

# Welcome

## Passive Sampling Technology Update



The Passive Sampling Update Guidance Document combines the previous ITRC Passive Sampling documents (DSP-1, DSP-3, DSP-4, DSP-5) along with updates to the technologies into one comprehensive document that evaluates 24 passive sampling technologies. The document explores the use of these technologies and application of the data gathered to all phases of environmental remediation. This document is intended to be used by regulators and stakeholders currently sampling environmental media at sites undergoing evaluation, remediation, or monitoring for compliance with applicable laws and regulations.

Listed below are a few of the topics of importance in the document that will aid the reader in selection and use of the passive sampling technologies.

The Media section of the document discusses different media types (groundwater, surface water or soil) and how to use the passive sampling technologies appropriately.

The document has three Analyte Tables (Table 5-1 Passive Grab Sampling, Table 5-2 Passive Equilibration Sampling, and Table 5-5 Passive Accumulation Sampling) that detail the analyte capabilities of the passive sampling technologies within each passive sampling technology type (Grab, Accumulation, and Equilibration). These tables provide the user a quick and easy way to search which sampling technology is most appropriate for your project based on the chemical being sampled.

All of the 24 passive sampling technologies are detailed in Section 5.

A video for each of the passive sampling technologies is also provided. These videos would be useful for any professional looking to learn additional information to aid in the use and selection of one of the passive sampling technologies.

The case studies section provides studies for all of the passive sampling technologies to aid the regulatory acceptance and user acceptability of the technologies.

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# 1. Introduction

## 1.1 Background

In previous years, the ITRC Passive Diffusion Sampling Team (later the Passive Sampling team) produced four informational and guidance documents (2001, 2004, 2006, and 2007) that explored the function and use of 12 passive groundwater sampling devices. The team concluded in 2007. In the ensuing years, emerging concerns about high-profile contaminants, interest in reducing purge water volume, sampling cost, and sampling of other media in addition to groundwater has driven interest in passive sampling techniques.

This growing interest in the benefits of passive sampling, and the availability of newer devices, has increased the number of requests for regulatory review, approval, and acceptance on project sites. Few, if any, specific regulations addressing the use of passive samplers have been written into promulgated documents. The use and/or approval process varies widely by agency and even by individuals within an agency due, in part, to a general lack of reliable, vetted information on the use and efficacy of passive sampling technologies.

The intent of this team is to replace the current ITRC Passive Diffusion documents (2001, 2004, 2006, and 2007) with a single new guidance document that will include 12 additional technologies, for a total of 24 passive sampling technologies. Devices that sample groundwater, surface water, pore water, sediment, soil gas, indoor air, outdoor air, soil, and nonaqueous phase liquid (NAPL) are included and each technology's use, operation, viability for specific contaminants, development or commercial status, project applicability, advantages and limitations are described. Case studies for each technology are included to demonstrate the use and effectiveness in real-world conditions. This guidance will help appropriately transition sites to passive sampling, build confidence in passive sampling, and enable more sustainable management of monitoring sites.

The inclusion of the following passive sampling technologies in this document does not constitute endorsement or approval from your state. The sampling technologies are provided for informational purposes only and are not all-inclusive or exhaustive. Additional technologies and information may be available or in development but not discussed in this document.

## 1.2 What is Passive Sampling?

ITRC defines passive sampling as using a device that acquires a sample from a discrete location without inducing active media transport. The passive technologies considered in this document rely on exposure of the sampling device to media in ambient equilibrium during the deployment period and are classified into three types of technology based on the sampler mechanism and nature of the collected sample. The technology classifications to be discussed include grab, equilibrium, and accumulation samplers, which are summarized below and further discussed in more detail in **Section 5**.

- **Grab Samplers (Section 5.1):** Devices that recover a sample of the selected medium that represents the conditions at the sampling point, including any chemicals and suspended material present in the sample interval, at the moment of sample collection or a period surrounding sample collection (for example, as presented in this document, HydraSleeve and Snap Sampler).
- **Equilibrium Samplers (Section 5.2):** Devices that rely on diffusion and equilibrium of the chemicals/parameters into the collecting medium for the sampler to reach equilibrium between the sample and the sample medium (for example, as presented in this document, Passive Diffusion Bag Sampler (PDB) and Dual Membrane Passive Diffusion Bag Sampler). Samples are time-weighted toward conditions at the sampling point during the latter portion of the deployment period. The degree of weighting depends on chemical- and device-specific diffusion rates
- **Accumulation Samplers (Section 5.3):** Devices that generally rely on diffusion and sorption, absorption, or precipitation to accumulate chemicals/parameters in the sampler (for example, as presented in this document, AGI Universal Sampler and Polar Organic Chemical Interval Sampler). Accumulation devices concentrate the target chemical on a selective collecting medium such as an adsorbent or absorbent solid, a solvent, or chemical reagent ( ITRC 2023<sup>[55DMC29X]</sup> ITRC. 2023. "PFAS Technical and Regulatory Guidance Document and Fact Sheets." Interstate Technology & Regulatory Council, PFAS Team. <https://pfas-1.itrcweb.org/>.). Target molecules continue to accumulate on the collecting medium during the exposure period and do not come to concentration equilibration with the surrounding medium ( ITRC 2023<sup>[55DMC29X]</sup> ITRC. 2023. "PFAS Technical and Regulatory Guidance Document and Fact Sheets." Interstate Technology & Regulatory Council, PFAS Team. <https://pfas-1.itrcweb.org/>.). 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

chemical concentrations in the sampled medium over the exposure period. Accumulation samplers are also sometimes referred to as integrative or kinetic samplers.

In addition to the passive sampling technologies, this document discusses the following three nonpassive sampling technologies, which are further discussed in Section 6 . These nonpassive samplers do not collect true passive samples because they induce active media transport.

- **Syringe Samplers (Section 6.1):** Devices designed to capture a groundwater sample by grabbing a sample of the water and everything in the water at the sample interval and isolating the sample to preserve the conditions at the selected depth. The sample is collected without contact with air by precluding sample aeration and pressure changes at the selected depth of sampling.
- **Deep Discrete Interval Samplers (Section 6.2):** Devices designed to obtain representative discrete groundwater samples from a specific sampling zone where the sampler is activated, with limited drawdown and negligible agitation of the water column.
- **Horizontal Surface Water Interval Samplers (Section 6.3):** Devices designed to collect surface water samples at a prescribed depth.

### 1.3 Passive Sampling vs. Active Sampling

In contrast to the passive sampling methodologies described in this document, active sampling methods rely on the movement of a medium by the sampling equipment to draw the medium and chemicals into the sampling device, causing deviations from the natural flow or ambient conditions. Active sampling methods are sometime thought of as traditional methods because they have been in use prior to the use of passive sampling methods. Traditional active sampling methods generally require a power source, such as gasoline generator or battery, for the operation, and a submersible or peristaltic pump for water sample acquisition. Active methods, by nature of changing the conditions in the sampling environment, affect sampling results; using a pump, vacuum, or physical removal method introduces variables (that is, pumping rate and duration, criteria for stabilization prior to sample collection, and variability in sampling equipment components between events) into the sample collection sequence that may not be reproducible between sampling events and will influence the results obtained. Passive sampling eliminates many of the active sampling variables by limiting the extent of the sampling method's interaction with media and, thus, the potential to influence sample results. The use of both types of samplers throughout the remedial phases of a project may yield insightful results to understand in greater detail the fate and transport of compounds through the medium under different conditions at a site. Passive sampling may then be used to provide consistent sampling methodology during long-term monitoring programs from an established sampling interval.

Passive sampling programs can result in several benefits, including elimination of a power source, reduction in investigation-derived waste (IDW), less equipment, and fewer personnel needed on site. These may also lead to the additional benefits of increased site accessibility and help achieve green and sustainable metrics. Despite these benefits, passive sampling may not be appropriate for all circumstances. For example, active methods are most efficient for groundwater monitoring programs requiring large sample volumes (such as for extensive radionuclide analysis or a particularly large analyte list) beyond the capacity of currently available passive sampling devices. Technology and device-specific benefits and limitations are described in detail in **Section 5**.





































Similar to active sampling methods, passive sampling is a reproducible methodology that can reassure samplers and regulators alike that the data obtained are a result of the environmental conditions present. In addition, appropriate quality assurance/quality control (QA/QC) procedures should be followed for all sampling methods.

## 2. Passive Sampling Used by Media

This ITRC Passive Sampling document details different passive sampling techniques across multiple media. Different types of media require specific considerations and have their own unique complications. The previous ITRC Passive Sampling documents identified passive sampling techniques that were mostly applicable to groundwater. The types of media discussed in this document are groundwater, surface water, pore water, sediment, soil gas, indoor/outdoor air, soil, and NAPL.

Table 2-1 includes a comprehensive list of passive sampling devices presented in this document, the type of sampling technology, and the applicable media. Although the technologies included below can produce quantitative results, qualitative data may also be acquired.

Table 2-1. Passive samplers by media type

Sampling Device	Technology Type	Groundwater	Surface Water	Pore-Water	Sediment	Soil Gas	Indoor Air*	Outdoor Air*	Soil	NAPL
Thin Walled Soil Sampler	Grab									
Snap Sampler	Grab									
HydraSleeve	Grab									
Rigid Porous Polyethylene Sampler (RPPS)	Equilibration									
Regenerated Cellulose Dialysis Membrane Sampler (RCDM)	Equilibration									
Polymeric Sampling Devices	Equilibration									
Peeper Sampler	Equilibration									
Passive Diffusion Bag (PDB)	Equilibration									
Nylon Screen Passive Diffusion Sampler (NSPDS)	Equilibration									
Dual Membrane Passive Diffusion Bag Sampler (DMPDB)	Equilibration									
Ceramic Diffusion Sampler / Ceramic Dosimeter	Equilibration									
Waterloo Membrane Sampler	Accumulation									

Sampling Device	Technology Type	Groundwater	Surface Water	Pore-Water	Sediment	Soil Gas	Indoor Air*	Outdoor Air*	Soil	NAPL
Sentinel	Accumulation	●	●	●						
Semipermeable Membrane Devices (SPMDs)	Accumulation	●	●	●		●	●	●		
Radiello Sampler	Accumulation						●	●		
Polar Organic Chemical Integrated Sampler (POCIS)	Accumulation	●	●	●						
Mineral Samplers (Min-Traps)	Accumulation	●								
Fossil Fuel Traps	Accumulation					●				●
Diffusion Gradient in Thin Films (DGT) Sampler	Accumulation	●	●	●						
Dart Sampler	Accumulation				●				●	●
Bio-Trap Sampler	Accumulation	●	◐							
Beacon Sampler	Accumulation					●	●	●		
AGI Universal Sampler (formerly the Gore Sorber)	Accumulation	●	●	●		●	●	●		
Passive In Situ Concentration Extraction Sampler (PISCES)	Accumulation		●							

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## 2.1 Terminology

For the purposes of this document each medium is described as follows:

- **Groundwater** is water that can be found in the subsurface in the pore spaces within soil, sand, and rock and is accessed by monitoring wells. Although groundwater does exhibit a flow direction, its velocities are typically much slower than surface water.
- **Surface water** is permanent or recurring water open to the atmosphere under either high-flow (for example, rivers or streams) or low-flow (for example, ponds, oceans, wetlands, or lakes) conditions. Surface water features are fed from a collection of sources, such as groundwater exfiltration, upstream tributaries, precipitation, storm water runoff, wastewater, or snowmelt. Surface water features can persist all year long, or in shorter durations, such as seasonally or tidally. Surface water is primarily differentiated from temporary stormwater features

because it is not a direct result of a single or short-term precipitation event. Although most surface water flows toward oceans, it may also undergo infiltration into groundwater aquifers where the ground surface is higher than the prevailing water table.

- **Pore water** in this document refers to *sediment* pore water rather than *soil* pore water. In the context of this document, pore water is described as water located within the pore spaces between sediment particles that may represent the mobile water interacting between groundwater and surface water within permanent surface water features or intermittently flooded features (such as seasonal streams, intertidal zones, or stormwater swales/basins).
- **Soil** is a solid medium consisting primarily of inorganic particles (but may contain organic matter, water, and air). Soil development involves time and a stable ground surface (bedrock or unconsolidated material), differentiating it from sediment.
- **Sediment** is a medium consisting of primarily solid minerals and/or organic particles that are deposited by water or wind transportation. Sediments may be deposited at the bottom of permanent surface water features (such as rivers or streams) or located along the surface of intermittently flooded features (such as seasonal streams, intertidal zones, or stormwater swales/basins). Sediments may be moved and deposited in new locations over short-term events, differentiating it from soil that remains in one location.
- **Soil gas (soil vapor)** is gaseous elements and chemicals in the spaces between soil particles within the vadose zone. The soil gas may contain chemicals in a gaseous phase that are targeted for environmental investigation.
- **Indoor air** is the air present within buildings and structures that may be closed or sealed from exterior air.
- **Outdoor air** in this document refers to the air present outside of buildings and structures or from within structures that cannot be sealed from external sources.
- **NAPL** is the acronym for “nonaqueous phase liquid” and refers to typically organic liquids that are immiscible or not soluble in water. There are two types of NAPL: light nonaqueous phase liquids (LNAPL), which are less dense than water, and dense nonaqueous phase liquids (DNAPL), which are denser than water.

## 2.2 Media Conditions Affecting Sampling Approach

Each medium is described by a specific set of physical conditions that affect the fate and transport of chemicals within the medium. These physical conditions must be considered when trying to extract a sample that represents the temporal-spatial extent and concentrations of the chemicals of interest. Some of these considerations affect decisions about the method of acquiring a sample. The considerations below serve as examples to encourage thoughtfulness about factors that can affect sample integrity on specific sites.

### 2.2.1 Groundwater Considerations

#### **Technical Considerations**

Groundwater flows directionally, at a slow rate, through a variable granular medium or through cracks and fissures within a solid medium, at some depth below the ground surface, frequently in defined geological strata. Because there is no direct access, a conduit-like structure (that is, a groundwater well) is typically required to provide access to groundwater.

This combination of hydraulic, geologic, and well construction conditions influences the transport of chemicals present in the soil and groundwater and whether a water sample taken from a specific monitoring well represents the water quality in the target aquifer (groundwater) or not. The location of the well casing and screen in relation to the groundwater level, target aquifer, and aquifer flow conditions are factors for consideration. Additionally, water in the blank casing is isolated from aquifer flow, interacts with air in the casing, may further interact with well construction materials over time, and may be subject to leakage from surface runoff ( Puls and Barcelona 1996<sup>[LBCSV95N]</sup> Puls, Robert W., and Michael J. Barcelona. 1996. “Ground Water Issue: LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES.” EPA/540/S-95/504. USEPA. <https://www.epa.gov/sites/default/files/2015-06/documents/lwflw2a.pdf>.) Therefore, to optimize the conditions needed to collect a sample representing the aquifer, the sampling device should be placed within the saturated portion of the screen of a cased well or in the water-bearing interval of an open-borehole well in fractured bedrock aquifers.

Allowing a sampling device to remain in the well until the well has returned to natural flow conditions is called the minimum residence time. This accounts for things such as displacement and mixing, and is dependent on the rate of groundwater flow through the well.

#### Vertical Interval Sampling Considerations

Hydrogeologic conditions may cause variations in flow rates and/or geochemistry at different vertical intervals when groundwater sampling. When hydrogeologic conditions vary vertically within an aquifer, it is possible that concentrations of targeted chemicals may also vary with depth.

When active sampling methods are used, the concentration of chemicals in the sample collected represents a flow-weighted average across the length of the saturated open interval ( ). Although this is also generally true of passive samples due to a typical condition of natural mixing within the saturated screen interval, passive samples also can be said to represent the groundwater at the depth of placement in the well (mixed or otherwise). In the case of horizontal flow through the screen at that (passive sample) interval, then the sample may represent the groundwater at that same depth in the adjacent aquifer.

When sampling long-screen wells, known conditions may suggest the use of a vertical flow meter and other geophysical logging tools to evaluate vertical flow and mixing in the open interval and whether passive samples may represent specific depths of the adjacent aquifer. In this case, the well may be suitable for vertical profiling to determine optimum sampler placement and to monitor discrete intervals. To determine the geochemical variation over the open or screened interval of a well with longer screens, it is suggested the initial use of multiple passive samplers over the length of the saturated screen to vertically and chemically profile the well. These chemical results, combined with the borehole flow meter and geophysical logging results, can give a better idea of the depth to deploy passive samplers during sampling events. Passive and active samples from wells with shorter screen intervals (for example, 10 feet or less) are generally expected to provide similar results without the need for vertical profiling.

#### Site-specific Considerations

Site conditions vary widely and are important to consider prior to, and during, groundwater sampling events because the conditions may affect the ability to acquire a representative sample, maintain personnel safety, and minimize the generation of waste for disposal. Although there are many additional considerations when setting up any groundwater sampling program, the following are several examples of site-specific conditions that may help determine whether or how to use passive sampling methods.

**Site Access:** If there are seasonal conditions (for example snow, ice, swampy, or tidal conditions) or environmental or biological concerns (for example, tick season, bird nesting season, etc.) that render the wells difficult to access, or limit the equipment that can be delivered to the wells during certain times of the year, passive sampling may be desirable because there can be less equipment involved and the equipment tends to be less bulky or heavy than pumping equipment, making it easier to reach the site. High-traffic sites can cause logistics problems, delays, and safety issues for personnel, so limiting the time and equipment needed at the site by using passive sampling devices is often desirable.

**Water Level Changes:** If water levels fall or rise, the installed depth of passive samplers may need to be adjusted so that the zone sampled by the passive device remains within the saturated screen as conditions change. The length of saturated screen should be reviewed to be sure the method can still obtain adequate sample volume. Consideration should also be given to how the vertical change affects the source and flow of water through the well because these may affect sample results. Active sampling methods may produce samples that result in greater blend from a longer screen interval or a more concentrated blend of water from a shorter interval. At sites with nearby pumping wells or major surface water affecting groundwater, localized changes in groundwater flow direction can result. Because passive samplers sample the water flowing through the well, they can provide insights into chemical movement affected by the surrounding conditions. Active sampling methods, such as pumping, add another variable to where the sample originates because they induce flow toward the well.

**Well Construction:** It is important to first determine whether the type of sampling equipment will fit within the constraints of the well casing diameter, the depth from which the sample must be recovered, and the required sample volume. There are not many options for pumps that will fit wells smaller than 2 inches in diameter, but there are several passive samplers that can be used in wells as small as 1-inch diameter. As well sampling depths increase, it becomes increasingly difficult for pumps to lift water to the surface and may add to the type and cost of sampling equipment required; most passive sampling methods simply require a longer suspension tether and reel to hold the tether. Because passive samplers are limited to the volume of water in the well and should be used only to sample within the screen interval, the length of saturated screen or water-producing fractured-bedrock interval in open-hole wells should be determined before selecting the sampling method to be sure there is adequate sample volume for the laboratory method. To facilitate the use of passive samplers, sampler selection should include coordination with laboratories to determine the minimum sample volume required to meet data quality objectives (DQOs). In the case where new wells are being designed, screen placement should intersect the zones of suspected contaminant contribution.

**Investigation-Derived Waste (IDW) Disposal:** Local regulations and site capabilities dictate how purge water from active sampling methods is disposed (ITRC 2023<sup>[55DMC29X]</sup> ITRC. 2023. "PFAS Technical and Regulatory Guidance Document and Fact Sheets." Interstate Technology & Regulatory Council, PFAS Team. <https://pfas-1.itrcweb.org/>). Passive sampling methods produce little to no purge water (IDW) for disposal.

## 2.2.2 Surface Water Considerations

Careful judgment must be used to balance safety precautions with sampling objectives when developing and implementing surface water sampling strategies. Surface water samples are typically collected by either (1) inserting or placing the sample bottle/jar directly into the water body or (2) decanting water from a clean (that is, contaminant-free) container such as a ladle, scoop, bottle, or bowl. The physical actions needed to collect the sample may seem simple. However, accessing ideal/preferred sampling locations and depth intervals needed to satisfy data objectives can often be dangerous or impractical because of difficult and/or remote site conditions. This is because streams, rivers, and lakes are often secluded and surrounded by uneven surfaces, steep/slippery slopes, steep drop-off points, eroded banks, jagged rock piles, deep soft/muddy areas, sinkhole-like conditions, and other dangerous or unnavigable terrain. Water current can be a safety hazard for medium to large rivers and streams. Other hazards may include watercraft traffic, fencing, sharp surfaces or jagged edges from debris or structures, insects, snakes or other wildlife, or property line/trespassing issues. For example, it can be difficult to collect a surface water sample from the middle of a large wastewater settling pond/impoundment that is hundreds of feet long and wide, has steep slippery walls covered with an expensive liner fabric that must be safeguarded to maintain liner integrity, and the surface of the wastewater is more than 30 feet below ground surface/walkways around the pond. In this example, there is no easy or safe way to deploy a boat to collect a sample further out than points along the sides of the impoundment. Even collecting a sample from the water's edge would be a challenge because of the slippery 30-foot drop with no proper footing that would allow samplers to reach the surface of the pond without harnesses and/or attaching the sampling devices to long poles that would increase the difficulty of the sampling task.

Limitations of sampling approaches vary when sampling fast-moving water, slow-moving water, or stagnant water. The sampling strategy must be carefully orchestrated to collect samples that are representative of conditions that address the project objectives. Logistics need to be planned and executed so that the sampling team can obtain quality samples from various depth intervals and/or representative of upstream/background water quality conditions. When the surface waters being sampled are shallow enough to allow samplers to wade into the water, especially when there is significant flow velocity, sampling should be performed carefully and methodically to reduce disturbance of bottom sediments. If multiple samples are to be collected in a river or stream, it is important to collect downstream locations first and move progressively upstream to collect additional samples so that downstream locations are not affected by suspended/disturbed upstream sediment material. If a river or stream is too deep to wade and/or conditions are deemed unsafe, samples can be collected from an elevated platform (bridge, retaining wall, etc.) or boat using supplemental sampling equipment such as a plastic bucket attached to a rope.

The logistics required to collect surface water samples for a particular project and whether the samples collected are used for screening purposes or to obtain quantitative data for site characterization will generally determine the most appropriate sampling devices needed to satisfy the DQOs. A strong and dynamic project work plan should identify strategic sampling locations that account for the site-specific conditions and provide enough flexibility to allow field personnel to make changes that account for unanticipated adverse conditions, including variations in flow patterns, areas of pooling/stagnant water, point-source discharges from adjacent/upstream locations, and other unforeseen conditions that may influence or impact concentrations within background and downstream locations. It is possible to select a sampling approach that will help simplify the sample collection process and determine how intermediate steps such as adding sample preservatives should be accomplished, thereby saving time and reducing hazards. There are many sampling devices available, including glass and plastic bottles/containers, various ladles/scoops, long-handled and/or measuring cup-type devices, peristaltic pumps with tubing of various materials, and other specialty devices such as Van Dorn samplers. There are numerous equilibrium and accumulation type passive sampling technologies that may be used to accomplish various surface water sampling objectives, each with advantages and limitations that need to be examined.

## 2.2.3 Porewater Considerations

Pore water sample collection may be completed to understand the interaction between surface water and groundwater, to understand the bioavailable fraction of contaminants, and to support ecological evaluations. Groundwater is generally low in dissolved oxygen and enriched in inorganic solutes compared to surface water, so collection of physical and chemical

parameters is recommended to compare each aqueous media. On-site collection of sediment pore water is completed by wading into surface water bodies, deployment by a diver, or from a platform or boat. Water currents and traversing soft sediment surfaces are often primary concerns when wading into shallow water bodies, and consideration should be taken when accessing sampling locations. Additional health and safety considerations related to working in and around water bodies include those described in the **Section 2.2.2** above, such as accessing water bodies, boat deployment considerations, biological hazards, and complying with local regulations. In deeper waters, divers may be required for sample collection, but this adds concerns for logistics as well as health and safety that are not discussed here. When wading into surface water bodies or collecting sediment samples, it is important to limit disruption of bottom sediments, which may bias results. Enter the sampling area from a downstream location and proceed upstream during sample deployment and/or collection.

In the case of having to revisit a location, whether it be to collect confirmatory samples or retrieve samplers, additional concerns may need to be addressed. Samplers may be affected by boat traffic or human disturbance in the time between access events. If there is a need to revisit a sampling location, careful consideration should be given to appropriate ways to mark the sampling location and protect it from external hazards. It is recommended that an accurate GPS unit be used to record location area in conjunction with flagging or marking of a sample location. Appropriate signage may be used to warn potential visitors to the sampling location and provide contact information.

A primary consideration during pore water sample collection is surface water intrusion into the sample. This is more of a concern for point samplers, as passive samplers have time to integrate ambient conditions, but it should be considered in all situations. Surface water may infiltrate the sample if a preferential pathway is provided by the sampling device. Mitigation strategies may be implemented, such as use of a sampling flange, especially if the target sampling interval is near the sediment surface. However, investigators should confirm that sampler and flange construction material will not cross-contaminate the sample. Aside from sampler or flange insertion, care should be taken to avoid disturbing the sampling area.

