	applicable or relevant and appropriate requirements
ASTM	American Society for Testing and Materials
BOD	biological oxygen demand
CEC	cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CGWMA	Committee on Ground Water Modeling Assessment
COC	Chain of Custody
COD	chemical oxygen demand
DOD	Department of Defense
DOE	U.S. Department of Energy
DSIC	Diffusion Sampler Information Center
ECOS	Environmental Council of States
EPA	U.S. Environmental Protection Agency
ERIS	Environmental Institute of the States
FML	flexible membrane liner
FR	Federal Register
GPS	global positioning system
GW	groundwater
ID	inside diameter
ITRC	Interstate Technology & Regulatory Council
LDPE	low density polyethylene
LTM	long term monitoring
MWCO	molecular weight cut-off
NAWC	Naval Air Warfare Center
OD	outside diameter
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	tetrachloroethene
PDB	polyethylene diffusion bag
PISCES	Passive In-Situ Concentration Extraction Sampler
POCIS	Polar Organic Chemical Integrative Sampler
PRC	Performance Reference Compound
PsMS	Polysulfone Membrane Samplers
PVD	passive vapor diffusion
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
RPPS	Rigid Porous Polyethylene Sampler
RPO	Remedial Process Optimization
SPMDs	Semi-permeable Membrane Devices
SSSA	Soil Science Society of America
SVOC	semi-volatile organic compounds

SW	surface water
TCE	trichloroethene
TIE	Toxicity Identification Evaluation
TSWG	Tribal and Stakeholder Working Group
UFGS	Unified Facility Guide Specifications
USGS	U.S. Geological Survey
VFA	volatile fatty acid
VOA	volatile organic acid
VOC	volatile organic compound

Appendix B

ITRC Team Contacts, Fact Sheet, and Product List

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