Quality assurance/quality control samples and background samples are another component of an investigation. Identifying locations for background and duplicate samples is a critical part of determining the performance and validity of samplers during investigation or remedial monitoring.

Pore water sampling data can be a tool used during an ecological evaluation to understand the bioavailable fraction of contaminants. Typically, this bioavailable fraction provides a stronger relationship (compared to bulk sediment) for predicting contaminant concentrations in benthic receptors. This subsequently can influence cleanup decisions and long-term monitoring at sediment sites. Freely dissolved concentrations ( $C_{free}$ ) of hydrophobic organic compounds (HOCs) in pore water represent the actual bioavailable fraction of those compounds and provide useful information for risk assessment rather than bulk sediment/soil concentrations ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.; Burgess 2012<sup>[DQ5ELCGU]</sup> Burgess, Robert. 2012. "Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites." OSWER Directive 9200.1-110 FS. USEPA. <https://semspub.epa.gov/work/HQ/175405.pdf>.)

). Polymeric sampling devices such as low-density polyethylene (LDPE) and solid phase microextraction (SPME) fibers coated with polydimethylsiloxane (PDMS), and polyoxymethylene (POM) have been used to determine  $C_{free}$  of HOCs in pore water.

### **Ex Situ vs. In Situ Pore Water Sampling**

Most of the passive samplers discussed in this document are deployed in environmental media in the field, which is called in situ deployment. For pore water sampling, in situ deployment is preferred when it is critical to understand the influence of the field conditions, such as groundwater intrusion, currents, bioturbation, depth-varying chemical concentration profiles, and sediment-water column gradients and fluxes ( Ghosh et al. 2014<sup>[T8GHY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." Integrated Environmental Assessment and Management 10 (2): 210-23. <https://doi.org/10.1002/ieam.1507>.) However, achieving equilibrium between polymeric sampling devices and pore water by the in situ approach is often difficult or practically impossible within a reasonable timeframe for strongly HOCs such as dioxin/furans because the uptake kinetics of strongly HOCs to polymeric sampling devices are particularly slow.

Placement of passive samplers is often difficult in deep waters or in water where divers are not easily deployed. In such

cases, conventional sediment grab or coring can be used to collect sediment samples, and passive samplers are placed in the collected sediments under controlled laboratory settings, which is called ex situ deployment. Polymeric sampling devices, diffusive gradient in thin films (DGT), or other passive samplers can also be deployed under controlled laboratory settings to determine dissolved-phase pore water concentrations of target chemicals ( Burgess et al. 2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://semsub.epa.gov/work/HQ/100000146.pdf>.) For example, in the ex situ deployment approach of polymeric sampling devices, field-collected sediments or soils are brought to a laboratory and polymeric sampling devices are deployed under static or well-mixed conditions to attain equilibrium partially or fully between the polymeric sampling devices and pore water.

Ex situ sampling with well-mixed sediment slurry samples can achieve equilibrium more quickly than in situ sampling, and it has been accepted for partitioning investigations, treatability testing, and sediment toxicity assessment ( Ghosh et al.

2014<sup>[T8GHY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." *Integrated Environmental Assessment and Management* 10 (2): 210–23.

<https://doi.org/10.1002/ieam.1507>; Michalsen et al. 2018<sup>[IEVDPQE]</sup> Michalsen, Mandy, Danny Reible, Adesewa Aribidara, Upal Ghosh, Mandar Bokare, Philip Gschwend, John MacFarlane, and Mingta Lin. 2018. "Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater." *Standardized Method Memo ER-201735*. ESTCP. <https://apps.dtic.mil/sti/pdfs/AD1084245.pdf>.) Pore water concentrations of HOCs based on in situ and ex situ sampling

generally agreed within a factor of two to three ( Apell and Gschwend 2016<sup>[CA63XU9R]</sup> Apell, J.N., and P.M. Gschwend. 2016. "In Situ Passive Sampling of Sediments in the Lower Duwamish Waterway Superfund Site: Replicability, Comparison with Ex Situ

Measurements, and Use of Data." *Environmental Pollution* 218:95–101.; Reininghaus, Parkerton, and Witt 2020<sup>[VYVK4C3]</sup> Reininghaus, M., T.F. Parkerton, and G. Witt. 2020. "Comparison of In Situ and Ex Situ Equilibrium Passive Sampling for Measuring Freely Dissolved Concentrations of Parent and Alkylated Polycyclic Aromatic Hydrocarbons in Sediments."

*Environmental Toxicology and Chemistry* 39:2169–79.). The ex situ deployment approach is simpler to perform but should be carefully planned and designed. Key steps involved in performing ex situ deployment of polymeric sampling devices are

described in detail elsewhere ( Ghosh et al. 2014<sup>[T8GHY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." *Integrated Environmental Assessment and Management*

10 (2): 210–23. <https://doi.org/10.1002/ieam.1507>; Burgess et al. 2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." *User's Manual EPA/600/R-16/357*.

Washington, DC: USEPA and SERDP-ESTCP. <https://semsub.epa.gov/work/HQ/100000146.pdf>; Michalsen et al. 2018<sup>[IEVDPQE]</sup> Michalsen, Mandy, Danny Reible, Adesewa Aribidara, Upal Ghosh, Mandar Bokare, Philip Gschwend, John MacFarlane, and Mingta Lin. 2018. "Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater." *Standardized Method Memo ER-201735*. ESTCP. <https://apps.dtic.mil/sti/pdfs/AD1084245.pdf>; Jonker et al.

2020<sup>[U4PNQM7R]</sup> Jonker, Michiel T. O., Robert M. Burgess, Upal Ghosh, Philip M. Gschwend, Sarah E. Hale, Rainer Lohmann, Michael J. Lydy, Danny Reible, and Foppe Smedes. 2020. "Ex Situ Determination of Freely Dissolved Concentrations of Hydrophobic Organic Chemicals in Sediments and Soils: Basis for Interpreting Toxicity and Assessing Bioavailability, Risks and Remediation Necessity" *15:1800–1828*. <https://www.nature.com/articles/s41596-020-0311-y>.)

Passive samplers described in this document for sediment pore water collection include a variety of equilibration and accumulation samplers.

## 2.2.4 Sediment Considerations

As described in the above sampling considerations sections for surface water and pore water sampling, similar health and safety concerns are applicable when collecting sediment samples to support environmental investigation or remediation activities. Accessing preferred sampling locations often poses logistic challenges, including but not limited to traversing across uneven or unnavigable surfaces, biological hazards, transportation of materials required for sampling, and complying with applicable regulations in and around water bodies. Prior to completion of sediment collection, a formalized health and safety plan and a field sampling plan should be prepared to address these considerations.

Sediment is often heterogeneous, so a variety of factors should be considered when determining appropriate sample depths and locations, such as surface water flow rates, tidal influence, physical and chemical properties of the sediments, and co-location of other sampling media, such as surface water or pore water. Investigators should also consider project goals when collecting sediments: are targeted discharges or discrete sample depths the focus of investigation versus understanding the greater ecological system?

Tidal influences may provide areas of higher contamination due to the presence of depositional or erosional environments, areas of sediment resuspension, and/or changes in chemical solubility resulting from varying salinity in surface water. Coarser media may not be representative of contaminant levels due to the physical properties of the sediments. It is important to confirm with the regulatory agency if there are sediment sample collection requirements such as grain size or total organic carbon analysis.

When collecting surface water and sediment concurrently, surface water samples should be collected first to avoid cross contamination from disturbed sediments during sampling activities. In addition, samples should be collected from the most downstream location first and continue sampling upstream. Care should be taken to minimize sediment disturbance during discrete sample collection to avoid cross contamination between depths, and appropriate techniques should be chosen to reduce loss of finer grained sampling media during collection. In addition, sampling personnel should be sure that any aqueous media entering the sample jar or bottle is representative of sediment conditions and has not been “washed” during sample extraction by overlying water.

If sediment samples are composited from multiple depths or homogenized as part of collection activities, considerations should include changes in chemical properties during mixing, thorough homogenization of the sample, and appropriate decontamination procedures.

The only passive sediment sampler that is described in this guidance document is the Dart sampler (**Section 5.3.10**).

## 2.2.5 Soil Gas Considerations

It is common to complete soil gas investigations for a wide range of uses, including vapor intrusion assessments, groundwater investigations, and subsurface source area delineations. Whether using passive sampling devices or collecting subsurface vapor in canisters, drilling is required to install a soil vapor point (temporary or extended use) and/or monitoring well. As such, health and safety concerns should be addressed ahead of time to ensure workers’ safety and that subsurface utilities are not encountered during the drilling and probe/well installation.

The overall costs and length of soil gas investigations are also important considerations. Active soil gas methods can require well construction at a greater depth below ground surface (bgs) than with a passive soil gas sampler to ensure enough packing material can be installed. Ambient air is not sampled through short circuiting and the screen interval is not within the groundwater-saturated zone ( Abreu and Schuver 2012<sup>[43UDNI2M]</sup> Abreu, Lilian, and Henry Schuver. 2012. “Conceptual Model Scenarios for the Vapor Intrusion Pathway.” EPA 530-R-10-003. USEPA, Office of Solid Waste and Emergency Response. <https://www.epa.gov/sites/default/files/2015-09/documents/vi-cms-v11final-2-24-2012.pdf>.). The active methods for sampling soil gas rely on pumps or vacuum pressure from evacuated canisters, tubing, and fittings, which are susceptible to leakage. Both the construction methods and required sampling equipment can have high costs and take several mobilizations to complete characterization. Shallow passive soil gas sampling has the potential to complete the lateral delineation of a contaminant plume at a reduced cost and in less time. However, you must also consider vertical delineation of a contaminant plume, for which active soil vapor sampling methods may be more appropriate.

The chemicals sampled as part of a site investigation need to be considered when selecting a sampling method for soil gas. Passive samplers often have a much narrower chemical list compared to canister samples. Analytical results obtained from passive samplers require known sampling rates to back-calculate soil vapor concentrations. Careful consideration is needed to determine whether the passive sampler has known uptake rates for given chemicals at a site. Additionally, environmental factors such as temperature, humidity, wind speed, and barometric pressure can positively or negatively influence the accuracy of the resulting data. Thus, it may be necessary to measure these factors in the field.

It is always important to consider the DQOs for a site when deciding whether to use passive or active sampling for soil gas. Many states are not accepting passive soil gas data for risk assessments but will for screening purposes. It is best to check your state’s guidance and contact the regulatory program when considering passive soil gas sampling for a specific remedial phase.

Compared to canisters, passive samplers are smaller and much easier to store, transport to the field, and ship to a lab for analysis. Additionally, passive samplers are often easier to deploy because they do not require power sources while sampling or field technician oversight during collection.

### 2.2.6 Indoor Air Considerations

There are some considerations specific to indoor air sampling, including variability of contaminant concentrations, flow and ventilation within a structure, background sources, and the added complication of human tampering. The same passive samplers can be used for soil gas and indoor air investigations. Sampler-specific considerations (for example, chemical selection, cost savings, etc.) identified in **Section 2.2.5** also apply to indoor air.

When assessing indoor air, many factors may influence contaminant concentrations within a structure and create significant temporal variability. Temporal variability may exist due to the structure's use by occupants, outside weather conditions, and/or heating ventilation, and air conditioning (HVAC) systems. Passive sampler deployment periods can range from days to weeks, which may help to overcome this variability compared to active/grab sampling methods. However, average concentrations representative of days to weeks may not adequately reflect short-term concentration spikes that could have toxicological significance for chemicals that represent short-term or acute exposure concerns.

Similar to soil gas considerations discussed in **Section 2.2.5**, contaminant uptake into passive samplers in an indoor environment is also influenced by temperature, humidity, and air flow. These factors are often influenced by how the building is used by occupants throughout a given day and even an entire season. Changes in the operational use of an HVAC system, frequency of doors and windows being opened, and changes in weather conditions can all influence seasonal variation. Differences can also be observed during varying shifts (that is, day versus night shifts) if processes change or even cease between shifts. It is important to understand how these influencing factors may affect the sampling accuracy for the passive sampler throughout the deployment period.

Indoor sources of chemicals being targeted may also provide an additional challenge when performing an indoor air survey. Field personnel should always consider the current building uses and perform building surveys that inventory all chemicals that are currently in use at the facility. Field personnel shall remove any products that may interfere with sampling results associated with the vapor intrusion assessment at least 24 hours before collecting a sample ( USEPA 2015<sup>[ZH2YKUR7]</sup> USEPA. 2015. "OSWER Technical Guide For Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air." USEPA, Office of Solid Waste and Emergency Response.

<https://www.epa.gov/sites/default/files/2015-09/documents/oswer-vapor-intrusion-technical-guide-final.pdf>; Guillot

2016<sup>[JUGE4LGB]</sup> Guillot, Richard. 2016. "Ambient Air Sampling." USEPA, Science and Ecosystem Support Division.

[https://www.epa.gov/system/files/documents/2022-06/Ambient%20Air%20Sampling%28SESDPROC-303-R5%29\\_0.pdf](https://www.epa.gov/system/files/documents/2022-06/Ambient%20Air%20Sampling%28SESDPROC-303-R5%29_0.pdf)). This can help identify indoor sources prior to sampling.

Passive sampling devices are discrete and inconspicuous compared to canisters, which can reduce risk perception and tampering from building occupants. Small devices may go unnoticed by occupants and therefore not cause workplace distractions or elevated risk concerns. Passive samplers are cheaper than canisters, so missing equipment is less of a cost burden.

### 2.2.7 Outdoor Air Considerations

Compared to most others, outdoor air is one of the most accessible media to sample. There is no need to enter a structure (that is, residential, commercial, and/or industrial building), drill into the subsurface, or install a conduit-like structure, such as a soil vapor probe or a groundwater monitoring well. In many cases, whether using active or passive sampling methods, all that is required is a sample collection device (that is, a passivated canister and flow controller for active collection or a sorbent tube for passive collection). However, there are several considerations to keep in mind when both planning and collecting outdoor air samples.

The primary considerations for outdoor air sampling pertain to the environmental variables for where and when to collect. The three most common are wind direction, season, and weather. Consider the wind direction to ensure that outdoor air samples are collected from upwind, downwind, and in some cases, crosswind locations. The season should be considered to assess variability between the warmer and colder months. Weather conditions may dictate if the sampling device(s) needs to be protected from the elements (that is, precipitation and direct sunlight), while conditions such as barometric pressure may also affect some physical samplers and/or the resulting data.

When planning and implementing an outdoor air survey, the types of industries at or around the sampling area must also be considered, as they may bias the analytical data. For example, collecting an outdoor air sample in a highly industrial area where there is constant trucking traffic may yield analytical data with higher concentrations of benzene. This consideration should be evaluated in tandem with wind direction to ensure that samples are not being collected downwind of a facility that may release chemicals into the air that could affect the data.

Health and safety conditions are another set of considerations that should be evaluated when planning and/or implementing outdoor air sampling. If possible, you should have a clear understanding of the potential hazardous chemicals that may be in the immediate atmosphere at and around the sampling locations and ensure that workers have the appropriate personal protective equipment (PPE). Many outdoor air samples are collected on the roofs of buildings, possibly necessitating additional PPE. Additionally, whether using an active or passive sampler, field personnel must consider public perception and ease any safety concerns. These sampling devices are not common in the everyday lives of most people and may lead to fear and/or curiosity.

Another set of considerations you must evaluate when planning and/or implementing an outdoor air survey is the equipment to be used. As mentioned above, in some cases, only an active or passive sampling device is required to collect outdoor air samples. However, many projects require field personnel to collect field screening levels using various monitoring devices (that is, a photoionization detector or multi-gas meter). When monitoring outdoor air for dust, field meters are typically the primary sampling method. Workers must ensure that they have the proper monitoring device(s) for the task at hand and that the devices are properly calibrated and charged. Additionally, security equipment may be needed to prevent tampering. These may include a chain and lock, a protective container, and caution tape. In the case of inclement weather, field personnel must consider what equipment will be needed to protect the sampling devices from sun, precipitation, or even winds that bring a higher than normal particulate level.

Outdoor air samples are often collected in tandem with indoor air samples to collect data that may prove integral in evaluating vapor intrusion versus outdoor air infiltration/background. It is important to consider the placement of outdoor air samplers in relation to the target building. Again, the wind direction becomes important for these projects, as it is common protocol to collect outdoor air samples upwind, downwind, and crosswind from the targeted building.

As discussed above, passive sampling devices are discrete and inconspicuous compared to canisters, which can reduce risk perception and tampering from the public. Passive samplers are cheaper than canisters, so missing equipment is less of a cost burden.

### **2.2.8 Soil Considerations**

Commonly, there are three types of soil samples: samples collected on the surface (0-6 inches below grade), shallow (up to 2 feet below grade), and at depth (> 2 feet below grade). Surface soil samples are generally quick to prepare for sample collection, not as destructive to the site, and less costly. Collecting the at-depth soil sample can be very expensive given the equipment required, and time consuming to prepare for. When planning a soil sampling event, consideration must be given to soil lithology, weather, site constraints, and equipment needed.

Soil can be grouped into three main categories: coarse-grained (sands and gravels), fine-grained (silts and clays), and highly organic soils (peat) (Kelechava 2018<sup>[D397EAY7]</sup> Kelechava, Brad. 2018. "ASTM D2487 Unified Soil Classification System." The ANSI Blog (blog). March 15, 2018. <https://blog.ansi.org/2018/03/unified-soil-classification-astm-d2487-17/>.; ASTM 2020<sup>[BWLJENR8]</sup> ASTM. 2020. "D2487 Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System)." ASTM. <https://www.astm.org/standards/d2487>.). Each group of soil has its own limitations and advantages when collecting surface and at depth soil samples. For example, collecting a deep sample from a fine-grained soil can be difficult because the soil might easily slide away/heave from the soil auger or soil collection sleeve/liner, making collection at the desired depth time-consuming and sometimes unlikely.

To collect soil at depth, certain equipment is needed and site constraints might make this difficult to maneuver. For example, certain locations may be inaccessible to a drill rig.

### **2.2.9 NAPL Considerations**

Although passive samplers can be used for NAPL collection, they do not provide a general advantage over nonpassive or active methods, such as bailers. One exception would be collection of NAPL-impacted soil for NAPL characterization testing that requires the preservation of the physical or geochemical properties of the media.

For NAPL in soil, it is important to retrieve an undisturbed section of the soil column to complete characterization of NAPL mobility or transmissivity within the unconsolidated material. Although standard soil collection methods can produce NAPL samples, it is important to collect soil that has not been disturbed by mechanical forces to retain the precise properties observed in situ.

There are also passive means of detecting NAPL in boreholes. The Ribbon NAPL sampler can be deployed to boreholes to assist in detecting NAPL. The FLUTe Profiler can also be used in open boreholes to detect NAPL. However, these technologies are not quantitative and are generally restricted for use in direct sensing during site characterization activities. See ITRC's document on advanced site characterization tools (ASCTs) for more information on these types of direct sensing tools.

When NAPL or sheen is present in association with groundwater or surface water, caution should be taken in the use of passive samplers, as is the case with nonpassive samplers, due to potential interference/contamination of the sampler or media being tested. Nonpassive methods used in the collection of a NAPL sample from a monitoring well or surface water are discussed in **Section 6**.

## 2.3 Contaminant Sampling Considerations

As with any sampling method, it is important to keep in mind the compatibility between the chemical and the sampling equipment. It is not uncommon for investigators to have to adapt sampling techniques and materials based on the contaminant of concern. For example, polytetrafluoroethylene (PTFE)-containing materials should not be used when sampling for per- and polyfluoroalkyl substances (PFAS). In situations where certain chemicals may adsorb to the sampler, it is possible that the sample may be biased low. In cases where certain chemicals adsorbing to the sampler could cause cross contamination, incorporating single-use materials may be a mitigation strategy to reduce that risk.

### 3. Regulatory Acceptance

Over the past 20+ years, passive sampling technologies have become more commonplace in the United States and other countries as research has advanced and technologies have been used in practical settings. As passive sampling has been adopted more frequently, and with the increasing number of contaminants of emerging concern, there has been an increase in the number and type of passive sampling devices that are commercially available and in use for collecting samples from different media.

In the United States, at the federal level, passive sampling data have been accepted in decision-making in the U.S. Environmental Protection Agency's (USEPA) Superfund Program at many contaminated sediment sites. Specifically, passive sampling has been used in several phases of the remediation process at more than 20 sediment sites around the United States. As such, sampling implementation at Superfund sites may require advisement and discussion as to what phase of the remedial process and applications the regulatory agencies may deem appropriate. In contrast, passive sampling of groundwater contaminants at Superfund sites is less developed and its use would require site-specific review and acceptance. Similarly, regulatory acceptance of passive sampling methods varies substantially by state, regulatory group within each state, sampled media, and other factors.

Unfamiliarity with the technologies, their use, or the state of the science can lead to a hesitance to accept the use of passive sampling technologies in practical applications. Even in states where passive sampling is commonplace within one department or for one application, it may be discouraged or not allowed in others. Lack of information sharing within or between organizations has resulted in a wide disparity in regulatory approaches and requirements for the use of passive sampling technologies. In some cases, limiting regulatory language, often written in previous years, around legacy methods may even discourage or altogether disallow the use of data collected using passive sampling in decision-making processes.

Using passive sampling methods can benefit both the regulated community and regulators. For instance, passive sampling technology can often be more representative of site conditions across multiple media compared with active sampling methods, allows for more efficient high-resolution characterization (interval sampling and rapid data collection), and uses methods that have undergone rigorous review through the scientific community. When deployed for long-term monitoring programs, the ease of use for passive sampling can allow for less variability in results due to small variations in sampling methodology and gives greater confidence that changes in data over time reflect actual changes in conditions rather than sampling variability. For some media, sampling events can be completed more quickly using passive sampling methods, providing a consistent snapshot of site conditions. Additionally, because the use of passive sampling in investigation and long-term monitoring can be more cost-effective and labor-efficient than active methods, the regulated community has greater resources available at hand to focus on completing remediation efforts. Incorporating high-resolution sampling, which can be completed using passive sampling programs for some media, allows for defensible and cost-effective remedy development overall.

To better understand the need for passive sampling guidance, ITRC surveyed state regulators with respect to current regulatory language surrounding passive technology use, asking if there was any regulatory language prohibiting the use of passive sampling. The team received responses from 48 states and Puerto Rico, and conducted research for the remaining states as summarized in Figure 3-1. Some states do not have any regulatory language prohibiting passive sampling but differ in acceptance across agency departments. Always check with the state's regulatory program to see if passive sampling is applicable for your site or project.

Figure 3-1

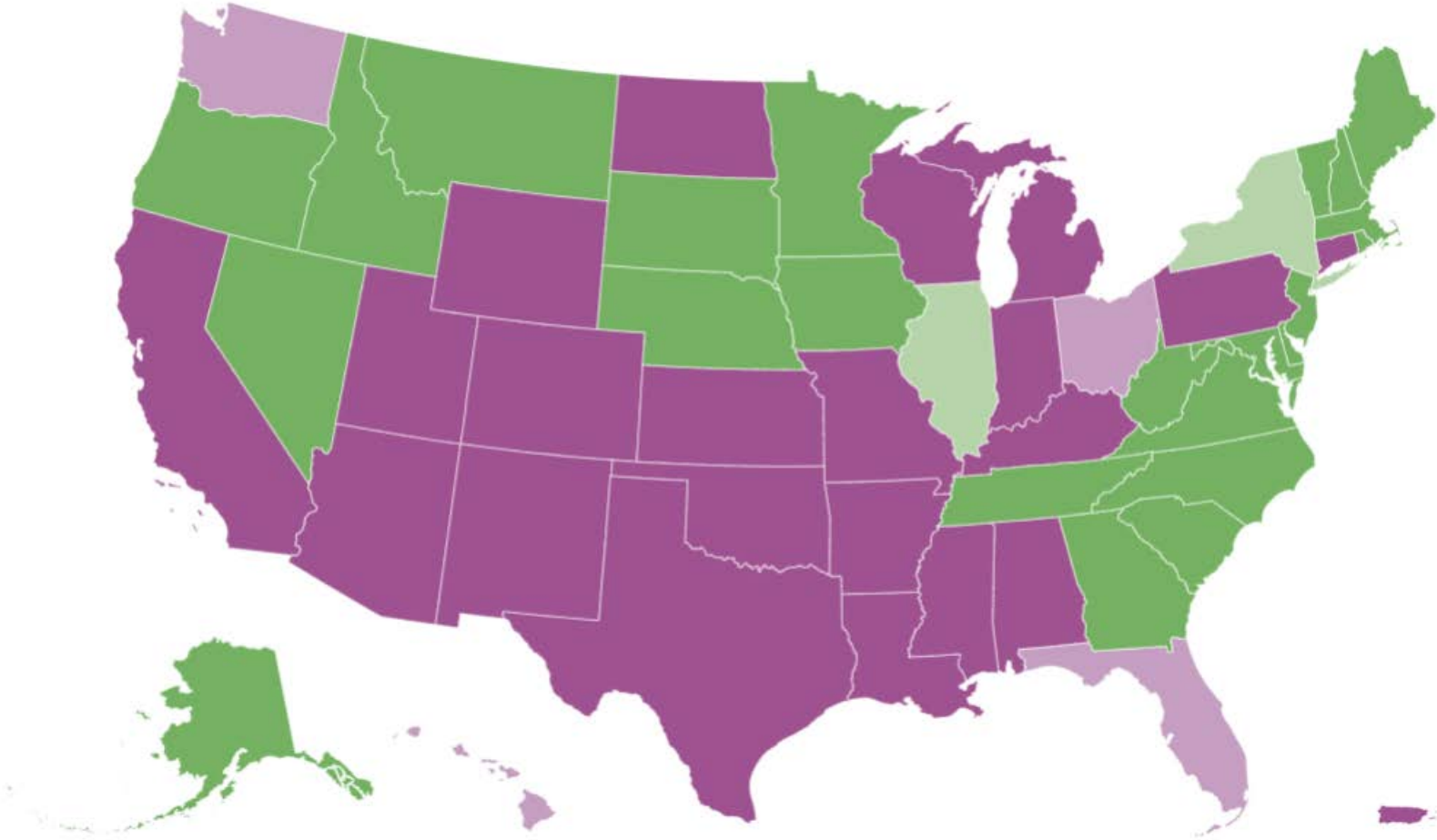


Figure 3-1 Key:

General State Acceptance of Passive Sampling (*no formal policy prohibiting the use of passive sampling at large within the state; check with your Project Manager if passive sampling is applicable*).

Passive Sampling Team conducted research as no state POCs were able to confirm

Site-Specific State Acceptance of Passive Sampling (*check with your project manager if passive sampling is applicable*)

Passive Sampling Team conducted research as no state POCs were able to confirm

### 3.1 Site-specific Regulatory Program Concerns

The use of passive sampling technologies can cause concern among regulators, deterring its use in that state. Some of these concerns are discussed in this section in hopes that passive sampling will become more widely used and accepted. Compliance monitoring in many states relies upon meeting specific regulatory levels. Generally, site-specific contamination is measured through grab or single point of time sampling. Many regulatory programs have little to no guidance or user experience with passive sampling technology. Regulatory use of passive samplers can include, but is not limited to, their use during investigative stages, compliance monitoring, and meeting closure requirements. In determining if passive sampling is appropriate, a key consideration is whether chemicals effectively move within the medium under natural (passive) conditions so that a sample taken at one location represents the spatial-temporal concentrations of target chemicals in the surrounding medium. These concerns tend to center around contaminant transport:

In determining if passive sampling is appropriate, a key consideration is whether chemicals effectively move within the medium under natural (passive) conditions so that a sample taken at one location represents the spatial-temporal concentrations of target chemicals in the surrounding medium. These concerns tend to center around contaminant transport:

- Does natural groundwater flow through a well carry chemicals through the well at the same concentrations found in the larger aquifer?
- Does the mechanism of the sampler—for example, diffusion through a membrane or grabbing from a column—acquire a representative sample of the specific chemicals?
- Will external factors, such as biofouling, scaling, or sediment load, affect sample validity?
- How to compare results from passive sampling to historical data, or what to expect from results on new sites—for example, how does a flow-weighted average (pumped) sample compare to an instantaneous (grab) sample, or a time-weighted average (equilibrated diffusion) sample compare to a time-integrated (accumulation) passive sample?

This document provides guidance based on data from research and case studies to address these concerns; to suggest when, where, and how to use passive samplers; and to support the appropriate use of passive sampling methods. It is always best to check with your state prior to using a passive sampling method.

### 3.2 Technology Acceptance

Regulators may be reluctant to accept passive methods due to a perception that the technology is new or untested. Individuals or organizations may apply an unfavorable experience with one passive technology to their views of all passive technologies, perceive a deficiency or uncertainty around sampling results, or have concerns about the consequences of changing methodologies. In reality, each passive sampling technology and specific device has its own history of use and applicability, and many have been in use for more than 20 years.

Although the data collected using passive sampling devices may differ slightly from data collected using traditional sampling methods, properly designed sampling programs with appropriately deployed devices will result in scientifically valid data demonstrating a level of precision and accuracy to meet performance standards for decision-making. This document provides case studies and general use guidelines to support acceptance of passive sampling with the latest information available.

### 3.3 Acceptance Varies by Media

The interconnection and coordination of environmental regulations across media (water, soil, sediment, and air, etc.) and regulatory groups differ significantly state to state. As such, the use of passive sampling technology may vary accordingly for different media and different applications in different places. Regulations governing multimedia investigations and remediation may differ from those governing routine monitoring. Further, the use of passive sampling for these different media can vary greatly, even across regulatory groups. Similarly, regulations for surface water sampling may differ considerably from those governing air or groundwater, each with its own barriers or flexibilities toward passive technology use. This document is intended to support the entire regulatory community, regardless of media or specific application, to help provide the technical basis for decision-making surrounding the use of passive sampling technology.

### 3.4 Remedial Phase Acceptance

Passive sampling techniques that are acceptable for collecting data throughout the entire remedial process, including site remedial characterization and monitoring, human health or ecological risk assessments, remedial action performance monitoring, long-term monitoring, and site closure activities, vary by state and regulatory agency. It is best to check your state's guidance and contact the regulatory program when considering passive sampling use for a specific remedial phase.

### 3.5 Performance Standard Acceptance/Approval

For states where the responsible party and the consultant are required to obtain written approval from the regulatory environmental agency prior to the implementation of remedial activities, the environmental consultants typically contact the assigned regulatory case manager for the site and/or the applicable regulatory agency program director to obtain approval to change data collection methods. Further details for regulatory approval are presented in Section 3.6.

For states with a regulatory program that is performance- and/or voluntary-based, where the regulatory state environmental agency delegates and/or relies on the environmental decision made by a licensed professional in that state, the licensed site professional must be able to demonstrate that the use of passive sampling technologies meets the state's performance standards during remedial activities. See Section 4 for comparison methods that can be helpful in analyzing and evaluating data from different methods when considering transition. In these states, the regulatory environmental agency typically performs periodic reviews and audits of report submittals certified by the licensed professional and responsible party performing the environmental work, and receives all documents associated with regulatory site closure requests.

The licensed professional and/or environmental consultant needs to properly design sampling programs (active and/or passive) with appropriately deployed devices. They should demonstrate that the data collection methods are scientifically valid and defensible, and that the level of precision and accuracy are commensurate with the intended use and meet performance standards for decision-making. The licensed professional and/or environmental consultant can rely on published and unpublished methods, sampling-device manufacturer studies, case studies, and/or site-specific data to demonstrate that passive sampling is representative of site conditions. Prior to the transition to a new method, the state should be consulted if preapproval is required.

### 3.6 Concurrent Regulatory Oversight

Due to the highly site-specific challenges across environmental sites, it is good practice to contact the state regulatory program when considering passive sampling or switching from active to passive sampling at individual projects. Each regulatory program may have policies, guidance, or standard operating procedures that explain the use (or nonuse) of passive sampling technologies within their respective programs. Including the regulatory team early in your project can address any regulatory conditions or approvals that may be required. Depending on the state where your project is, additional concurrence from the regulatory agency may be required prior to using passive sampling. Some states have little to no restrictions on the use of passive sampling. Other states have some limitations for the application of the data collected from passive sampling devices or restrict the use of devices to certain phases. (See Figure 3-1 for a map of states and their approach to the use of passive sampling.) The regulatory agency may typically require documentation to demonstrate that the data collected by the passive sampling devices are representative of the conditions of the actual media and are better than or comparable to other methods of sampling. The review team may require side-by-side comparisons of both active and passive sampling data, or a review of data collected and criteria for passive sampling data to meet the applicable state regulation performance standard. The data comparison methods (Section 4) provide guidance on how to present site data to support a change to passive sampling methods.

## 4. Data Comparison Methods

The key concerns when changing site sampling methods are (1) whether the results acquired using the new method will be substantially the same as those acquired by the previously used and accepted method and (2) whether the regulators will accept results acquired by the passive sampling method. Various media can be sampled via passive sampling. Groundwater sampling is subject to the most constraints when evaluating and comparing the data collected. However, many of the considerations and methods described in this section could be applied across all media.

### 4.1 Site Data Quality Objectives

Before undertaking an evaluation of the results between sampling methods, the site DQOs should be reviewed to determine how the sampling results are used in site decision-making, the key points of comparison between the existing and new method, and what the regulators want to see to allow a change in sampling method. In most cases it is a simple process to discuss the evaluation objectives with the regulators up front so that criteria can be developed prior to beginning an evaluation.

#### 4.1.1 Project-Specific Criteria

Methods used to compare the data should be based on project objectives. For example:

- If groundwater sample data are being used to determine whether, or to what extent, a site has specific chemicals, the comparison may be focused on whether both active and passive techniques indicate similar concentrations at low levels across a wide range of chemicals.
- If the data are part of a long-term monitoring program, the comparison may be specific to whether the different sampling methods lead to the same decision, based on exceedance of regulatory screening levels or criteria for a known set of chemicals.
- A comparison of monitoring data at an active remediation site may be more directed toward the general changes and trends in the concentration of a limited number of chemicals within a treatment area, rather than having agreement on achieving chemical action levels.

#### 4.1.2 Field Data Collection Requirements

Field data collected on site can be used to compare and support the method transition. Sampling results should be evaluated in the context of other field factors that can influence the sample results. A project-specific plan should consider site-specific field data, hydrogeologic differences, and additional information that will help inform whether data variability may be attributable to factors other than the change in method. Following QA/QC procedures may help account for some of these factors, including:

- Physical factors: groundwater elevation, well/probe construction details, tidal influences, seasonality, sampling depth, weather conditions
- Geochemical factors: medium temperature, pH, turbidity, oxidation-reduction potential (ORP), aerobic/anaerobic conditions, dissolved gases
- Other factors: vandalism, user experience, equipment malfunction, equipment fouling

## 4.2 Results Comparison Methods

Below are three techniques for comparing results that can be effective when considering changing sampling methods.

- Historical comparison: Sample using the proposed (passive) technique and compare the results to historical data. This is the least costly method of comparison and may be suitable when there are long-term, consistent, and stable data available.
- Bracketed comparison: Sample some of the locations by alternating between the proposed (passive) and current (active) sampling methods for three or more rounds of sampling. This strategy provides results from the passive method that are “bracketed” between two active sampling results occurring before and after the passive result. Although samples are not taken contemporaneously, changes in detected chemicals or concentration trends may be noted and evaluated. This method takes longer but is less costly than side-by-side evaluations.
- Side-by-side comparison: Perform the proposed (passive) and the current (active) sampling methods

sequentially during a single sampling event to ensure equivalent sample conditions. The passive sampler should be deployed in advance of the scheduled sampling event (to account for sufficient minimum residence time). On the sampling date, the passive sampler is recovered, and immediately after, the active method is implemented, and a sample is collected. Due to the collection and analysis of two samples, this comparison method will be more costly. Because of time and cost considerations, side-by-side evaluations are usually employed at a representative set of locations, rather than all the sampling locations.

When conducting side-by-side groundwater comparisons of active sampling to passive sampling methods, similar results would be expected in wells with 5- to 10-foot screens, unless there were exceptional hydrogeologic differences in the borehole. As screens get longer than 10 feet and the hydrogeologic or geochemical conditions vary, results may vary somewhat between active and passive methods. When contaminant concentrations are variable, the differences in results can usually be explained by further study of the local hydrogeologic and geochemical conditions.

## 4.3 Result Comparisons between Sampling Technologies

What methods will be employed to compare each data pair?

The U.S. Geological Survey (USGS) provides guidance for groundwater on how to evaluate the data from a side-by-side sampling event, suggesting the following general guidelines for acceptable relative percent differences (RPD) between sample concentrations ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>). RPD is a common statistical tool used to compare two data points in side-by-side sampling evaluations for technology usability for a site.

The USGS recommended the following RPDs based on chemical concentrations:

- RPD up to +/- 25% VOCs & trace metal concentrations > 10 ug/L
- RPD up to +/- 50% for VOC & trace metal concentrations < 10 ug/L
- RPD up to +/-15% major cations & anions concentrations mg/L range

Lower RPDs mean the two data points are similar. RPDs begin to fail as a practical comparison when concentrations are low. For example, comparing 2 µg/L to 5 µg/L yields a difference of 3 µg/L, which for many regulated chemicals would not be a significant difference that leads to different site decisions. In this example, the calculated RPD is an unacceptable 86%. Therefore, in these cases of low concentration results (for example, within several times the quantitation [or reporting] limit), other evaluation techniques may be appropriate, such as comparison of the two method results and absolute difference between them to the target chemical's project screening value.

The Techniques and Methods 1-D8 USGS publication also states "one of the more effective ways to compare concentration results" is to plot the data on a 1:1 correspondence on an X-Y plot with the passive results on one axis and the active results on the other axis ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>). "If the two sampling methods collect the same concentrations, the points will plot on or close to the 1:1 correspondence line" ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>). Outliers may represent well-specific anomalies such as turbidity.

To determine statistical confidence intervals around the data comparison, standard linear regression methods may be applied depending on normality of data sets. Other nonparametric-based methods—for example, Passing-Bablok regression ( Passing and Bablok 1983<sup>[YM82DEUZ]</sup> Passing, H., and null Bablok. 1983. "A New Biometrical Procedure for Testing the Equality of Measurements from Two Different Analytical Methods. Application of Linear Regression Procedures for Method Comparison Studies in Clinical Chemistry, Part I." *Journal of Clinical Chemistry and Clinical Biochemistry. Zeitschrift Fur Klinische Chemie Und Klinische Biochemie* 21 (11): 709–20. <https://doi.org/10.1515/cclm.1983.21.11.709>.; Passing and Bablok 1984<sup>[WTFATPGG]</sup> Passing, H., and W. Bablok. 1984. "Comparison of Several Regression Procedures for Method Comparison Studies and

Determination of Sample Sizes. Application of Linear Regression Procedures for Method Comparison Studies in Clinical Chemistry, Part II." *Journal of Clinical Chemistry and Clinical Biochemistry. Zeitschrift Fur Klinische Chemie Und Klinische Biochemie* 22 (6): 431-45. <https://doi.org/10.1515/cclm.1984.22.6.431>.) or Lin's concordance correlation coefficient ( Lin 1989<sup>[LGS7F6P]</sup> Lin, L. I. 1989. "A Concordance Correlation Coefficient to Evaluate Reproducibility." *Biometrics* 45 (1): 255-68.; McBride 2005<sup>[C7KBPCY]</sup> McBride, GB. 2005. "A Proposal for Strength-of-Agreement Criteria for Lin's Concordance Correlation Coefficient." *NIWA Client Rep.* <https://www.scienceopen.com/document?vid=46b1768a-002f-48fa-a238-673d8373ee6a>.)—may also be used to understand comparability and usability of results. The appropriateness of specific statistical methods and acceptance criteria for data usability are expected to vary by constituent, the sampling methods compared, and project DQOs.

## 4.4 Other Comparison Considerations

There are a few things that should be considered when comparing the results from sampling events.

- Do the data appear to follow the trend from the past several active sampling events?
- Are any site conditions or insights from prior sampling activities noted on field sampling sheets, such as "high turbidity" or "well pumped dry," that might point to localized well influences?
- Do the passive sampling results lead to the same site decisions as the historical data?
- If multiple passive samplers were used to profile a well, are the results from the samplers similar to each other? If not, do the active sampling results fall somewhere between the points? For long-screen wells or transmissive zones/lithological changes surrounding the saturated well screen, additional considerations or analysis may be needed.
- Were equivalent QA/QC methods employed for all methods being compared?
- If comparison of results is favorable, what other practical considerations for the different methods might be relevant to evaluate for the site (for example safety, cost/efficiency, equipment and staffing needs, sustainability, IDW management)?

## 5. Passive Sampling Technologies

The passive samplers in the previous ITRC documents were classified based on sampler mechanism and nature of the collected sample, as follows:

- Grab sampler: A device that recovers a sample of the selected medium that represents the conditions at the sampling point, including any chemicals present, at the moment of sample collection.
- Equilibrium sampler: A device that relies on diffusion of the analytes for the sampler to reach and maintain equilibrium with the sampled medium.
- Accumulation sampler: A device that relies on diffusion and adsorption to accumulate analytes in the sampler.

Over the last few decades, a variety of passive samplers have been developed and applied to measure chemical concentrations in different media. The classification of passive samplers slightly varies among different documents depending on the focus of the documents. For example, the focus of the previous ITRC documents was on passive sampling of groundwater in monitoring wells. As noted in the Introduction, the scope of this new guidance document is expanded to incorporate passive sampling of other media.

In this new guidance document, the three different classification names adopted in the previous ITRC documents are maintained for consistency and simplicity, but their definitions have been slightly modified to be accurate in terms of sampler mechanisms and consistent with other references. Please refer to Table 2-1 for details on the applicable media for each of the samplers listed in this section.

Equilibrium and accumulation samplers are often confused with each other. Therefore, before getting into the description of each passive sampling technology, the distinction between the two samplers is explained in detail below.

### **Equilibrium Samplers**

Equilibrium samplers, such as the Passive Diffusion Bag (PDBs), Dual Membrane PDBs (DMPDBs), Nylon Screen Passive Diffusion Sampler (NSPDS), Peeper Samplers, Regenerated Cellulose Dialysis Membrane Sampler (RCDM), Rigid Porous Polyethylene Sampler (RPPS), and Regenerated Cellulose Dual Membrane PDBs (RC-DMPDBs), rely on diffusion of chemicals from the surrounding water, through a semipermeable membrane(s), into a collecting medium inside the samplers. In these equilibrium samplers, the collecting medium is usually deionized (DI) water. When a concentration gradient exists between the water inside the membrane and the water outside the membrane, diffusion through the membrane eventually results in equilibrium on both sides. Because the collecting medium in the sampler is the same as the surrounding environment, the concentration of chemicals in the sampler will be equivalent to the concentration outside the sampler when equilibrium is reached. The type of semipermeable membrane determines which chemicals can be successfully sampled. The standard PDB, for example, uses a single LDPE membrane and can sample only for nonpolar VOCs.

The equilibrium samplers used to measure inorganic chemicals, metals, and polar organic compounds in water (for example, PDBs, DMPDBs, NSPDS, peeper samplers, RCDMs, RPPS, RC-DMPDBs) use semipermeable membranes with larger pores or different membrane characteristics that allow inorganic chemicals, metals, and polar organic compounds to pass through and diffuse into the water inside the samplers, as shown in Figure 5-1. In some devices the pores do not exclude water molecules, allowing any chemicals in the water, along with suspended material smaller than the pores, to diffuse into and out of the sampler.

# Passive Sampler Collection Mechanisms

## Equilibrium Samplers (e.g. PDBs, NSPDS, Peeper)

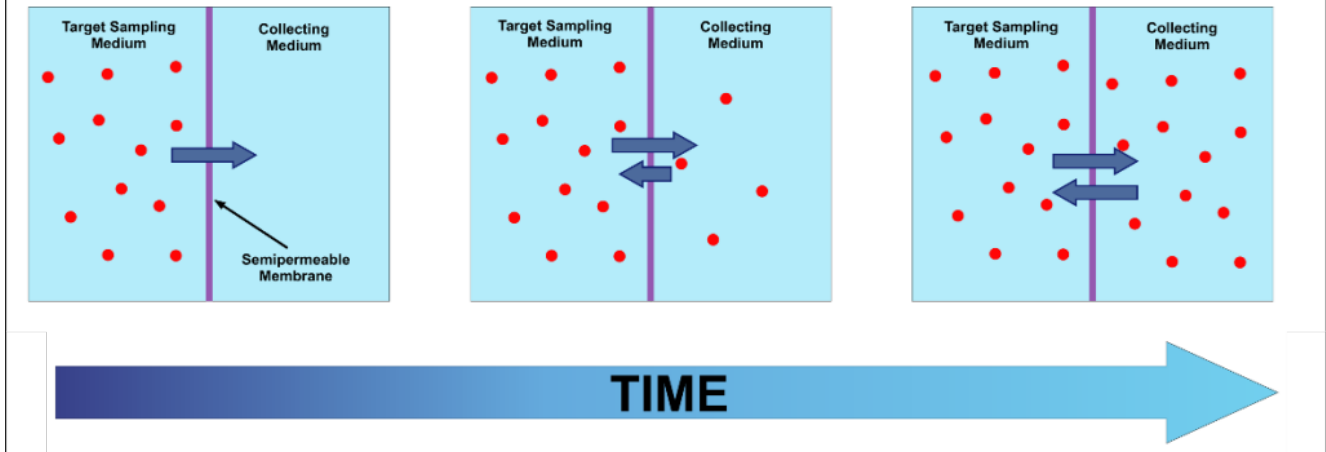


Figure 5-1. Passive sampler collection mechanisms for equilibrium samplers.

Source: New Jersey Department of Environmental Protection (NJDEP), figure used with permission.

The deployment time necessary for equilibrium samplers to reach partition equilibrium varies by target chemicals, sampled medium, and site conditions. In groundwater monitoring wells, the deployment time should be long enough to include the time the groundwater flow returns to its natural condition after being disturbed by the installation of the sampler and the time it takes for partition equilibrium to be reached. A conservative deployment time of 14 days is often recommended for some equilibrium samplers to reach partition equilibrium in groundwater; however, the minimum deployment time is dependent on site-specific conditions and sampler types, and longer deployment times may be required. Once those equilibrium samplers reach partition equilibrium, they will reflect the chemical concentrations of the sampled medium during the final days of residence time.

Because equilibrium samplers maintain dynamic equilibration—that is, they continually adjust to the surrounding concentration changes—it is common practice to leave the samplers in place beyond the minimum residence time and collect them at the next sampling event to eliminate a separate field mobilization for deployment of samplers.

When it is expected that the type of diffusion sampler selected and the deployment time will not allow the sampler to reach equilibrium, reverse tracers (often referred to as performance reference compounds (PRCs) can be used to evaluate the fractional state of equilibrium achieved during deployment (Equation 1). For example, a bromide tracer is commonly used as a PRC for NSPDS and peepers, and the sample collection medium is spiked with the tracer at a known concentration inside the sampler ( Risacher et al. 2023<sup>[Q4VDTGP2]</sup> Risacher, Florent F., Haley Schneider, Ilektra Drygiannaki, Jason Conder, Brent G. Pautler, and Andrew W. Jackson. 2023. "A Review of Peeper Passive Sampling Approaches to Measure the Availability of Inorganics in Sediment Porewater." *Environmental Pollution* 328 (July):121581.

<https://doi.org/10.1016/j.envpol.2023.121581>). Bromide has not been rigorously evaluated as a tracer in high salinity environments or for use with some metals in sediment environments. A detailed discussion of considerations for applications of reverse tracers is available in Thomas and Arthur ( Thomas and Arthur 2010<sup>[VLP6CY6N]</sup> Thomas, Burt, and Michael A. Arthur. 2010. "Correcting Porewater Concentration Measurements from Peepers: Application of a Reverse Tracer." *Limnology and Oceanography: Methods* 8 (8): 403–13. <https://doi.org/10.4319/lom.2010.8.403>). During the residence time, the PRCs diffuse out of the sampler at a known rate, sometimes called the dissipation rate, to correspond to the uptake rate of a target analyte, assuming isotropic exchange kinetics ( Ghosh et al. 2014<sup>[TBGHY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." *Integrated Environmental Assessment and Management* 10 (2): 210–23. <https://doi.org/10.1002/ieam.1507>). For example, when the concentration of a PRC in an NSPDS is decreased from 100 mg/L to 50 mg/L during deployment, you can infer that a target chemical reached 50% of equilibration. The concentration of any known background chemical should be considered if those background

chemicals are the same as the PRC used in the sampler.

PRCs should be analytically noninterfering and have similar diffusivity as target analytes. Measurement of the remaining PRC at retrieval to the initial concentration provides a direct indication of the fraction of equilibrium as shown in the equation below ( Burgess et al. 2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://semspub.epa.gov/work/HQ/100000146.pdf>.):

### Equation 1

$$f_e = 1 - \frac{C_t}{C_0}$$

where:

$f_e$  = fraction of equilibrium (-)

$C_t$  = PRC concentration in passive sampler at time t

$C_0$  = initial PRC concentration in passive sampler

Put simply, chemicals diffuse from the surrounding water with higher concentrations to the water inside the sampler with lower concentrations due to concentration gradients and eventually reach equilibrium over time between the two aqueous phases.

Other passive equilibrium samplers use a collection medium that is different from the sampled medium. These may be nonaqueous organic solvents, or solid-phase polymer materials that come to equilibrium with the sampled medium over time. A target chemical diffuses into the device and is absorbed into polymer or organic solvent and concentrates in the material until equilibrium is reached. When different phases are involved, chemical partitioning occurs, in which the chemical concentration in the sampled medium will be different from the chemical concentration in the sampling medium, at equilibrium. The partitioning coefficient expresses the ratio of concentrations of a chemical in two different phases at equilibrium. The ratio of target chemical molecules inside the sampler compared to target chemical molecules in the target medium may not be 1:1 when the collecting medium is not the same as the sampled medium, though the ratio will remain constant once equilibrium has been reached.

The equilibrium samplers discussed below (polymeric sampling devices (the LDPE sampler, POM, and PDMS-coated SPME fiber) and PISCES) use the partition equilibrium of chemicals, specifically HOCs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), DDX (the pesticide DDT and its breakdown products), and dioxin/furans, between water and an organic polymer/solvent or between air and an organic polymer/solvent. Chemical partitioning between two phases is generally reversible and driven by intermolecular attraction energies such as the van der Waals force and the dipole-induced dipole forces. When an organic polymer is used as the collection medium, HOCs present in environmental media partition into the polymer and the resulting mass of HOC collected in the polymer is used to calculate freely dissolved concentrations.

The fundamental processes behind all equilibrium samplers are thermodynamically equivalent in terms of chemical potential and fugacity. Hence, the passive samplers discussed further below have also historically been referred to as equilibrium samplers ( Mayer et al. 2023<sup>[6DVRH658]</sup> Mayer, Paul M., Kelly D. Moran, Ezra L. Miller, Susanne M. Brander, Stacey Harper, Manuel Garcia-Jaramillo, Victor Carrasco-Navarro, et al. 2023. "Not yet Peer Reviewed: Where the Rubber Meets the Road: Tires as a Complex Pollutant."; Cornelissen et al. 2008<sup>[QHJKURY2]</sup> Cornelissen, Gerard, Arne Pettersen, Dag Broman, Philipp Mayer, and Gijs D. Breedveld. 2008. "Field Testing of Equilibrium Passive Samplers to Determine Freely Dissolved Native Polycyclic Aromatic Hydrocarbon Concentrations." *Environmental Toxicology and Chemistry* 27 (3): 499-508.

<https://doi.org/10.1897/07-253.1>; Grundy, Lambert, and Burgess 2023<sup>[BP2FNJUH]</sup> Grundy, James S., Matthew K. Lambert, and Robert M. Burgess. 2023. "Passive Sampling-Based versus Conventional-Based Metrics for Evaluating Remediation Efficacy at Contaminated Sediment Sites: A Review." *Environmental Science & Technology* 57 (28): 10151-72.

<https://doi.org/10.1021/acs.est.3c00232>.). Although the driving processes are the same, there is a notable difference in determining the concentration of the sampled medium. Passive samplers that use a collection medium that is the same as the sampled medium produce a sample with a partitioning ratio of 1:1, and the concentration in the sampler directly represents the surrounding medium at equilibrium. Devices that use a collection medium that is different from the sampled medium have a partitioning ratio that is not 1:1 and the concentration in the sampler must be calculated by measuring the collected mass and using the uptake rate to calculate the concentration.

Figure 5-2 illustrates the chemical uptake by a passive sampler. Generally, equilibrium samplers are deployed into environmental media for a certain period aiming to nearly or fully achieve chemical equilibrium.

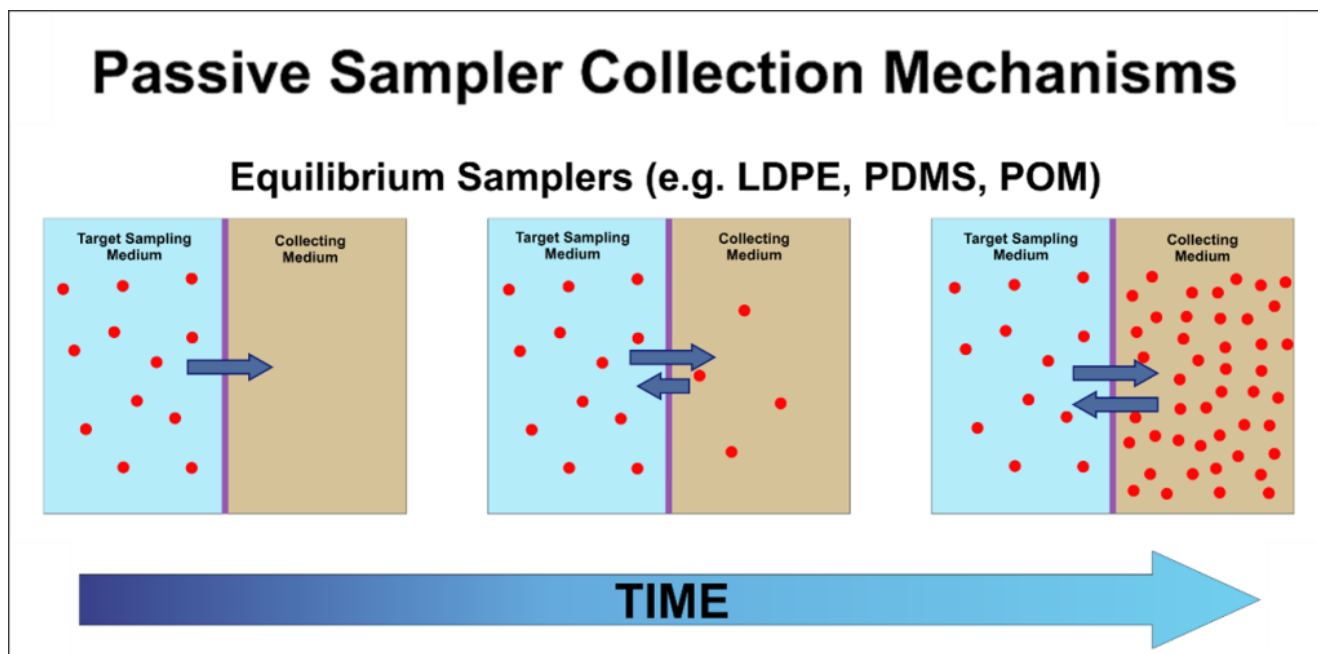


Figure 5-2. Passive sampler collection mechanisms for equilibrium samplers with absorption sampling mechanisms. Source: NJDEP, figure used with permission.

Equilibrium samplers collect samples optimally in the equilibrium sampling media (see above Figure 5-2). However, some also work in kinetic and transient sampling if the fraction of equilibrium is estimated using PRCs. This is often the case for passive sampling of strongly hydrophobic organic compounds (for example, octanol-water partition coefficient,  $\log K_{OW} > 6$ ) by polymeric sampling devices because the partitioning of those compounds to polymeric sampling devices is kinetically slow. Kinetically slow partitioning can be overcome by ex situ methods, employing passive samplers ( Ghosh et al.

2014<sup>[T8GHY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." *Integrated Environmental Assessment and Management* 10 (2): 210-23.

<https://doi.org/10.1002/ieam.1507>.). Polymeric sampling devices are often spiked with PRCs, which include deuterated PAHs, <sup>13</sup>C-labeled PCBs, or rare congener PCBs, to determine the fraction of equilibrium for HOCs. Some things to consider when evaluating PRCs include similar hydrophobicity and kinetics compared to target analytes, loss of PRCs can be precisely measured, PRCs are not present in the environment, PRCs are stable/nonreactive, and PRCs do not interfere with target analytes or compounds added to the samplers for QA/QC purposes ( Tomaszewski and Luthy 2008<sup>[DJVYK9K]</sup> Tomaszewski, Jeanne E., and Richard G. Luthy. 2008. "Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment | *Environmental Science & Technology*" 42 (16): 6086-91.

<https://doi.org/10.1021/es800582a>.). Although the PRCs introduced are considered de minimis, the relevant state agency and commercial laboratories should be contacted to discuss acceptance.

### **Accumulation Sampler**

Accumulation samplers function differently from equilibrium samplers. Accumulation samplers defined in this document are also called "kinetic samplers," "transient samplers," or "integrative samplers" in other references. Accumulation samplers rely on diffusion through a diffusion-controlling membrane or barrier and adsorption, precipitation, or other interfacial accumulation of chemicals on collecting media (for example, adsorbents, resins) to concentrate chemicals in the samplers

over time. Reactions occurring in the collecting media are practically irreversible during the sampler deployment, in contrast to chemical partitioning in equilibrium samplers in which chemicals reversibly partition between different phases. In accumulation samplers, target chemicals do not significantly desorb, degrade, or diffuse out from accumulation samplers. Binding sites in the collecting media will be eventually used up by target chemicals once the reaction between target chemicals and reaches chemical equilibrium. Therefore, accumulation samplers are valid only in the kinetic or transient sampling regimes, as shown in Figure 5-3. Whereas equilibrium samplers rely on diffusion and in some cases, absorption, to accomplish the intraphase collection of chemicals, accumulation samplers rely on diffusion and adsorption or precipitation to accomplish the interphase accumulation of chemicals. Accumulation samplers provide a time-integrative concentration during the deployment period.

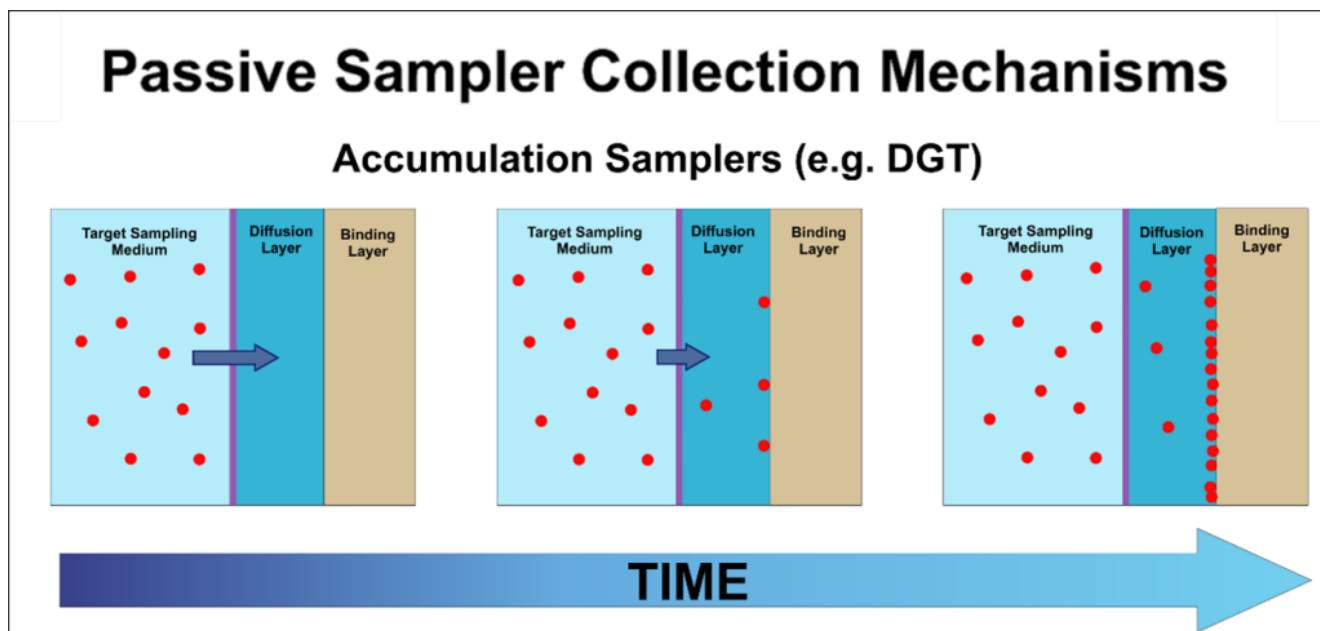


Figure 5-3. Passive sampler collection mechanisms for accumulation samplers.

Source: NJDEP, figure used with permission.

## 5.1 Grab Sampling Technologies

A passive grab sampler collects an instantaneous, whole media (the media and everything in it, at the interval where collected) sample by “grabbing” or capturing the medium without inducing movement of the medium itself. Two of the grab samplers in this document are designed for groundwater sampling because of the unique challenges presented by groundwater conditions that may not exist when sampling other media (see Section 2.2.2).

There are, however, several technologies that do not meet the criteria for passive samplers but that may produce a sample with less disturbance than traditional active sampling methods where large volumes of water are not acquired. To give further representation to technologies for other media, such as surface water and air, Section 6 includes grab samplers that do not meet the full criteria for passive samplers but can be considered in cases where it might be acceptable to induce flow to acquire a small volume sample. Media conditions and project DQOs should be considered before using nonpassive samplers.

Some of the advantages common to all passive grab samplers in aqueous media include:

- are relatively easy to use
- can be deployed in most groundwater wells
- can be deployed in surface water greater than 3 feet deep
- can sample multiple discrete intervals in a groundwater well to provide a vertical contaminant profile
- reduce field sampling variability, resulting in highly reproducible data
- decrease field time (sample collection without purging)
- reduce or eliminate IDW

Disadvantages for all passive samplers are listed in the individual technology sections.

In Section 5.1 below on grab sampling, HydraSleeve, Snap Sampler, and thin-walled soil sampler will be discussed. Table 5-1, adapted from USGS's Table 4 ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.), lists chemical families that can be analyzed using the noted passive sampling technologies. Always check with the relevant state agency, sampler manufacturer, and laboratory to confirm that the selected technology meets your DQOs.

<b>Passive Grab Sampling Technologies</b>	<b>HydraSleeve</b>	<b>Snap Sampler</b>	<b>Thin-Wall Soil Samplers</b>
<b>Chemical Constituents and Characteristics</b>			
<b>Field physiochemical characteristics</b> (Temp, pH, SC, DO, ORP)	Most	Most	N/A
<b>Major cation and anions</b> (Ca, Mg, Na, K, HCO <sub>3</sub> , Cl, SO <sub>4</sub> , F, Br)	Most	Most	Most
<b>Nutrients</b> (NO <sub>3</sub> , NO <sub>2</sub> , NH <sub>4</sub> , PO <sub>4</sub> )	Most	Most	Most
<b>Trace elements (metals)</b> (Fe, Mn, Al, Ag, Zn and others)	Most	Most	Most
<b>Perchlorate</b> (ClO <sub>4</sub> )	Most	Most	Most
<b>Organic carbon</b> (dissolved or total)	Most	Most	TOC Only
<b>Dissolved hydrocarbon gases</b> (Methane, ethane, ethene)	Most	Most	N/A
<b>Volatile organic compounds</b> (Chlorinated solvents, BTEX)	Most	Most	Most
<b>Semivolatile organics</b> (1,4-Dioxane, BN, Phenols, PAH, PCB, dioxins, furans)	Most	Most	Most
<b>Pesticides, herbicides, and fungicides</b> (organo Cl, organo PO <sub>4</sub> )	Most	Most	Most
<b>Explosive compounds</b> (RDX, HMX, TNT)	Most	Most	Most
<b>Poly- and perfluoroalkyl substances</b> (PFAS)	Most	Most	Most
<b>Pharmaceuticals</b> (Drugs, fragrances, hormones)	Most	Most	NT
<b>Minerals</b> (pyrite, mackinawite)	Most	Most	Most
<b>Microbial population sampling</b> (e.g., Dehalococcoides)	Most	Some	NT

<b>Table 5-1 Key</b>	
Most	Most compounds are compatible with the sampler
Some	Some compounds are compatible with the sampler
NT	Not tested (no study to support)
N/A	Not applicable to this sampler

**Table 5-1 Acronym Key**

[Temp, temperature; SC, specific conductivity; DO, dissolved oxygen; ORP, oxidation-reduction potential; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO<sub>3</sub>, bicarbonate; Cl, chloride; SO<sub>4</sub>, sulfate; F, fluoride; Br, bromide; NO<sub>3</sub>, nitrate, NO<sub>2</sub>, nitrite; NH<sub>4</sub>, ammonium; PO<sub>4</sub>, phosphate; Fe, iron; Mn, manganese; Al, aluminum; Ag, silver; Zn, zinc; ClO<sub>4</sub>, perchlorate; BTEX, benzene, toluene, ethylbenzene and xylene; BN, base-neutral organics; PAH, polycyclic aromatic hydrocarbons; PCB, polychlorinated biphenyls; organoCl, organochlorine; organoPO<sub>4</sub>, organophosphate; RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane; TNT, trinitrotoluene; TOC, total organic carbon; Hg, mercury; CO<sub>2</sub>, carbon dioxide]

## 5.1.1 HydraSleeve

### 5.1.1.1 Description and Application

HydraSleeve groundwater samplers are passive grab-sampling devices that collect water samples from groundwater wells and surface water without purging or mixing fluid from other intervals. The HydraSleeve collects a “whole water” sample of the water flowing through the saturated screen and all chemicals in the water within the sample interval at the instant it is retrieved. Because everything in the water is collected, the HydraSleeve can be used to sample for most groundwater chemicals (for example, volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), metals, pesticides, anions, cations, explosive compounds, perchlorate, 1,4-dioxane, PFAS) and physical parameters (for example, pH, dissolved oxygen), as long as an adequate volume of sample is recovered for analysis (“HydraSleeve ‘No Purge’ Grab Sampler,” n.d.). In addition, the sampler causes minimal agitation of the water column prior to sample collection.

There are three versions of the HydraSleeve (Figure 5-4) that are constructed with the same valve and are operated in the manner described above, but they vary by sampler dimensions, volume capacity, and method of attachment to the tether line. These are the HydraSleeve, the HydraSleeve-SuperSleeve and the HydraSleeve-SpeedBag. SuperSleeve samplers have reusable top collars, can be manufactured in longer lengths to hold more volume, and can be made from high density polyethylene (HDPE), which is an accepted material when sampling for PFAS. SpeedBag samplers have a feature that shortens the wait time required between deployment and retrieval, so they can be used to sample shortly after installation.

# HydraSleeve™

# HydraSleeve™ SpeedBag

# HydraSleeve™ SuperSleeve

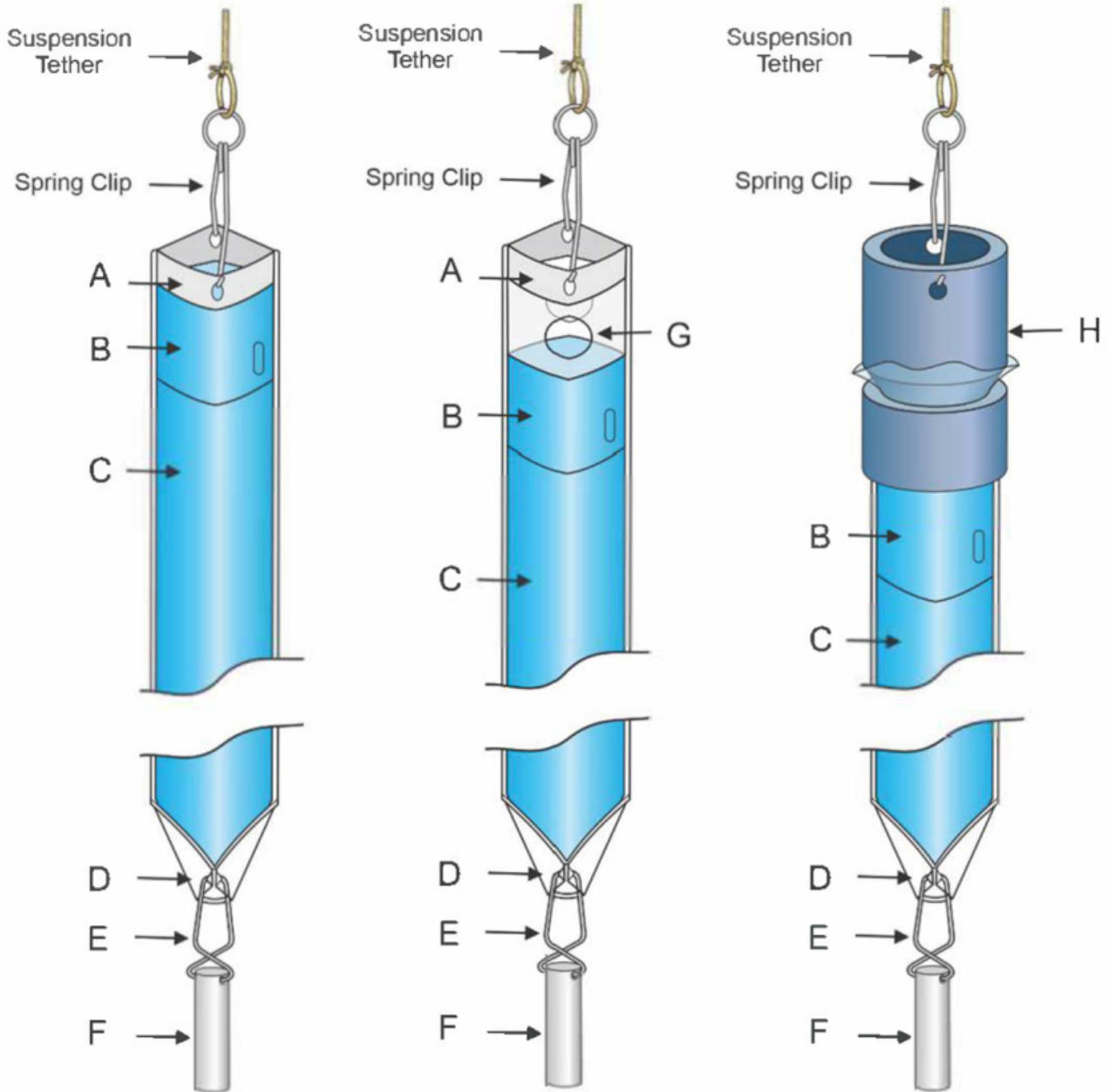


Figure 5- 4. HydraSleeve samplers.

Source: NJDEP, figure used with permission.

### Figure 5-4 Key

A	Reinforcing strips
B	Self-sealing, reed-type flexible polyethylene check valve
C	Sample sleeve
D	Bottom of sample sleeve (2 holes)
E	Weight clip (a zip tie can be used in place of a weight clip)

**Figure 5-4 Key**

F	Reusable stainless steel weight
G	Flushing ports
H	Reusable PVC top collar assembly ( <i>can also include stainless steel top weight</i> )

All HydraSleeve samplers are made from a collapsible, flexible tube of LDPE or HDPE that is sealed at the bottom end and has a self-sealing reed valve at the open top end. The HydraSleeve sampler is installed in the water column within the screen interval of the well, flat, empty, in a ribbon-like form, creating very little displacement or disturbance. Hydrostatic pressure keeps the device closed until it is pulled upward through the water during retrieval, and then the sample seals the valve shut when the HydraSleeve is full, ensuring that only a specific interval is sampled.

During deployment, one or more HydraSleeves can be attached to a reusable weighted suspension tether and situated in a well at the chosen sampling intervals or target horizons within the saturated well screen (see Section 5.1.1.2 for HydraSleeve placement relative to sample interval).

Following deployment, the samplers are left in place in the monitoring well to allow the water surrounding the sampler to restabilize after any minor vertical mixing that may have occurred during installation. HydraSleeves are installed empty and have a very thin profile in the water, so a standard 2-inch diameter HydraSleeve with an 8-ounce weight displaces only about 75 ml of water. Because of the very small amount of displacement, there is very little change in well flow and therefore almost no wait is required for the well to return to normal flow conditions.

It is recommended to allow a minimum of 12 hours' residence time to allow the groundwater in the well screen to return to its ambient condition after the sampler is installed. In cases of very low recharge wells, a minimum residence time of 24 hours is suggested. In some cases of high-flow wells or partially saturated screens, less residence time may be required. There is no maximum residence time under any conditions, so new HydraSleeves may be installed after one sampling event and left in place indefinitely before initiating a sample.

The HydraSleeve SpeedBag can be used to collect a sample immediately after installation with no residence time required. This is because two, 1-inch diameter holes are fabricated into the sides of the sleeve above the valve so that the small volume of water that entered the space during installation is flushed out the sides of the sleeve before the valve opens as the SpeedBag is pulled upward to collect a sample. Because of this feature, SpeedBags require a slightly longer pull distance to fill than do HydraSleeves. SpeedBags can be used to sample quickly during one-time events such as site assessments and when advanced installation of the sampler is not possible.

To retrieve the HydraSleeve and acquire the water sample, the device is pulled up by the tether through the sample zone, at a rate of one foot per second or faster. During sampling, the sampler moves within the water column without causing or changing groundwater flow. Once the HydraSleeve is full, the self-sealing reed valve closes, preventing loss of the sample or the entry of extraneous fluid as the HydraSleeve is recovered. At the surface, the HydraSleeve is discharged, and the sample transferred to suitable containers for shipment to the laboratory, where the analysis provides a direct measure of concentration using standard laboratory methods. If there is sufficient water in the screen above the sleeve at the time of retrieval, the HydraSleeve will always represent the water in the sample interval at the instant it is pulled upward during retrieval, regardless of when it was deployed.

The HydraSleeve can be made in different lengths, diameters, and materials to accommodate various well diameters, volume requirements, and chemicals. To test for vertical stratification within a well, multiple HydraSleeve samplers can be suspended on the same cable and deployed simultaneously. In short water columns or to sample as close to the bottom of the well as possible, a stainless steel top collar weight may be used to compress the top of the HydraSleeve or SuperSleeve to within 1–2 feet of the bottom of the well. Double-walled "armored" HydraSleeves are also available for wells with sharp, jagged casing or screen.

The HydraSleeve performs the same in surface water as groundwater. Just as in groundwater, the depth of water must be adequate to accommodate the length of the sampler below the intended sample interval. Top collar weights can be used to compress the sleeve closer to the bottom of the water body if there is a stable surface at the bottom of the water for the bottom weight to rest upon so the sleeve can be compressed from the top down. Because HydraSleeves are lightweight and require only a rapid upward pull to acquire a sample, they are highly suited for use with drones to sample ponds, lakes, and other water bodies with adequate depth (see Section 5.1.1.2 for more information). Adapters are available to use

HydraSleeves for sampling discrete intervals from surface water and to use HydraSleeves with a drone for remote surface water sampling. Additional instructions on the use of the HydraSleeve are presented in the HydraSleeve Field Manual and the HydraSleeve SOP, available through the vendors.

Individual HydraSleeve volume varies by the diameter and length selected to fit the available saturated screen. A single HydraSleeve can acquire greater than 2 liters from a typical 2-inch monitoring well with 10 feet of saturated screen. A single HydraSleeve sized for a 2-inch well with 5 feet of saturated screen can recover more than 1 liter of sample. Larger diameter HydraSleeves that hold more than 3 liters are available for 4-inch diameter and larger wells. HydraSleeve samplers are also available for wells as small as 1 inch. Multiple HydraSleeves can be attached to the same suspension tether to add sample volume or to sample discrete intervals in wells with longer saturated screens.

### **Illustration of the HydraSleeve**

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The basic HydraSleeve (Figure 5-5) consists of the following components\*:

- Directly above the self-sealing check valve at the top of the sleeve are two white reinforcing strips with holes (A) to provide attachment points for the spring clip or suspension tether.
- A reusable spring clip is fixed to a suspension line or tether and attaches to the holes in the white strips to deploy the device into and recover the device from the well.
- A transparent, self-sealing, reed-type flexible polyethylene check valve (B) is built into the top of the sleeve, preventing water from entering or leaving the sampler when not acquiring the sample.
- The sample sleeve (C), a long, flexible, 4-mil thick lay-flat polyethylene, is open at the top and sealed at the bottom to form a sample chamber.
- The bottom of the sample sleeve has two holes (D) to attach the weight clip (E) and weight (F).
- A reusable stainless steel weight (F) with clip or disposable zip tie (E) attaches to the bottom of the sleeve, drawing it down the well to its intended depth in the water column.
- A discharge tube is included and is used to puncture the HydraSleeve after recovery from the well so the sample can be decanted into sample bottles (not shown).
- An optional top collar weight (not shown in Figure 5-5) may be connected to the top of the HydraSleeve to compress the sleeve closer to the bottom of the well.

\*SuperSleeves require two-piece top collars, instead of the white reinforcing strips, to attach the sleeve to the spring clip.

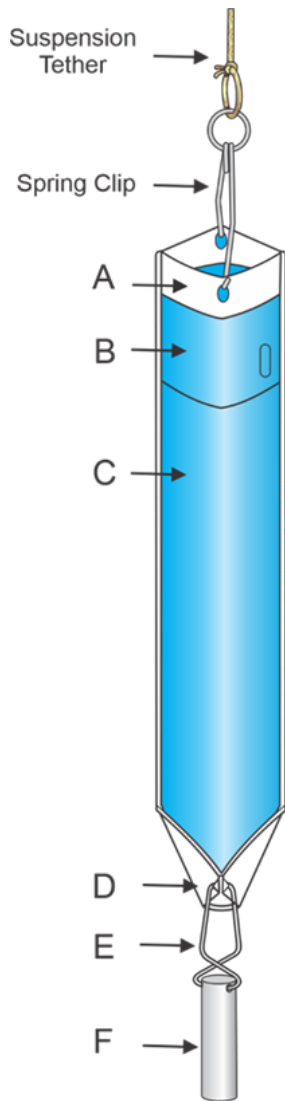


Figure 5-5. HydraSleeve™ sampler and components.

Source: NJDEP, figure used with permission.

**Note:** The sample sleeve and the discharge tube are designed for one-time use and disposable. The spring clip, weight, weight-clip, and factory-built suspension tethers are dedicated to the well and may be reused.

### 5.1.1.2 Installation and Use

The HydraSleeve is first installed to a position just below the intended sample interval. To retrieve the HydraSleeve and acquire the water sample, use the tether to pull the device up through the sample zone, at a rate of ~1 ft per second\* or faster. As the sleeve moves upward, the valve at the top opens and the sides of the sleeve expand around the stationary core of water in the sample interval. The effect is similar to pulling a sock over a foot; the sock moves around the foot as the sock is pulled upward, but the foot does not move. When the sampler is completely filled with water, the valve automatically closes, sealing the sample inside and preventing entry of water from overlying zones as the sampler is removed from the well.

The captured sample represents the interval above the starting position of the top of the HydraSleeve, upward for a distance approximately equal to (or slightly greater than, depending on the specific sampler and retrieval method) the length of the sampler, when properly sized to the well diameter. Upon retrieval, the HydraSleeve is punctured near the bottom with the provided straw and the sample is carefully transferred to the appropriate containers for laboratory analysis. A new HydraSleeve can then be attached to the tether for the next sampling event.

### Installation

1. HydraSleeve is installed empty, on a suspension tether below the sample interval in the saturated screen (Figure 5-6). Residence time is usually 24–48 hours but is dependent on groundwater well flow conditions.
  2. Leave in place (still empty) until the well restabilizes/equilibrates.
  3. Return to the site to sample and pull upward rapidly on the tether (~1 ft per sec)\* to fill the HydraSleeve.
  4. The valve at the top automatically closes and seals when HydraSleeve is full.
- \* ~1 ft per second is about the speed that a person can quickly move their straightened arm in an arc from alongside their leg to over their head. Some have also compared this to the motion used to “set the hook” when fishing.

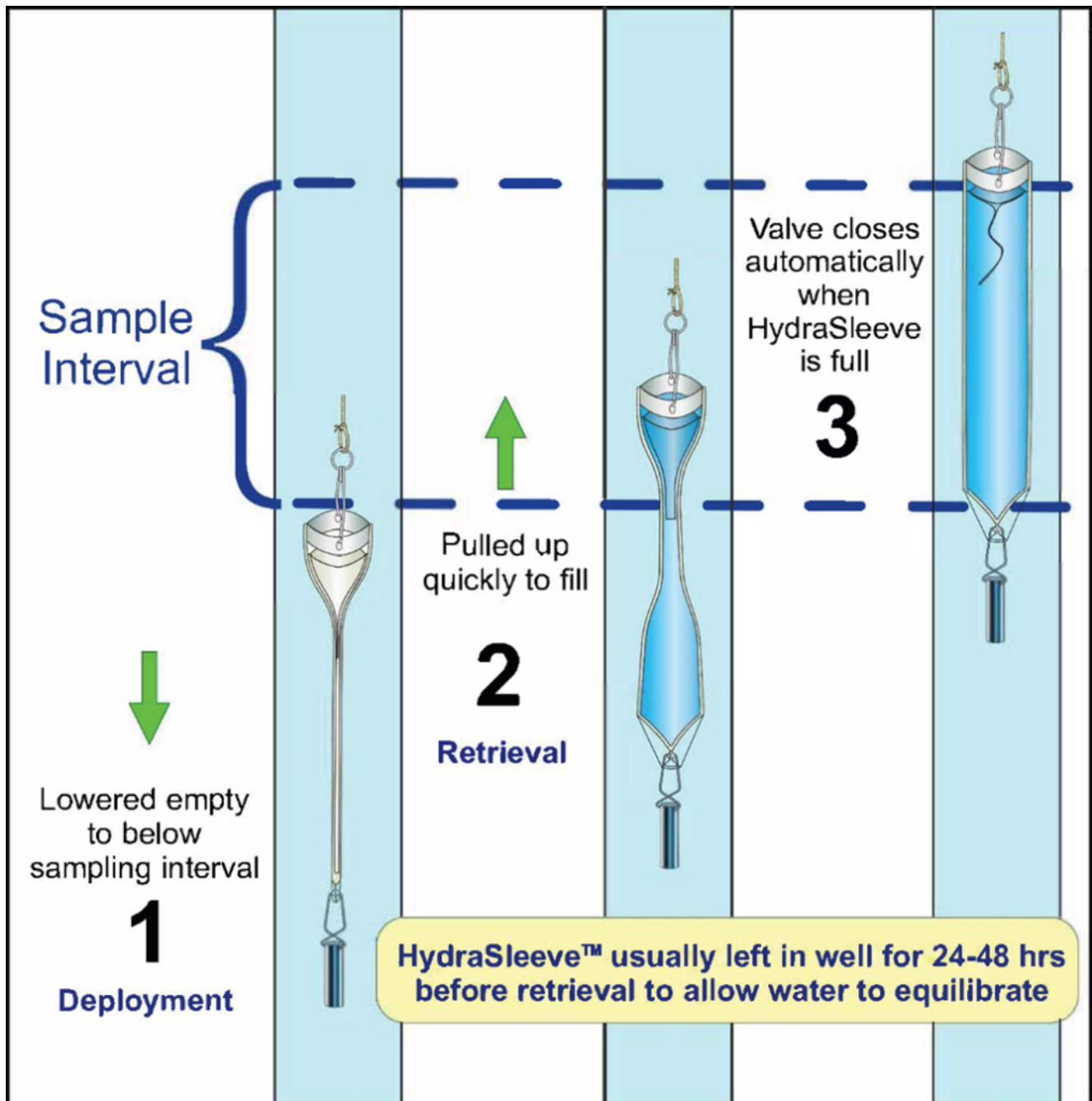


Figure 5-6. HydraSleeve installation steps.  
Source: NJDEP, figure used with permission.

### Use

In all cases where the HydraSleeve is used in groundwater, the installed position of the top of the HydraSleeve must be in the saturated screen and the length of saturated screen above the HydraSleeve must be at least as long as the HydraSleeve, preferably at least 6-inches longer.\*\* The sampler needs to fill with water before reaching the top of the saturated screen.

This will ensure that only water from the screened interval is collected in the HydraSleeve (Figure 5-6).

To optimize sample recovery in wells with short saturated screen length (5 feet or less), the HydraSleeve should be placed at the very bottom of the well so that the top of the HydraSleeve is as close to the bottom of the well screen as possible to leave at least one sampler length between the position of the top of the installed sampler and the top of the saturated screen. The use of a top weight on the HydraSleeve to help compress the top of the sleeve at the bottom of the well allows for sufficient saturated screen to fill the sleeve before it reaches the top of the saturated interval of the screen (Figure 5-7). In wells where multiple intervals are sampled (profiling) only the bottom HydraSleeve is compressed by a top weight

*\*\* The actual length of saturated screen required to fill a HydraSleeve varies by model and method of recovery.*

# HydraSleeve™ with Top Weight for Sampling Short Water Column

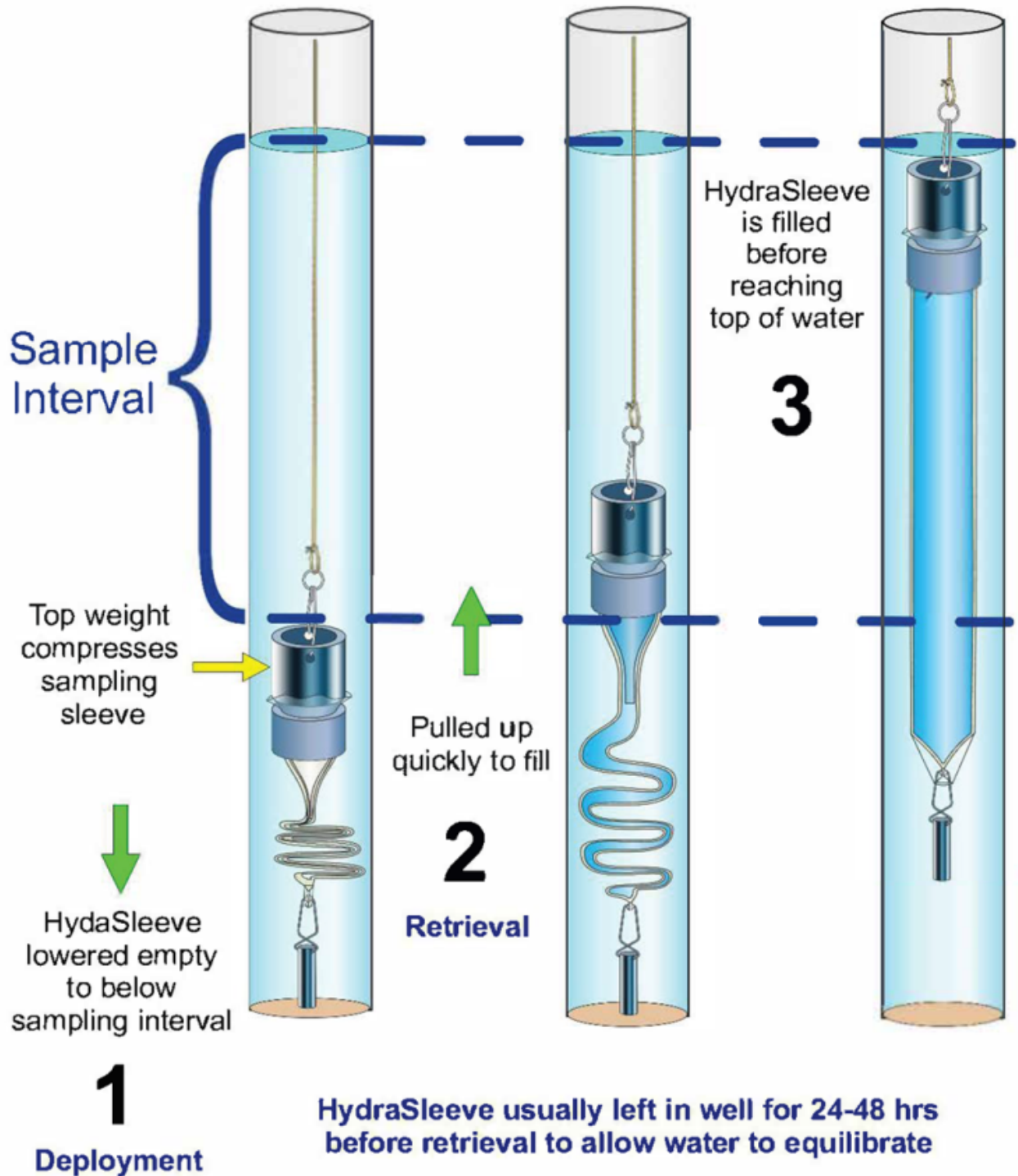


Figure 5-7. HydraSleeve sampling in a short water column.  
Source: NJDEP, figure used with permission.

## 5.1.1.3 Advantages

- HydraSleeves have been shown to be the lowest cost passive sampling method for groundwater (Parsons

2005<sup>[IKZXKLEL]</sup> Parsons. 2005. "FINAL: Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California." F44650-9900005. [https://clu-in.org/download/char/passsamp/mcclellan\\_final\\_results\\_report.pdf](https://clu-in.org/download/char/passsamp/mcclellan_final_results_report.pdf).)

- They provide the largest sample volume capability of passive samplers for the same saturated screen length.
- HydraSleeves collect a "whole water" sample containing everything in the water within the sample interval, so no limit to contaminants of concern.
- They collect an unfiltered sample (this may be an advantage or limitation depending on site DQOs. HydraSleeve samples can be filtered after sample recovery if needed).
- HydraSleeves are suitable for sampling wells for assessment, short-term, and long-term groundwater monitoring.
- They can be more representative of aquifer water in low-yield wells if purging causes the well to go dry and/or aerate during the purging or stabilization process.
- They are available in difference sizes for use in narrow or constricted wells as small as 1-inch diameter.
- HydraSleeves can be manufactured to custom lengths to fit project-specific screen lengths or sample volumes.
- HydraSleeve-SuperSleeves have available options for sampling PFAS.
- They can also be used to sample discrete intervals from surface water. A simple adapter allows using the HydraSleeve with a drone for remote surface water sampling.

#### 5.1.1.4 Limitations

- An unfiltered sample is collected. (This may be an advantage or limitation depending on site DQOs. HydraSleeve samples can be filtered after sample recovery if needed).
- Residence time of the HydraSleeve depends on aquifer and well flow conditions.
- Sample volume may be limited to the amount of water in the saturated screen and the size of the selected sampler device. For 2-inch wells, the maximum sampling volume is 1.5 liters; for 4-inch wells, the maximum sampling volume is 2.1 liters.
- 2-liter samplers that are 5 feet long may pose logistic challenges during retrieval and when filling sample bottles.
- Special considerations should be taken when evaluating using at sites with NAPL.
- Sampler handling and transfer to sample jars may need two technicians and may be challenging due to the nonrigid nature of device and spillage.

### 5.1.2 Snap Sampler

#### 5.1.2.1 Description and Application

The Snap Sampler is a grab-sampling device that collects a whole water sample at a fixed sampling depth up to 2,500 feet bgs. The Snap Sampler (Figure 5-8) uses removable Snap Sample bottles that are open on both ends to allow passive groundwater movement into and through the bottle. Each bottle contains spring-activated caps that are set in an open position during deployment. The samplers are deployed prior to collecting the sample and left in the well to allow the well to restabilize and the contents of the bottles to come to equilibrium with the surrounding water after insertion of the device. The sample is collected under in situ conditions, without purging or moving the device prior to bottle closure. When it is time to retrieve the sample, the caps are triggered to close the bottle by a mechanical trigger system or by a downhole pneumatic actuator initiated at the surface. Multiple samplers can be connected in series to collect several sample bottles at the same time. After retrieval from the well, Snap Sampler bottles can be sent directly to the analytical laboratory, in many cases without transferring samples into separate containers or exposing the sample to the atmosphere. Alternatively, samples can be transferred to laboratory-supplied containers if desired or required for transport and storage protocols. The fixed sampling depth of the Snap Sampler allows the user to collect an undisturbed sample from a precise depth without the potential for mixing with other depths in the water column. The in situ sealing feature avoids the surface bottle-filling step and exposure of the sample to ambient air. The downhole sample bottles are open to the well environment; thus, the sampler can be used to sample for any chemical, subject to total sample volume considerations.

Data quality is improved through several features of the Snap Sampler device. The sample is sealed while submerged, which prevents exposure to ambient air. Differences in surface handling by different personnel or different weather conditions are eliminated with containers sealed before collection from the well. Further, the sampling position is fixed with dedicated trigger system lengths. Samples are collected at the same fixed position in the well during each sampling event, improving

consistency between events. No disturbance of the water column when bottles are snapped shut also limits artifacts such as turbidity from motion in the water column.

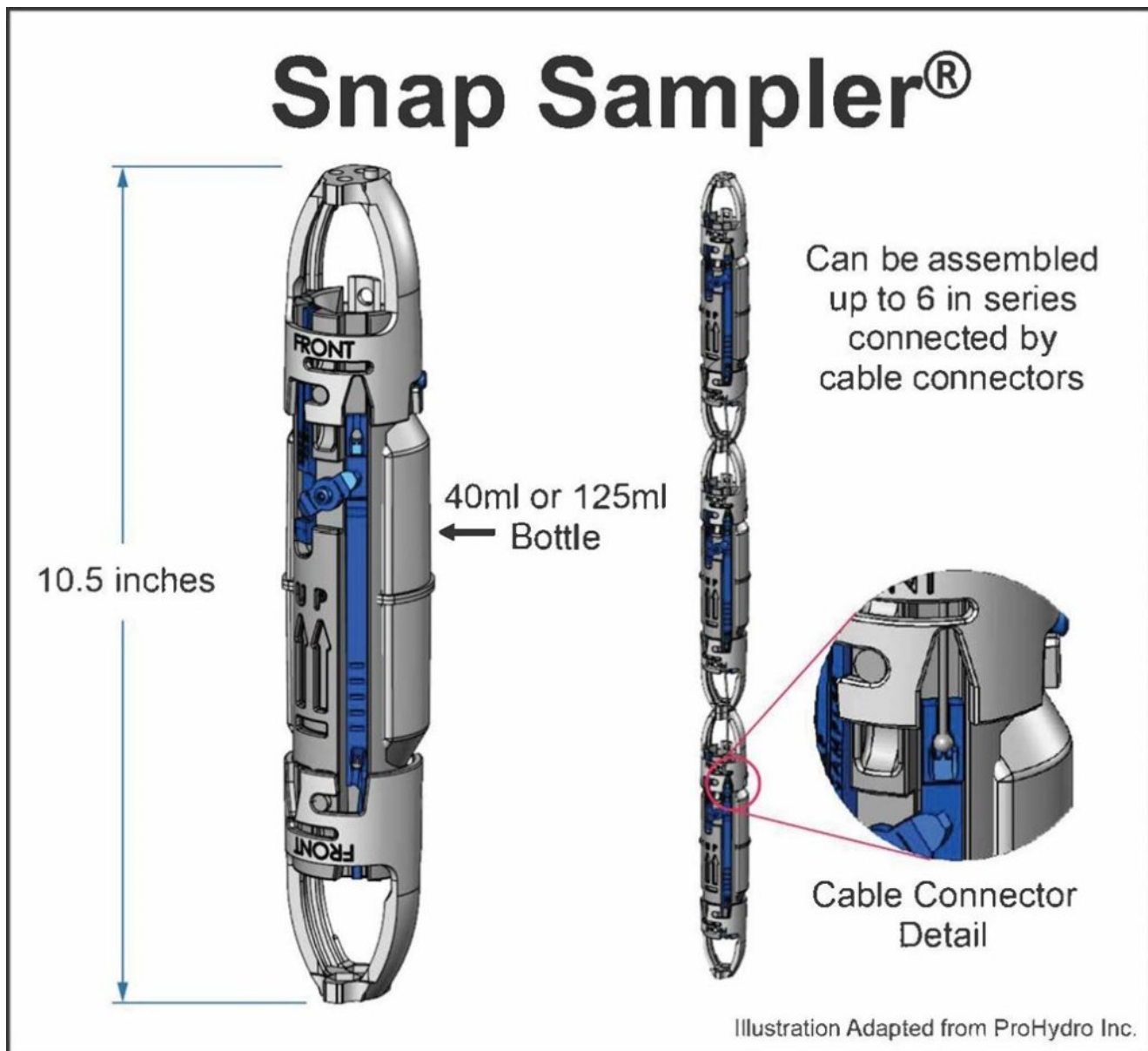


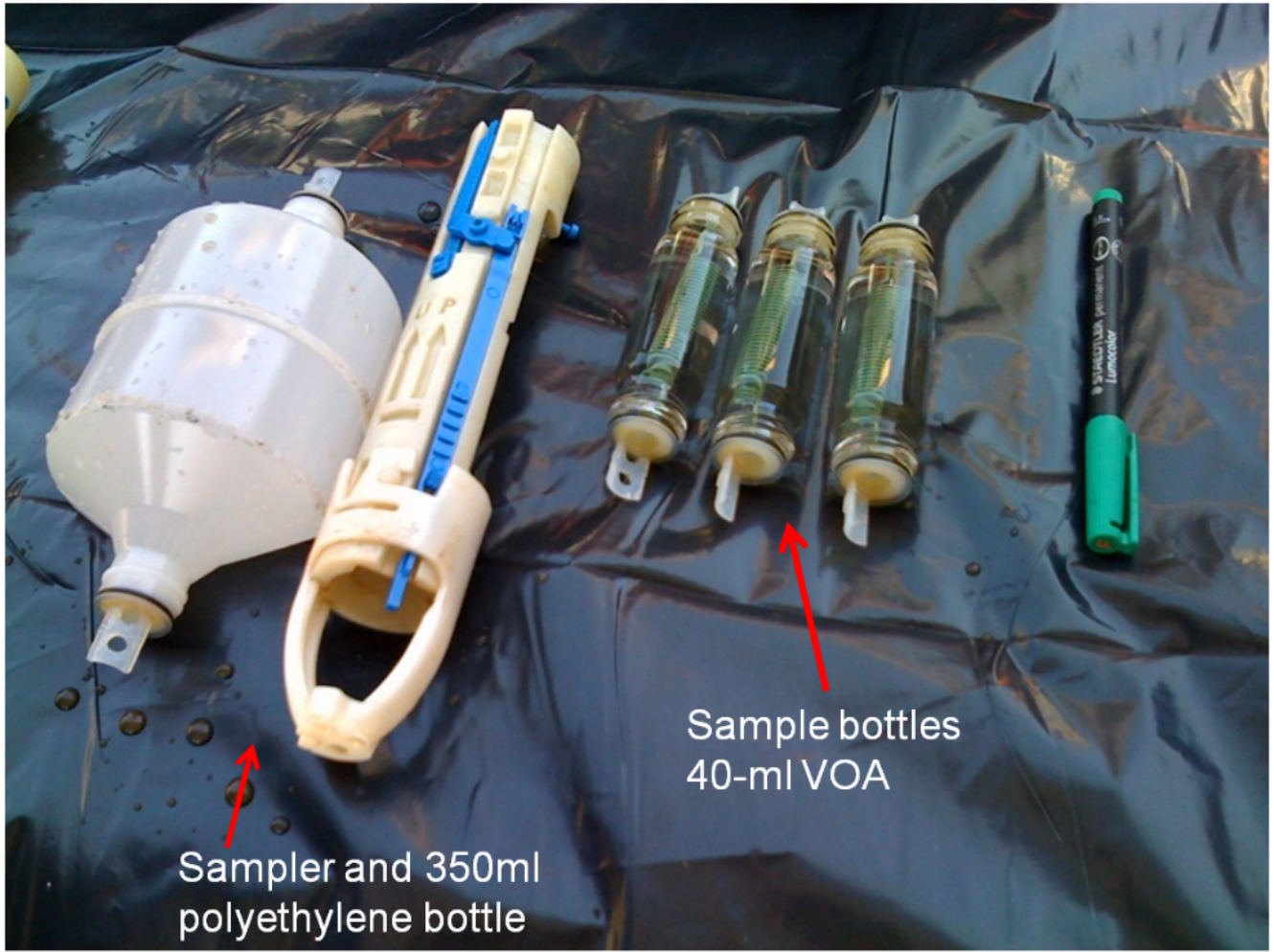
Figure 5-8. Snap sampler.

Source: NJDEP, figure used with permission.

### 5.1.2.2 Installation and Use

The Snap Sampler is a dedicated sampling device/method in which up to six individual bottles are loaded into sampler “modules” designed to hold the specialized double-ended bottles in an open position during deployment. Downhole equipment is selected based on well characteristics, depth, and chemicals to be tested.

There are three types of Snap Sampler modules (Figures 5-9 to 5-11): a 40 ml size that holds the double-ended 40 ml glass VOA vial; a 125/250/350 ml size that holds 125 ml, 250 ml, or 350 ml double-ended HDPE bottles; and a narrow 250 ml size that holds a single 250 ml double-ended HDPE bottle. Two-inch diameter wells are limited to 40 ml–250 ml bottles. Four inch or larger wells are not limited by bottle size.



Sampler and 350ml  
polyethylene bottle

Sample bottles  
40-ml VOA

Figure 5-9. Snap sampler bottle sizes.  
Source: Sandy Britt, used with permission.

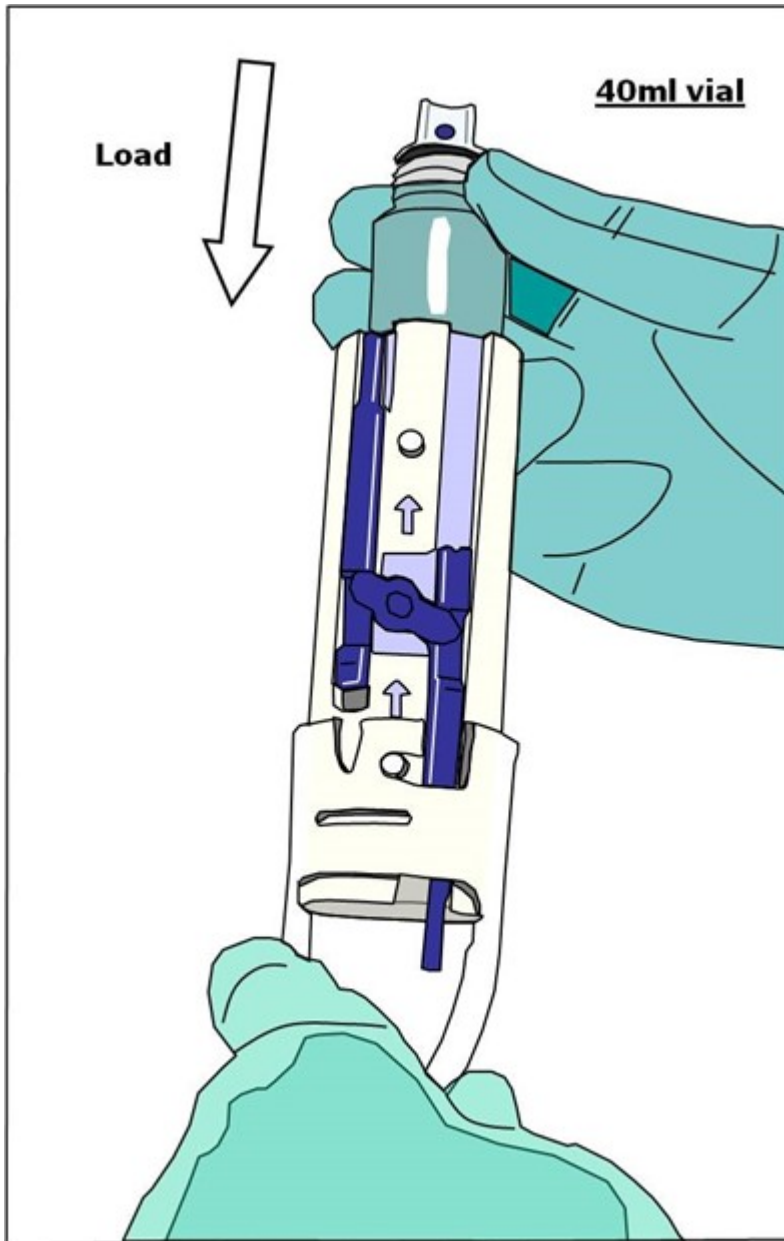


Figure 5-10. Snap sampler 40 ml bottle installation.  
Source: Sandy Britt, used with permission.

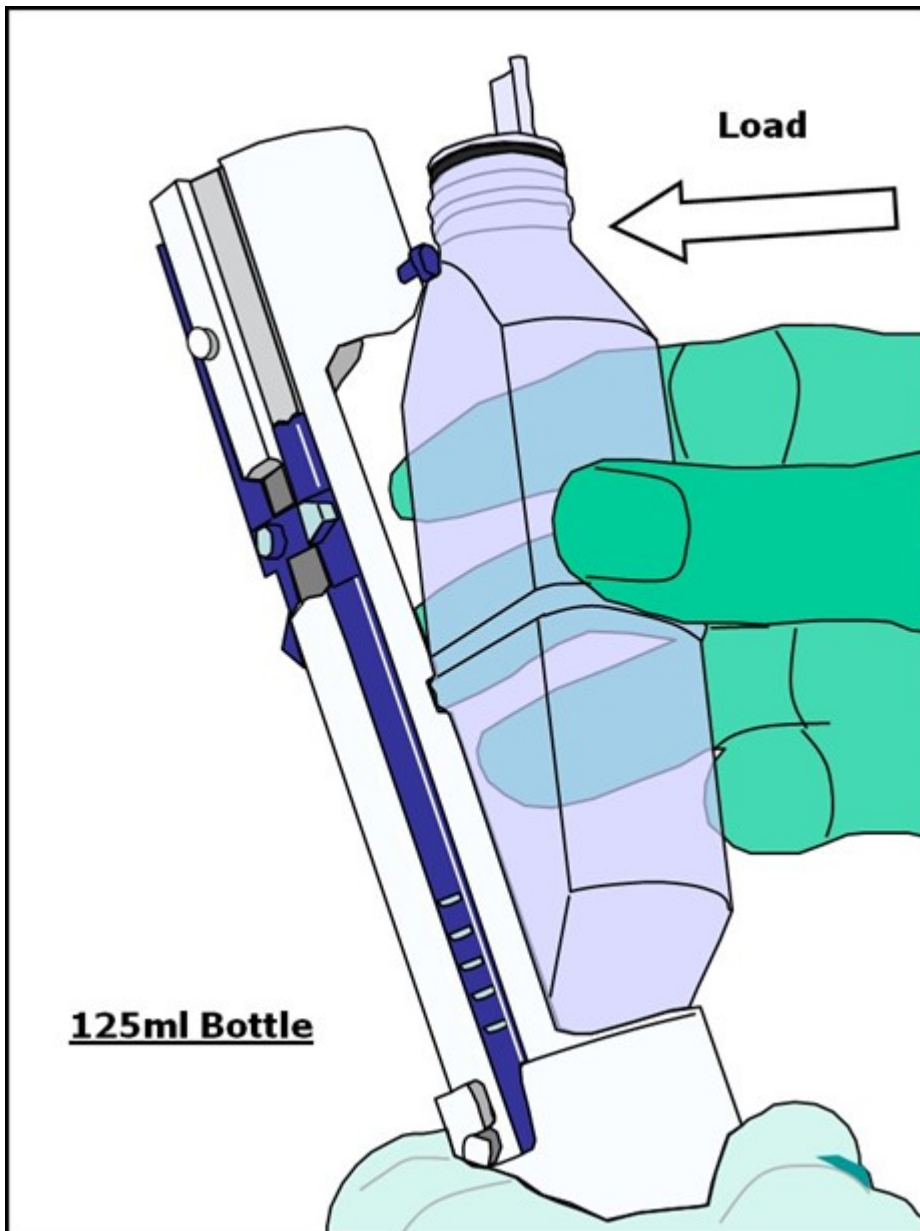


Figure 5-11. Snap sampler 125 ml bottle installation.

Source: Sandy Britt, used with permission

Single bottles or combinations of varied sizes and types are deployed to collect the chemical suite. Up to six modules can be connected in any combination per well assuming adequate water column in the well. A minimum of 12 inches of water column is required per module. You collect only the water needed for analysis. Normally there is little or no “extra” water requiring disposal. Bottle selection and chemical lists can allow the user to collect sufficient water for field parameter measurements.

The equipment setup for a well/site is determined in advance of sampling to ensure that the dedicated equipment is assembled and deployed in advance of the first sampling event. Well construction details, including diameter, depth of screen and target sample position, depth to water, and chemical list, are used to determine the equipment set up. These details are shared with the equipment vendor to generate the well-specific equipment specification. Modules and triggering mechanisms are built for the well to ensure that samples are collected at the specified fixed position in the well during each event.

Deployment of any type of sampling device into a well will disturb the natural flow conditions of resident groundwater. As a result, a well restabilization period is recommended for the Snap Sampler for passive deployments. It may take as little as 24 hours to restabilize for passive sampling, varying 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. Retrieval time 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 upon triggering.

When ready to collect samples, the user activates the manual or pneumatic trigger system to release the bottle closure mechanism. The mechanism releases the Snap Caps, which close on both ends of the Snap Sampler bottle(s). The sampler device is then retrieved from the well with the closed bottle(s). Individual bottles are removed from the sampler modules and prepared to go to the laboratory in many cases without opening or exposing the sample to ambient air. In particular, for the Snap Sampler VOA, this unique feature prevents VOC loss during sample handling. Different compounds volatilize differently, so handling can be variable between individuals, and ambient conditions change daily and seasonally. VOA vials sealed downhole avoid variability and artifact associated with such surface handling. This is a unique feature of the Snap Sampler method.

If preservative is required, the acid or similar compound can be added to the sample through a specially designed cavity in one of the Snap Caps. Standard septa screw caps are then placed on each end of the bottle to complete the collection process. In cases where the sample needs to be transferred to a different container, the Snap Cap is opened at one end and the sample transferred. Preservatives in this instance can be contained in the receiving bottle.

The Snap Sampler VOA vial can be used directly in common laboratory auto sampler equipment, preventing samples from being exposed to ambient air during retrieval, field preparation, or analysis at the lab (unless manual dilutions or re-analyses are required) ( Belluomini et al. 2008<sup>[HM2506CJ]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency. [https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf)). Larger capacity HDPE bottles can be used for most other analytical purposes, either directly or after transfer to lab-supplied containers.

After sample collection, bottles are reloaded into the individual Snap Sampler modules, the string of samples and trigger system is reattached, Snap Caps are set into the open position, and the string is redeployed downhole. As such, the system is ready for sampling at the next event. All equipment is stored within the well assembly.

### 5.1.2.3 Advantages

- Snap Samplers collect a whole water sample, allowing analysis for any dissolved or suspended chemical, including field parameters.
- They collect an unfiltered and undisturbed sample in a container sealed at the moment of bottle closure, largely avoiding sampling artifacts, such as turbidity, or collecting sample inadvertently from a nontarget sample position.
- They collect from a consistent depth position without sampler motion.
- Snap Samplers allow accurate sample point collection from extreme depths.
- Open bottles only need to be submerged to collect samples; they can be used to sample low-yield and short water column wells.
- Snap Samplers require one mobilization for long-term sampling event to both collect and replace bottles.
- They eliminate or reduce IDW.

### 5.1.2.4 Limitations

- Snap Samplers must be deployed in wells 2 inches in diameter or larger.
- Some components of this sampler may contain PFAS, which should be considered based on project DQOs.
- They collect a maximum volume of 1.5 L of water with a single string of samplers in a 2-inch well and 2.1 L in a 4-inch well.

## 5.1.3 Thin-Walled Soil Samplers

### 5.1.3.1 Description and Application

Thin-walled soil samplers are designed to collect representative, undisturbed subsurface soil samples in cohesive soils and clays. These samplers are also known as Shelby tubes (Figure 5-12) or Acker thin-walled samplers and are made from steel,

stainless steel, galvanized steel, or brass. The thin-walled samplers minimize soil disturbances (for example, friction, compaction, and other soil displacements) compared to other types of samplers (for example, auguring, split spoon, or direct push). If used for collecting samples for chemical analyses, the tube is normally constructed of inert material such as stainless steel. Acetate liners can be used with the samplers if needed.

Although the use of Shelby tubes is typically associated with geotechnical investigations, they are also applicable to environmental investigations for purposes such as NAPL verification and characterization. Some examples include laboratory testing for NAPL presence and NAPL mobility. Testing for NAPL presence includes soil core photography with white light for structural information combined with ultraviolet light for the detection of NAPL-impacted locations within the core using an ultraviolet optical screening tool (UVOST). NAPL mobility/saturation testing is used to determine the volume of NAPL in the soil at greater than residual saturation levels and is performed with either centrifuge-based tests or water-drive tests. Providing undisturbed soil samples is pertinent for such analysis to provide depth-specific results to assist with determining site risk characterization, remedy selection, and/or remedial design.

# Shelby Tube

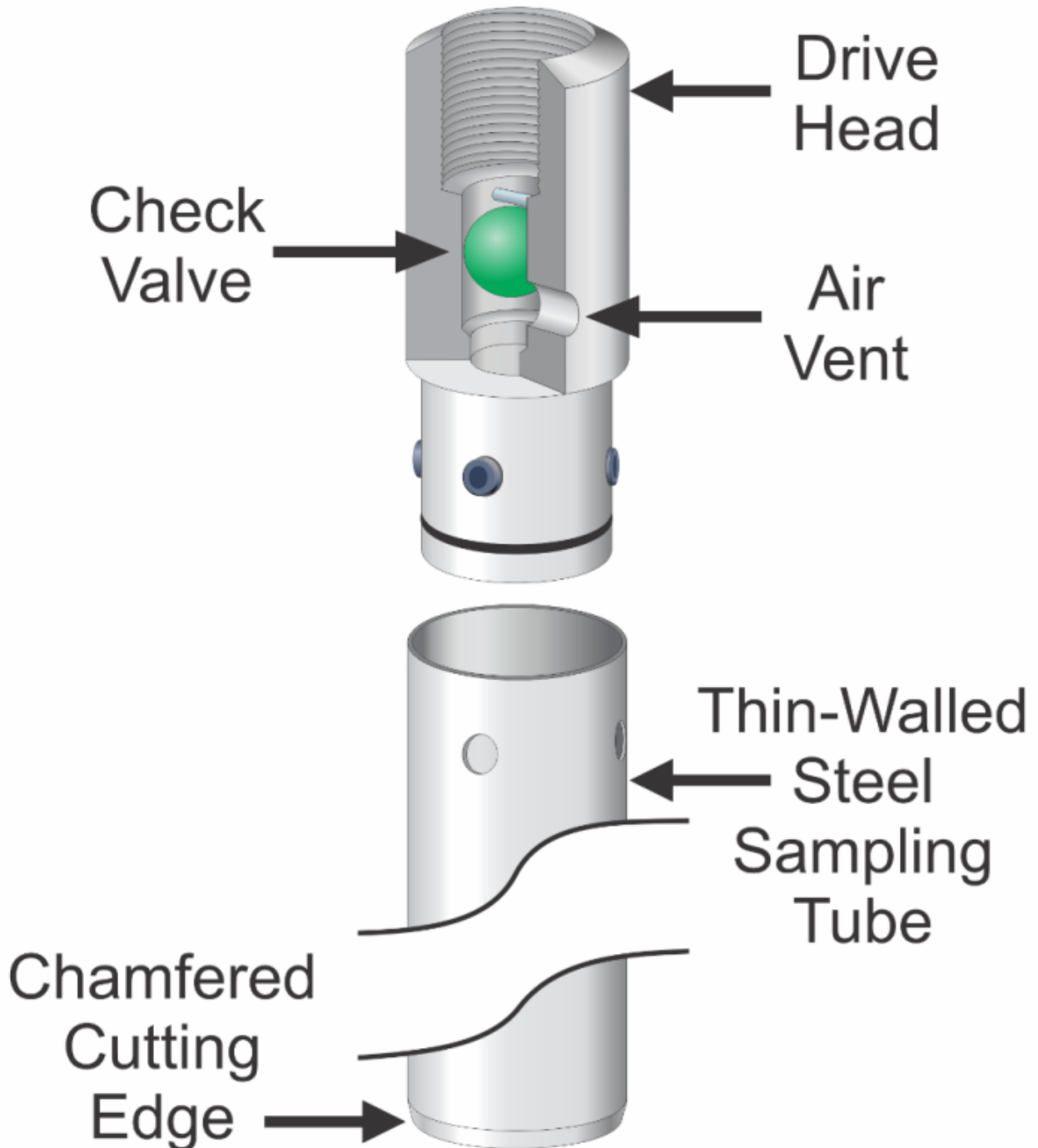


Figure 5-12. Thin-walled soil samplers: Shelby tube.  
Source: NJDEP, figure used with permission.

## 5.1.3.2 Installation and Use

The Shelby tube is the most common type of thin-walled sampler; it is 30 inches in length and comes in various outer diameter (OD) dimensions. Tubes with at least a 3-inch OD and 2.875-inch inside diameter are typically recommended for environmental testing. The downward cutting edge is sharpened and beveled such that its diameter is slightly smaller than the inside of the tube, allowing the sample to slide easily in the tube with little disturbance. The upper end is secured to a drive head, such as direct push tooling or hollow stem auger.

To deploy the sampler, the tube is fastened to a drill rod and is lowered into the borehole to the predetermined depth. At this point, the sampler is pressed into the undisturbed soil by hydraulic force. The tube is pushed 24 inches with a smooth, continuous thrust. If it becomes difficult to retrieve the sample—that is, the sample is partially or completely unretrievable—then leave the tube in place for approximately 10–15 minutes. During this waiting period, the sample should expand slightly to fill the sampler, increasing the probability of preserving the sample during retrieval. After retrieval, the tube containing the sample is removed from the drive head. If an acetate sleeve is used, the sleeve must be removed from the sampler and capped. Doing so keeps the sample in its relatively undisturbed state, and then it can be shipped to the appropriate laboratory. The cap may be a sealed plastic cap or a poured hot wax cap, depending on the project specifications. If no sleeve is used, the tube is then capped and shipped to the laboratory. For more specific instructions on preservation and transportation processes for soil samples, consult with the laboratory to be used. Tubes can be used multiple times following decontamination. Acetate liners are used on a one-time basis.

### 5.1.3.3 Advantages

- Thin-walled soil samplers can sample at discrete depths.
- Thin-walled soil samplers provide an undisturbed soil and/or NAPL sample.
- They provide location- and depth-specific NAPL verification and characterization.

### 5.1.3.4 Limitations

- Thin-walled soil samplers are limited to soils that can be penetrated by the thin wall of the sampler.
- They are not recommended for soils containing gravel, larger size soil particles, or hard, cemented soils.
- Very soft and wet soils tend to drop out of the sampler.
- The use of fluids is prohibited for many of the tests that use this sampling method, limiting the collection method.

## 5.2 Equilibration-based Passive Samplers

Equilibrium-based samplers function in aqueous media (groundwater, surface water, sediment pore water) and gas media where chemicals diffuse, usually through a semipermeable membrane, to equilibrate in the medium present in the sampler under naturally occurring conditions during the sampling period. Samplers that are used for determining trace metals should be deoxygenated (both the receiving media and sampler body if PTFE or polycarbonate) to reduce introduction of oxygen into potentially reducing environments, especially for relatively short deployment times.

During equilibration, molecules may continue to move in and out of the sampler, in response to changing concentrations, to maintain a dynamic equilibrium with the surrounding medium. Contaminant concentrations are measured directly from the receiving media of the equilibrium device.

The type of membrane determines which chemicals can be sampled, and different devices incorporate different membranes and configurations.

Samplers must be in place for at least the minimum residence time, which is the length of time from installation until equilibrium of the target chemicals can be reasonably achieved. Residence time for certain samplers and chemicals may be project-specific. The minimum residence time must include the time for the sampling environment to restabilize hydraulically, if it is disturbed when the sampler is placed, and the time it takes for diffusion of the target molecules to reach chemical equilibrium. Most equilibrium samplers have no functional maximum residence time. For example, many groundwater samplers can be left in place at one event and recovered at another, eliminating the time and cost of an additional mobilization for sampler recovery. Site-specific considerations such as loss or vandalism may be evaluated to understand the security and integrity of the sampler. The resulting sample can be analyzed by standard lab methods to directly produce a concentration result that represents the time-weighted average of the past few days of residence.

Table 5-2, adapted from USGS's Table 4 ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.), lists chemical families that can be analyzed using the noted passive sampling technologies. Always check with the relevant state agency, sampler manufacturer, and laboratory to confirm that the selected technology meets the project's DQOs.

<b>Passive Equilibration Sampling Technologies</b>	<b>PDB</b>	<b>DMPDB</b>	<b>NSPDS</b>	<b>Peeper*</b>	<b>Regenerated Cellulose Dialysis Membrane Sampler (RCDM)</b>	<b>RPPS</b>	<b>Polymeric**</b>	<b>PISCES</b>	<b>Ceramic Diffusion</b>
<b>Chemical Constituents and Characteristics</b>									
<b>Field physiochemical characteristics</b> (Temp, pH, SC, DO, ORP)	Some	Most	Some	Some	Some	Some	N/A	N/A	Some
<b>Major cation and anions</b> (Ca, Mg, Na, K, HCO <sub>3</sub> , Cl, SO <sub>4</sub> , F, Br)	N/A	Most	Most	Most	Most	Most	N/A	N/A	N/A
<b>Nutrients</b> (NO <sub>3</sub> , NO <sub>2</sub> , NH <sub>4</sub> , PO <sub>4</sub> )	N/A	Most	Most	Most	Some	Some	N/A	N/A	N/A
<b>Trace elements (metals)</b> (Fe, Mn, Al, Ag, Zn, and others)	N/A	Most	Some	Most	Most	Most	N/A	N/A	N/A
<b>Perchlorate (ClO<sub>4</sub>)</b>	N/A	Most	Most	Most	Most	Most	N/A	N/A	N/A
<b>Organic carbon</b> (dissolved or total)	N/A	Most	Most	Some (Dissolved)	Most	Most	N/A	N/A	NT
<b>Dissolved hydrocarbon gases</b> (Methane, ethane, ethene)	Most	Most	Most	Most	Most	Most	N/A	N/A	NT
<b>Volatile organic compounds</b> (Chlorinated solvents, BTEX)	Some	Most	Some	Most	Some	Some	N/A	N/A	Some
<b>Semivolatile organics</b> (1,4-Dioxane, BN, Phenols, PAH, PCB, dioxins, furans)	Some	Some	Some	NT	Some	Some	Some	Some	Some
<b>Pesticides, herbicides, and fungicides</b> (organoCl, organoPO <sub>4</sub> )	N/A	Some	NT	NT	NT	NT	NT	Some	NT

<b>Passive Equilibration Sampling Technologies</b>	<b>PDB</b>	<b>DMPDB</b>	<b>NSPDS</b>	<b>Peeper*</b>	<b>Regenerated Cellulose Dialysis Membrane Sampler (RCDM)</b>	<b>RPPS</b>	<b>Polymeric**</b>	<b>PISCES</b>	<b>Ceramic Diffusion</b>
<b>Explosive compounds</b> (RDX, HMX, TNT)	N/A	Some	Some	NT	Some	Some	N/A	N/A	NT
<b>Poly- and perfluoroalkyl substances</b> (PFASs)	N/A	Some	NT	Some	Some	NT	Some	N/A	Some
<b>Pharmaceuticals</b> (Drugs, fragrances, hormones)	NT	Some	NT	NT	NT	NT	N/A	N/A	Some
<b>Minerals</b> (pyrite, mackinawite)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>Microbial Population sampling</b> (e.g., Dehalococcoides)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

\*For information regarding the applicable analytes for the specific peeper technologies, please see Table 5-3.

\*\*For information regarding the applicable analytes for the specific polymeric technologies, please see Table 5-4.

<b>Table 5-2 Key</b>	
Most	Most compounds are compatible with the sampler
Some	Some compounds are compatible with the sampler
NT	Not tested (no study to support)
N/A	Not applicable to this sampler

<b>Table 5-2 Acronym Key</b>
[Temp, temperature; SC, specific conductivity; DO, dissolved oxygen; ORP, oxidation-reduction potential; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO <sub>3</sub> , bicarbonate; Cl, chloride; SO <sub>4</sub> , sulfate; F, fluoride; Br, bromide; NO <sub>3</sub> , nitrate, NO <sub>2</sub> , nitrite; NH <sub>4</sub> , ammonium; PO <sub>4</sub> , phosphate; Fe, iron; Mn, manganese; Al, aluminum; Ag, silver; Zn, zinc; ClO <sub>4</sub> , perchlorate; BTEX, benzene, toluene, ethylbenzene and xylene; BN, base-neutral organics; PAH, polycyclic aromatic hydrocarbons; PCB, polychlorinated biphenyls; organoCl, organochlorine; organoPO <sub>4</sub> , organophosphate; RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane; TNT, trinitrotoluene; TOC, total organic carbon; Hg, mercury; CO <sub>2</sub> , carbon dioxide]

## 5.2.1 Passive Diffusion Bag Sampler (PDB)

### 5.2.1.1 Description and Application

Passive diffusion bag (PDB) samplers are a relatively mature passive diffusion technology, having been developed in the late 1990s. The technology has been evaluated against traditional purge sampling techniques in groundwater and has become a

widely accepted technique for determining concentrations of VOCs in groundwater, surface water, and sediment pore water. PDB samplers can be used to collect samples for analysis of most nonpolar VOCs, in addition to select SVOCs (including naphthalene) and dissolved hydrocarbon gases (methane, ethane, ethene) ( USGS 2020<sup>[F4X9NMPG]</sup> USGS. 2020. Passive Sampling of Groundwater Wells for Determination of Water Chemistry. Collection of Water Data by Direct Measurement. U.S. Department of the Interior.).

PDBs operate using the principles of molecular diffusion across the semipermeable polyethylene membrane. The DI water in the PDB contains no organic compounds when installed. Therefore, a concentration gradient exists between the compounds in the target aqueous media (groundwater, surface water, or pore water) and the interior of the membrane. Compounds diffuse through the membrane until the concentration between the target media and the water in the sampler equilibrates. The PDB maintains dynamic equilibrium so if chemical concentrations in the target media change, the concentrations in the sampler will adjust accordingly ( Ertel et al. 2011<sup>[WRA2SQGD]</sup> Ertel, T, H.J. Kirchholtes, P.V. Schnakenburg, U. Schollenberger, S. Spitzberg, and W. Schäfer. 2011. "FOKS Handbook for Integral Groundwater Investigation: Toolbox for the Identification of Key Sources of Groundwater Contamination." CENTRAL EUROPE Programme.

[http://projectfoks.zuova.cz/wp-content/uploads/2012/06/toolbox\\_for\\_the\\_identification\\_of\\_key\\_sources\\_of\\_groundwater\\_contamination.pdf](http://projectfoks.zuova.cz/wp-content/uploads/2012/06/toolbox_for_the_identification_of_key_sources_of_groundwater_contamination.pdf)). Diffusion rates vary by compound, and the sample in the PDB typically represents the concentrations in the target media over the last several days prior to removal ( Ertel et al. 2011<sup>[WRA2SQGD]</sup> Ertel, T, H.J. Kirchholtes, P.V. Schnakenburg, U. Schollenberger, S. Spitzberg, and W. Schäfer. 2011. "FOKS Handbook for Integral Groundwater Investigation: Toolbox for the Identification of Key Sources of Groundwater Contamination." CENTRAL EUROPE Programme. [http://projectfoks.zuova.cz/wp-content/uploads/2012/06/toolbox\\_for\\_the\\_identification\\_of\\_key\\_sources\\_of\\_groundwater\\_contamination.pdf](http://projectfoks.zuova.cz/wp-content/uploads/2012/06/toolbox_for_the_identification_of_key_sources_of_groundwater_contamination.pdf)).

A PDB sampler consists of an LDPE sleeve filled with DI water. The LDPE sleeve (typically 2-4 mil [0.002-0.004 inch] in thickness) serves as a semipermeable membrane to allow for molecular diffusion of VOCs from the target media (that is, groundwater, surface water, or sediment pore water). PDB samplers are commercially available, either prefilled with DI water by the manufacturer or filled at a laboratory or in the field with a fill port and plug. To prevent damage during deployment and retrieval, commercially manufactured samplers typically come in a protective polyethylene mesh sleeve (Figure 5-13). PDB samplers are typically 12-24 inches long and diameters range from 0.75 to 1.75 inches, which allows deployment into 1-inch diameter or larger monitoring wells (Eon Products, n.d.). Sample volumes vary with the length and diameter of each sampler; for example, a 1-inch diameter and 18-inch-long sampler provides approximately 230 milliliters of sample (Eon Products, n.d.). The standard size PDB for a 2-inch diameter monitoring well is 1.7 inch diameter and 18 inches long (350 ml). PDB samplers are deployed on a reusable weighted polypropylene suspension tether that can be configured and provided by the PDB manufacturer to ensure repeated placement at the desired depth (Eon Products, n.d.). Other tether materials can be used if they meet project DQOs.

# Passive Diffusion Bag (PDB) Sampler

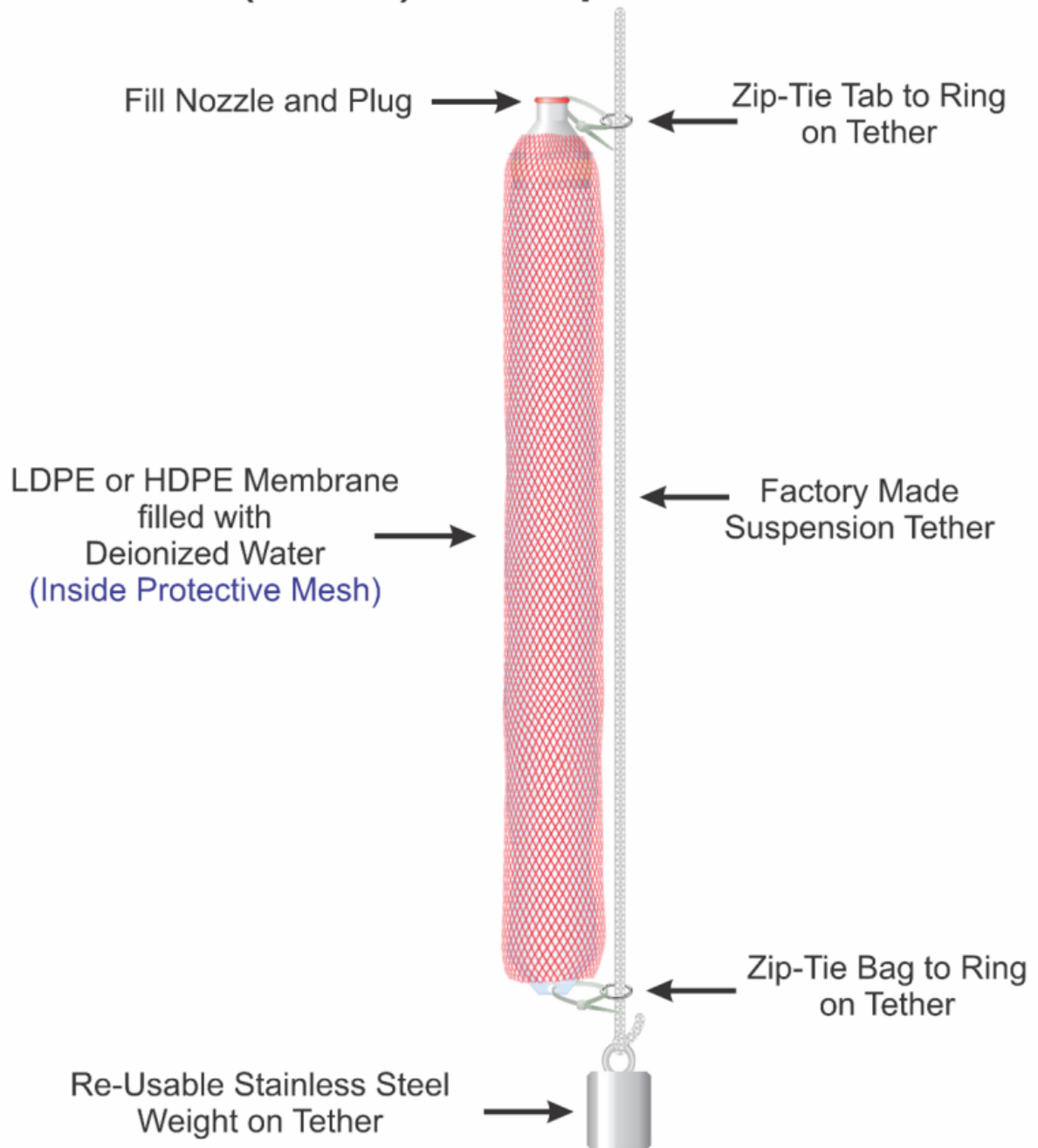


Figure 5-13. Passive diffusion bag sampler.  
Source: NJDEP, figure used with permission.

## 5.2.1.2 Installation and Use

Operating a PDB is straightforward. To deploy the device in monitoring wells, the PDB sampler must first be attached to a premeasured suspension tether and weight. It is then lowered to the predetermined location within the screened interval of the sampling well. For deployment in surface water or sediment (for pore water), PDB samplers are typically placed within protective canisters, which are tethered to a polypropylene or equivalent line and secured to a stationary object (for example, onshore) or to a flotation device to facilitate location and retrieval. Placement of PDBs in surface water and/or

sediment should consider current and future flow and/or tides to ensure the samplers will be sufficiently inundated with water during the entire deployment period. For surface water, PDBs should be placed at the desired depth interval. Additional weights and/or lines can be used to secure the sampler at the desired interval. For sediment pore water, PDBs are deployed by manually pushing the protective canister into the sediment (if soft) to the desired depth. For coarser sediment, a trowel or shovel can be used to gently lift the sediment to allow the PDB to be inserted. Sediment should be placed back around the PDB to ensure it is completely covered by sediment. In deeper water, a push-pole device may be used to push the PDBs into the sediment, although it is recommended to use video surveillance to verify that the PDB has indeed been deployed completely. Alternatively, divers may be used to deploy the PDBs.

Equilibration times are well- and compound-dependent. The recommended minimum equilibration period for PDBs is 10–14 days, although equilibration of many VOCs may occur within 1–4 days. Additional time may be required for low-yield groundwater aquifers. The installation of the sampler can cause the water in the monitoring well to become stratigraphically mixed. To account for this, it is necessary to allot an appropriate amount of time for the chemical concentrations in the well to re-stratify and for flow to resume according to the natural conditions ( Ertel et al. 2011<sup>[WRA25QGD]</sup> Ertel, T, H.J. Kirchholtes, P.V. Schnakenburg, U. Schollenberger, S. Spitzberg, and W. Schäfer. 2011. "FOKS Handbook for Integral Groundwater Investigation: Toolbox for the Identification of Key Sources of Groundwater Contamination." CENTRAL EUROPE Programme. [http://projectfoks.zuova.cz/wp-content/uploads/2012/06/toolbox\\_for\\_the\\_identification\\_of\\_key\\_sources\\_of\\_groundwater\\_contamination.pdf](http://projectfoks.zuova.cz/wp-content/uploads/2012/06/toolbox_for_the_identification_of_key_sources_of_groundwater_contamination.pdf).) Samplers can be left in monitoring wells between sampling events, then removed and replaced with a new sampler to abate mobilization and augment efficiency.

Recovery is a simple matter of pulling the sampler out of the monitoring well, water column, or sediment and transferring the contents to appropriate containers, typically VOA vials. Samples can be transferred directly into sample containers by carefully cutting or slicing the PDB or using discharge "straws" to pierce the membrane. This needs to be done within minutes of removing the sample from submersion to prevent a loss of volatiles to the air. Transfer of water from the PDB to sample containers is required before shipping samples to the laboratory.

In groundwater monitoring wells, PDBs can be installed at one or more intervals in the well screen and left in place under natural flow conditions ( Belluomini et al. 2008<sup>[HM25Q6C]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency. [https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf).) Natural flow transports target chemicals in the aquifer into the well through the screen. As compared to purge and pump procedures, this technique results in significant cost savings due to less field mobilization time and reduced wastewater disposal.

PDBs also provide depth-specific profiling for compounds and concentrations. The PDBs' ability to reflect dissolved target chemicals concentrations at a discrete depth allows the determination of stratification and vertical concentration gradients of target chemicals in groundwater. A PDB sampler should not be assumed to represent more than 5 feet of a saturated well screen unless longer intervals in a given well have been determined to be homogeneous. Interval target chemical concentrations can be measured at specific well screen depths by positioning PDB samplers in series, as shown in Figure 5-14. Hanging the samplers as such can result in the collection of information about the well's hydrogeologic attributes and determining the correct positioning of future single PDB samplers.

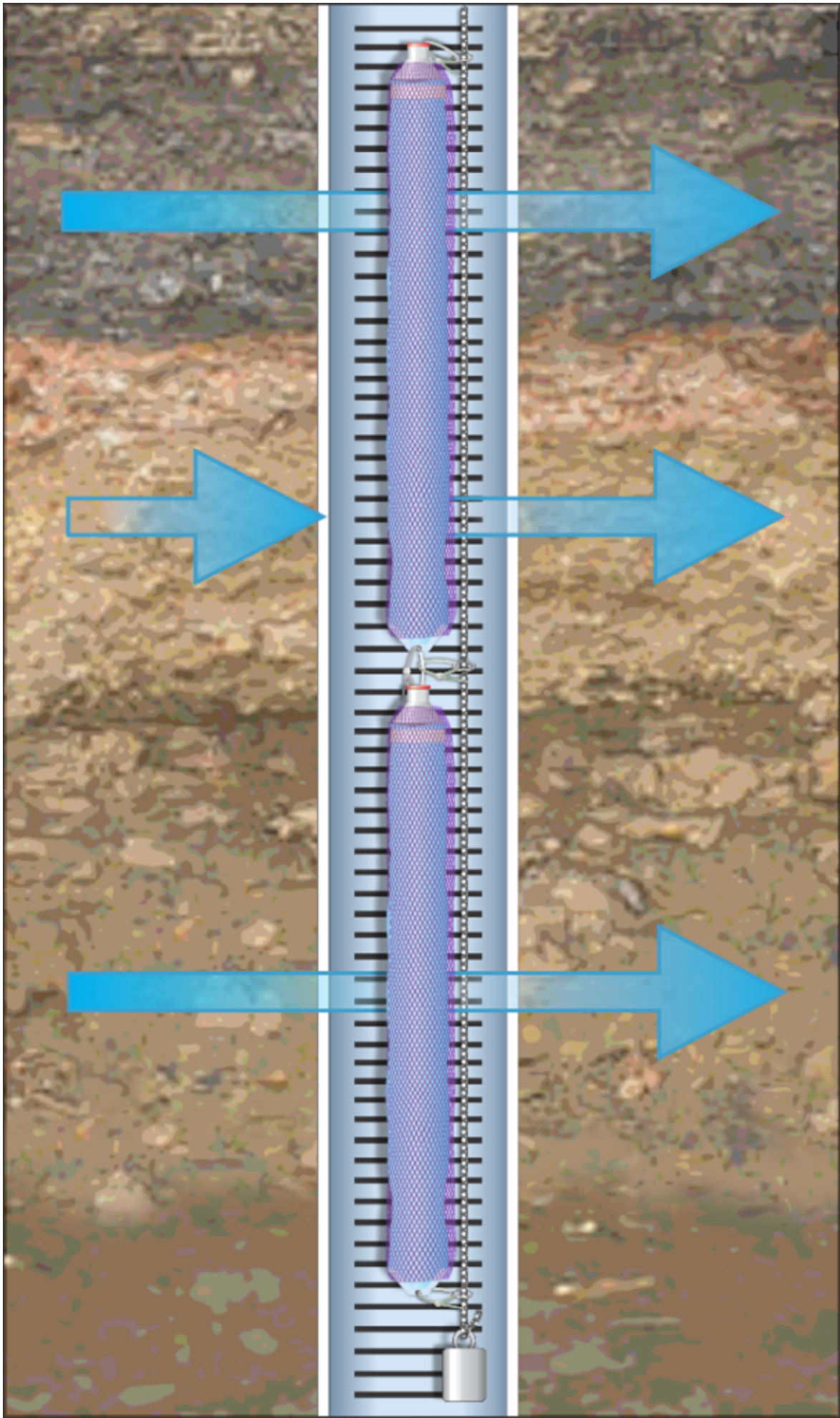


Figure 5-14. Deployment of multiple PDB samplers in a vertically profiled well.

Source: NJDEP, figure used with permission.

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 also successfully used PDBs to collect representative VOC concentrations from surface water and sediment pore water. Because polyethylene-based PDBs are semipermeable, certain compounds are restricted from diffusing through the membrane. Because the semipermeable PDB membrane allows diffusion only of nonpolar VOCs, the PDB can be used during active remediation to screen out non-VOC and oxidizing agents such as potassium permanganate while allowing residual VOCs, such as tetrachloroethylene (PCE), to be collected to measure remediation progress or effectiveness.

Metals and other nonorganics are not generally sampled using a PDB sampler because they cannot diffuse through the membrane. Compounds with a molecule size less than 10 angstroms, such as nonpolar VOCs, are recommended.

### 5.2.1.3 Advantages

- PDB samplers have become a commonly accepted method for establishing concentrations of VOCs in groundwater monitoring wells as well as surface water and sediment pore water.
- PDBs are easy to deploy and retrieve, allowing for rapid installation and sample collection.
- Sample collection in groundwater monitoring wells does not require purging, which provides ease of use and reduced labor costs and purge water disposal costs.
- PDBs reduce matrix interference from turbidity due to the small pore size of the LDPE membrane.
- PDB samplers are commercially available and are inexpensive to purchase or construct.
- PDB samplers have been manufactured to sample groundwater monitoring wells as small as 0.75-inch inside diameter.
- The samplers can be deployed for long residence times (that is, annual or biannual sampling events).
- Samplers can collect samples from discrete intervals in groundwater monitoring wells or surface water to produce a vertical contaminant profile.
- Samples have been successfully retrieved at depths more than 700 feet bgs.
- The PDB is a disposable sampler, reducing decontamination time.

### 5.2.1.4 Limitations

- Because the range of chemicals that can diffuse into PDB samplers is limited, these samplers should not be used for initial investigations where the chemicals of concern have yet to be identified. PDBs should be deployed mainly at well-characterized sites where the chemicals of concern have been identified as VOC compounds.
- PDBs collect a time-weighted discrete interval sample. Once the samplers have reached the minimum residence time, the samples are representative of concentrations present near time of removal. This is advantageous in aquifers with low hydraulic conductivity where chemicals migrate slowly but is limited in capturing contaminant spikes in aquifers with high hydraulic conductivity (that is, karst aquifers).
- PDBs require a minimum equilibration time of 2 weeks, which may not be suitable for rapid response situations

## 5.2.2 Dual Membrane Passive Diffusion Bag Sampler (DMPDB)

### 5.2.2.1 Description and Application

The Dual Membrane Passive Diffusion sampler (DMPDB) (Figure 5-15) is an equilibrium-based passive diffusion sampler that has been commercially available since 2014 for monitoring aqueous media, particularly groundwater (Eon Products, n.d.<sup>[DDXS64KH]</sup> Eon Products. n.d. EON Dual Membrane Passive Diffusion Samplers (DMPDBTM). <https://store.eonpro.com/eon-dual-membrane-passive-diffusion-samplers-dmpdb-2900.aspx>). The DMPDB operates using the same diffusion principles of established PDB sampling, but it uses two different semipermeable membranes on the same sampler, allowing for the diffusion of large or polar molecules and the sampling of an expanded list of compounds and water quality parameters.

# Dual Membrane™ Passive Diffusion Bag (DMPDB™) Sampler

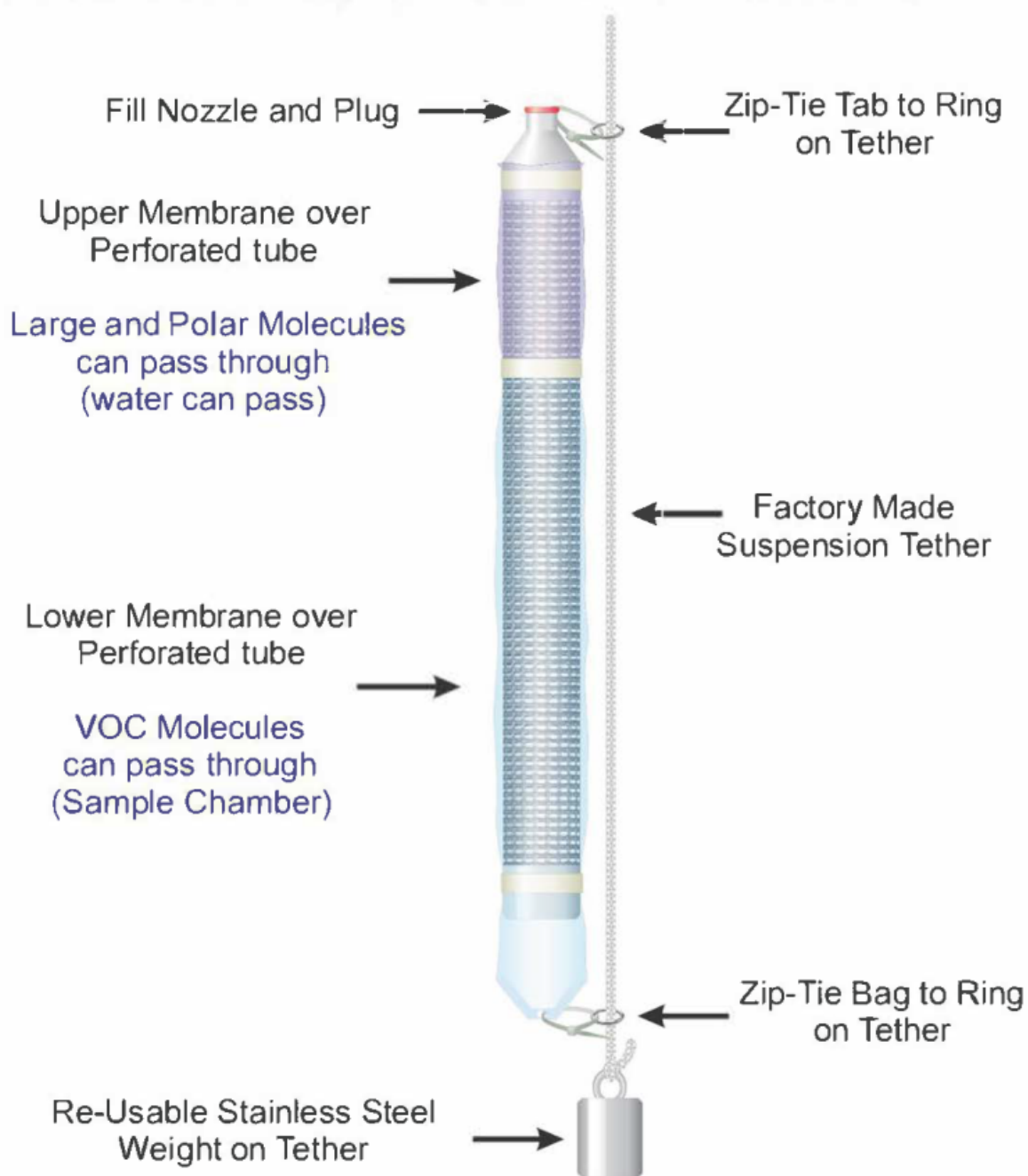


Figure 5-15. Dual membrane passive diffusion sampler.

Source: NJDEP, figure used with permission.

The DMPDB consists of two semipermeable membranes wrapped in series around a frame made of a rigid, perforated polypropylene tube (1.75" diameter), forming a single sample reservoir. The membrane on the lower section of this tube is made of LDPE or HDPE, which allows the diffusion of VOCs. Because the polyethylene portion is hydrophobic, it does not allow water molecules to pass, forming the reservoir where the sample is held. The membrane on the upper portion of the tube is made from more porous material that allows the diffusion of large or polar molecules between the surrounding aqueous media and the DMPDB. The upper membrane of the standard DMPDB is made of hydrophilic polyamide material (150-micron ( $\mu\text{m}$ ) pores). The upper membrane porosity allows information on field parameters (pH, dissolved oxygen, etc.)

to be collected. This document primarily refers to this standard version of the DMPDB. However, custom DMPDB versions have been made with other upper membrane materials with pores as small as 18 angstroms to meet specific site or contaminant conditions.

DMPDBs may be used in sampling of aqueous environments, including but not limited to groundwater and sediment pore water. The sampling technique allows for collection of samples from turbid aqueous media where traditional sampling methods may bias sample results or produce samples that require additional laboratory steps prior to undergoing analysis. DMPDBs do not create flow that could mobilize sediments, and the sampler membranes ensure that the aqueous sample represents only an unfiltered representation of suspended particulates smaller than the membrane pores.

When using DMPDBs in groundwater, the samplers act similarly to other equilibrium-based samplers. The DMPDB is deployed into the saturated screen or fractured bedrock in groundwater monitoring wells, where it is in contact with the natural groundwater flow through the well. The disturbance created during deployment is minimal, and the sampler can be used to target a specific interval of groundwater within the well screen. In cases where contaminant stratification may be present, passive sampling via the DMPDB allows for targeted interval sampling by deploying multiple samplers on a single suspension tether at target intervals along the saturated screen. The DMPDB will provide interval-specific results without mixing that may occur during active purging or low-flow pumping.

The DMPDB may be deployed in sediment for sampling of pore water through installation of a screened canister. Canisters should be installed to ensure the DMPDB remains submerged for the entirety of the equilibration period and should be flagged and anchored to ensure they remain in place. Diffusion/deployment times may be extended on a case-by-case basis for different chemicals.

#### **5.2.2.2 Installation and Use**

The DMPDB is filled with DI water during field mobilization and lowered into the interval of interest in the well, on a weighted suspension tether, where it intercepts natural water flow. Molecules enter the DMPDB by diffusing through the membranes into the sample chamber/reservoir. Although VOCs can enter the sampler through either membrane, larger or polar molecules, including water, as well as background colloids, diffuse through the larger pores of the upper membrane. Once inside the sampler, molecules diffuse throughout the water column in the DMPDB's reservoir until equilibrium is reached within the sampler and with the surrounding aqueous media. The recommended minimum residence time for the DMPDB to reach equilibrium and provide a representative sample is 21 days, which includes time for the surrounding environment to restabilize and return to natural flow conditions after being disturbed by sampler placement, as well as time for individual contaminant molecules to come to equilibrium within the DMPDB. Actual diffusion time (excluding surrounding area restabilization) ranges from approximately 1 day to 2 weeks, depending on the diffusion coefficients of the molecules of each contaminant of concern. Once the minimum residence time is met, the samplers can be left in place indefinitely and will represent the time-weighted average concentrations of the time surrounding retrieval. Some compounds, such as PFAS and 1,4-dioxane, equilibrate within about a week after well stabilization. Others, such as most SVOCs, will take longer. There is no standard maximum residence time for sample accuracy, because the diffusion process keeps the samplers in a dynamic equilibrium with the surrounding water, and the DMPDB materials are all chemically resistant to typical chemicals found in aqueous environments. Site-specific conditions may warrant a maximum residence time for deployment.

When the DMPDB is retrieved from the well or other casing, water in the upper portion of the sampler flows out through the pores in the upper membrane as the sampler exits the water column, leaving the equilibrated sample in the lower reservoir. The polyethylene sample chamber of the DMPDB is then punctured with a "juice box"-like straw, and the sample is discharged through the straw directly into laboratory-provided sample containers. Because there is no maximum deployment time for the DMPDB, it is common practice at many sites to replace the DMPDB being sampled at the current event with the sampler for the next event.

Compound-specific information:

- Can be used for all VOCs, similar to previous standard PDB technology
- Cations, anions, metals (dissolved and total), nitrate/nitrite, SVOCs
- Emerging contaminants: 1,4-dioxane *and* PFAS

Data from DMPDB use for a variety of compounds and water quality parameters are steadily increasing over time as more side-by-side field and case studies are conducted. For the most up-to-date information on studies and sampler capabilities,

contact the manufacturer.

Individual DMPDB sample volume varies by the sampler diameter and length selected to fit the available saturated screen. DMPDBs are approximately 1.7 inches in diameter to fit 2-inch schedule 40 and larger wells and are available in standard lengths of 16 inches (250+ ml), 24 inches (500+ ml), 28 inches (650+ ml), 31 inches (750+ ml), and 40 inches (1+ L). Custom sizes are available. A single DMPDB can acquire greater than 1 liter of sample from a 2-inch monitoring well with 5 feet of saturated screen. Multiple DMPDBs can be attached to the same suspension tether to add sample volume or to sample discrete intervals in wells with longer saturated screens. Custom installation configuration is required for 2-inch schedule 80 wells.

### 5.2.2.3 Advantages

- DMPDBs are effective for sampling a multitude of chemicals in groundwater, including VOCs, some SVOCs, trace metals, anions, cations, and contaminants of emerging concern, including 1,4-dioxane and PFAS, according to lab and/or field studies.
- They allow consistency in collection depth over repeated sampling events due to predetermined sample location (tether for groundwater or sampler housing for other media).
- They allow for easier vertical profiling to investigate stratified contaminant zones, multiple well screens, and bedrock fracture zones using discrete predetermined sample depths.
- DMPDBs allows the collection of field parameters, including dissolved oxygen, pH, and temperature, due to upper membrane design.
- They are constructed of nonbiodegradable materials, allowing the sampler to remain in place for extended time periods.
- DMPDB samples will include representative background colloids/suspended solids, without contributing additional, method-induced turbidity. Filtration practices should be followed if required for specific project and/or lab analysis.
- DMPDBs reduce cross-contamination risk because samplers are single use and are deployed using systems dedicated to sample locations (for example, tethers or sediment canisters).
- They eliminate or substantially decrease the generation of IDW.
- Sampling apparatus (tether, sediment canister, etc.) is reusable with only the sampler replaced for each sampling event and eliminates the use of gasoline or battery-powered sources often required by pumps. Although the DMPDB itself is single use, it has a smaller material footprint than most single-use bailers and tubing used for groundwater monitoring.
- When retrieved for sampling, they can be immediately replaced with a new DMPDB on the designated tether and can reside in place until the next sampling event, decreasing labor costs associated with sample collection activities.

### 5.2.2.4 Limitations

- DMPDBs provide limited sample volume, requiring consideration of laboratory sample volume requirements.
- The standard version requires field personnel to fill sampler with DI water in the field. Due to the hydrophilic polyamide upper membrane, the sampler cannot be transported prefilled and must be handled and deployed upright once filled to prevent spilling.
- They are restricted by monitoring well or sampler housing construction, requiring an inside diameter of at least 2 inches or larger to avoid abrasions if obstructions or rough edges are encountered.
- DMPDBs require extended deployment time of 2–3 weeks for equilibration of some chemicals both into and within the sampler, depending on the type of contaminant and well recharge rates. Investigations requiring shorter sampling frequencies may not be feasible.
- The standard version does not collect a “dissolved-only” sample. Use of a custom upper membrane may provide a dissolved-only sample.
- Prior to using in environments with exceptionally high solvent concentrations, contact the manufacturer to discuss options for maintaining integrity of sampler materials.
- DMPDBs should be deoxygenated (both the receiving media and sampler body if PTFE or polycarbonate) to reduce introduction of oxygen into potentially reducing environments, especially for relatively short deployment times.

## 5.2.3 Nylon Screen Passive Diffusion Sampler (NSPDS)

### 5.2.3.1 Description and Application

The nylon screen passive diffusion sampler (NSPDS) (Figure 5-16) is a passive equilibrium sampler for surface and groundwater. NSPDSs were developed to sample for a broader array of analytes than the PDB sampler ( Belluomini et al. 2008<sup>[HM2506CJ]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency.

[https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf).) The NSPDS is constructed using polypropylene wide-mouth bottles, a ring style cap, and a square of nylon mesh screen with a typical pore size of 125–250  $\mu\text{m}$ .

The bottles are filled with the appropriate type of DI water based on the project goals. A sheet of nylon screen is placed over the mouth, and the cap is screwed on. The sample bottle can be deployed alone or can be stacked in a polyethylene mesh bag. The number of bottles is dependent on the required sample volume for the project.

NSPDSs operate using the principles of molecular diffusion across the nylon screen mesh. The NSPDS bottles are filled with analyte-free DI water prior to installation. Therefore, a concentration gradient exists between the compounds in the target aqueous media (groundwater, surface water, or pore water) and the interior of the NSPDS bottles. Compounds diffuse through the nylon screen mesh until the concentration between the target media and the water in the sampler equilibrates. The NSPDS maintains dynamic equilibrium so that if chemical concentrations in the target media change, the concentrations in the sampler will adjust accordingly. Diffusion rates vary by compound, so the sample in the NSPDS bottles typically represents the concentrations in the target media over the last several days prior to removal.

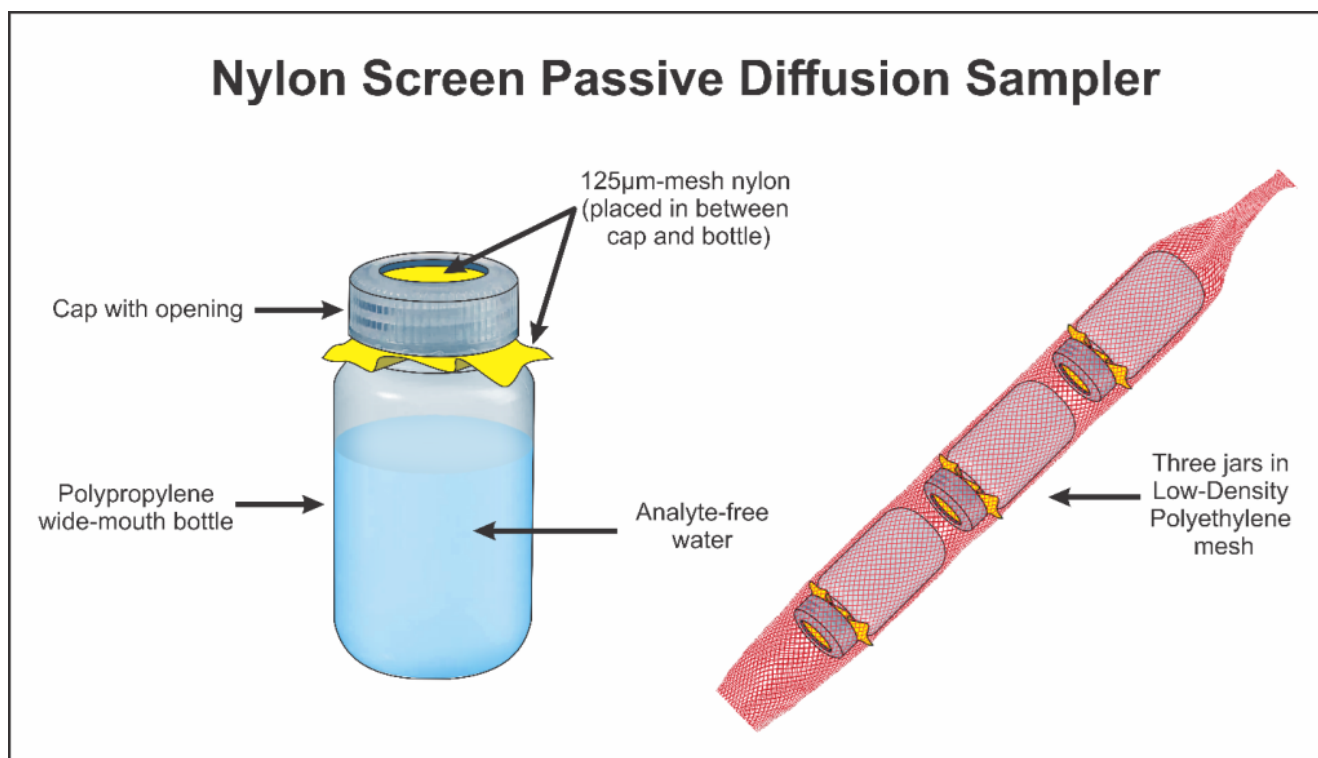


Figure 5-16. Nylon screen passive diffusion sampler.

Source: NJDEP, figure used with permission.

### 5.2.3.2 Installation and Use

For deployment in wells, the NSPD 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 micron nylon mesh of the bottle(s) should be faced downward to minimize mixing of water in the samplers with shallower well water during recovery ( Vroblesky, Petkewich, and Campbell 2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-

Resources Investigations Report 02-4031. U.S. Geological Survey.

<https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>). If the micron nylon mesh is not facing downward, it is possible that stagnant water from the casing or chemically different water from above the sample interval may be incorporated into the sample through the mesh as the bottle is pulled upward through the screen and casing. Care should be taken so that bottles do not block each other when the samplers are used in series. When the sampler is not submerged, it retains the water as a result of surface tension (between the water and the screen) and the vacuum that develops in the inverted bottle

( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>). Over time, chemicals diffuse across the nylon screen and equilibrate with the water inside the sampler. After retrieval, the sampled media must be prepared to be sent to the laboratory for analysis by either. The content of the sampler is transferring from the sampled media to laboratory sample containers, and sent to the lab for analysis, or the cut out cap on the sampler that holds the screen is replaced with blank caps, and the sampler bottles are sent for analysis

The direction the bottles are facing within the well can also affect their function ( Vroblesky, Petkewich, and Campbell

2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-Resources Investigations Report 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>).

As seen by the work from Webster, Teasdale, and Grigg. ( Webster, Teasdale, and Grigg 1998<sup>[L4CH5QFU]</sup> Webster, I.T., P.R. Teasdale, and N. Grigg. 1998. "Theoretical and Experimental Analysis of Peeper Equilibration Dynamics." *Environmental Science and Technology* 32:1727-33.), samplers facing down in water with a high ionic strength are unsuccessful in equilibrating as a result of

density differences between the sampler and ambient water ( Vroblesky, Petkewich, and Campbell 2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-Resources Investigations Report 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>).

It is ideal to orient the sampler so that the sampler membrane faces the well screen. According to Vroblesky, Petkewich, and Campbell ( Vroblesky, Petkewich, and Campbell 2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-Resources Investigations Report 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>), bottles should be oriented downward in wells with 2-inch diameters where horizontal deployment is not possible and the water is not strongly ionic. The stated purpose of this orientation was to minimize mixing of water in the samplers with shallower well water during sampler recovery ( Vroblesky, Petkewich, and Campbell 2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-Resources Investigations Report 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>). In addition, NSPDS placed with the screen mesh facing upward in groundwater may risk infiltration of water from above the sampling position, possibly water from the casing, as the samplers are pulled upward during the recovery process.

In January 2003 Columbia Analytical Services, in cooperation with criteria developed by Vroblesky of the USGS, conducted equilibration studies for NSPDS and included VOCs such as benzene, tetrachloroethene (PCE), trichloroethene (TCE), and 1,4-dioxane, as well as inorganic chemicals such as perchlorate, chloride, arsenic, and iron ( Vroblesky, Scheible, and Teall

2003<sup>[RU727V73]</sup> Vroblesky, D, W Scheible, and G Teall. 2003. "Laboratory Equilibration Study of Nylon-Screen Passive Diffusion Samplers for VOCs, and Select Inorganics." In ITRC Spring Meeting. Annapolis MD.). All chemicals 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 2003 on a suite of metals, and again, with the exception of silver, the

NSPDS showed good transfer from test jars into sampler water ( Vroblesky, Scheible, and Teall 2003<sup>[RU727V73]</sup> Vroblesky, D, W Scheible, and G Teall. 2003. "Laboratory Equilibration Study of Nylon-Screen Passive Diffusion Samplers for VOCs, and Select Inorganics." In ITRC Spring Meeting. Annapolis MD.). 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 volume of up to 175 mL) showed

poor comparisons with water in test jars ( Vroblesky, Scheible, and Teall 2003<sup>[RU727V73]</sup> Vroblesky, D, W Scheible, and G Teall. 2003. "Laboratory Equilibration Study of Nylon-Screen Passive Diffusion Samplers for VOCs, and Select Inorganics." In ITRC Spring Meeting. Annapolis MD.). Literature searches have been unsuccessful in finding citations that reference a nylon

screen sampler being used for SVOC collection ( "Passive No Purge Samplers" 2020<sup>[L84MVLPO]</sup> "Passive (No Purge) Samplers." 2020. Contaminated Site Clean-Up Information (CLU-IN). June 4, 2020.

[https://clu.in.org/characterization/technologies/default.focus/sec/Passive\\_\(no\\_purge\)\\_Samplers/cat/Diffusion\\_Samplers/.](https://clu.in.org/characterization/technologies/default.focus/sec/Passive_(no_purge)_Samplers/cat/Diffusion_Samplers/)

Webster, Teasdale, and Grigg ( Webster, Teasdale, and Grigg 1998<sup>[L4CH5QFU]</sup> Webster, I.T., P.R. Teasdale, and N. Grigg. 1998. "Theoretical and Experimental Analysis of Peeper Equilibration Dynamics." *Environmental Science and Technology* 32:1727-33.) 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 more quickly than bottles oriented with the opening up or down. Sampler orientation is dependent on well constriction and site-specific details ( Webster, Teasdale, and Grigg 1998<sup>[L4CH5QFU]</sup> Webster, I.T., P.R. Teasdale, and N. Grigg. 1998. "Theoretical and Experimental Analysis of Peeper Equilibration Dynamics." *Environmental Science and Technology* 32:1727-33.).

### 5.2.3.3 Advantages

- NSPDSs are good for most analytes.
- They eliminate or reduce IDW.
- They do not require specialized equipment (for example, generator, compressed gases).
- They can sample at discrete intervals to prevent groundwater mixing.
- Users can stack devices to profile screen length.
- NSPDSs have a small sampling interval, which provides good profile location for identifying contaminant stratification.
- They require minimal decontamination of the sampler. A disposable device is common for similar types of other passive diffusion samplers.

### 5.2.3.4 Limitations

- These samplers are not commercially available. However, NSPDSs can be easily constructed with typical laboratory sampling bottles and using mesh materials from industrial suppliers.
- Limited sample volume may be a concern if using these devices to test for a wide range of chemicals.
- These samplers are better suited to larger wells, where the larger volume samplers may be used. Smaller volume jars used for 2-inch wells have shown inconsistent results.
- Sampling for reduction-oxidation (redox)-sensitive metals, such as lead, iron, and manganese, is subject to several uncertainties and should be approached with caution. 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. Insufficient work has been done to determine whether prefilling with anaerobic water is effective.
- The sampler should be deoxygenated (both the receiving media and sampler body if PTFE or polycarbonate) to reduce introduction of oxygen into potentially reducing environments, especially for relatively short deployment times.

## 5.2.4 Peeper Sampler

### 5.2.4.1 Description and Application

Peeper samplers (that is, dialysis cells or Hesslein In Situ Pore Water samplers) (Figure 5-17) are rigid structures that are equipped with one or more water-filled chambers that are covered with a semipermeable membrane or mesh and rely on diffusion of chemicals from the pore water into the water-filled peeper chamber to reach equilibrium. Peeper samplers were developed for in situ monitoring of dissolved chemicals in saturated sediments ( Hesslein 1976<sup>[TKD2SRMX]</sup> Hesslein, Raymond H. 1976. "An in Situ Sampler for Close Interval Pore Water Studies." *Limnology and Oceanography* 21 (6): 912-14. <https://doi.org/10.4319/lo.1976.21.6.0912>). The efficiency of peeper samplers depends on equilibration time of the target chemical(s), which is a function of diffusion coefficient, adsorption-desorption properties, surrounding ambient-solution temperature, and sediment porosity. Peeper samplers have advantages over older centrifugation methods, including in situ monitoring of trace elements, quick and efficient sampling times, increased depth resolution, and minimal temperature and O<sub>2</sub> (g) diffusion effects. The primary advantage of the peeper sampler is that it measures dissolved fraction, which can be compared to risk-based standards (i.e., risk-based corrective action (RBCA)) or federal/state cleanup criteria.

Peepers can be stacked in a specially designed corer to sample discrete depths, direct-driven for near-surface (1-3 m) evaluation, or placed in a shallow rectangular array for near-surface area distribution determinations (Table 5-3). Prior to deployment, peepers are filled with an appropriate grade of water (for example, distilled, DI, or milli-Q) that can be spiked with a known concentration of PRC. PRCs are typically compounds that behave conservatively in the environment, meaning they do not have strong adsorption/reaction qualities, and can be used as simple tracers. Bromide is a common PRC. Addition of a PRC is useful for calculating percent equilibrium achieved between the peeper chamber and the pore water when the peeper is retrieved and sampled. Following deployment, peepers are left in place for a designated amount of time to achieve equilibrium with the surrounding pore water. Peepers equilibration time can range from hours to a month, depending on peeper construction, target chemicals, and site-specific soil/sediment properties. Peepers are available commercially and are also fabricated by universities and other researchers. General and specialized peeper sampler designs are described in the following sections.

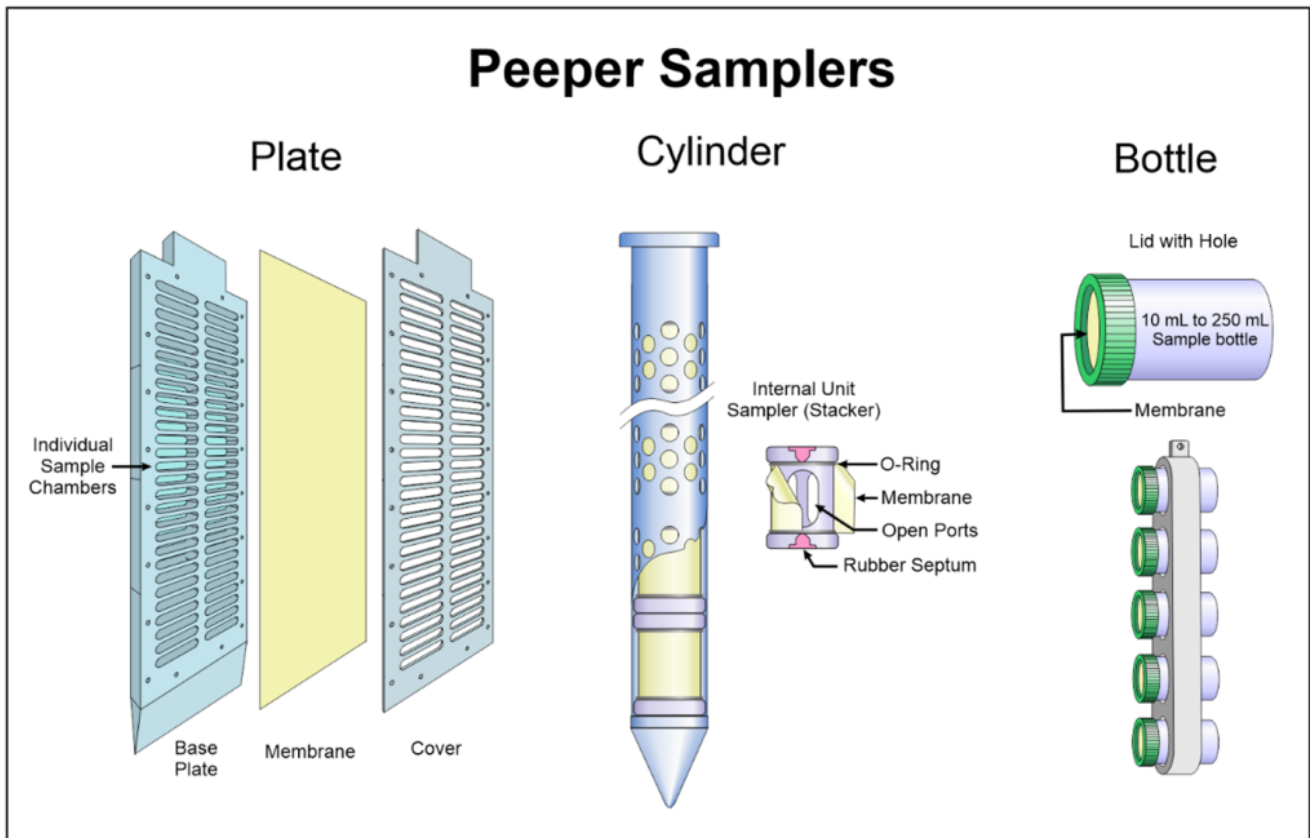


Figure 5 17. Peeper sampler, showing the three types: plate, cylinder, and bottle. Source: NJDEP, figure used with permission.

Table 5-3. Applications of peeper samplers.

Style	Type	Application	Installation	Chemical Constituents
Plate	Hesslein	shallow sediments	hand-push, slide hammer	Inorganics, VOCs, WQ parameters, (PFAS)
	sHRPP (sediment High-Resolution Passive Profiler)	shallow sediments	hand-push, slide hammer	PFAS (McDermott et al. 2022), metals, and organics (Andrew Jackson et al. 2022)
Cylinder	Standard	shallow sediments	hand-push, slide hammer	Inorganics (Risacher et al. 2023)
	HRPP (High-Resolution Passive Profiler)	deep sediments, shallow groundwater	slide hammer, diverless push-pole, dive team, direct-push rig tooling	PFAS (McDermott et al. 2022), inorganics, VOCs, microbial community and genes, hydrophobic organic compounds

Style	Type	Application	Installation	Chemical Constituents
<b>Bottle</b>	PsMS (polysulfone membrane sampler)	monitoring wells	lower using rope/cable	Metals (metalloids and some nonmetals) (Peijnenburg et al. 2014)
	SPeeper	shallow sediments, surface water, monitoring wells	hand-push, diverless push-pole, lower using rope/cable	Metals, dissolved organic carbon, phosphorus, major anions, and WQ parameters (Vachon 2023a)
	PFASsive	shallow sediments, surface water, monitoring wells	hand-push, diverless push-pole, lower using rope/cable	PFAS

Edit

#### 5.2.4.2 Installation and Use

Typical peeper samplers employ a rigid body with an opening or openings that are covered with a permeable membrane or mesh ( Jackson 2003<sup>[DA6W5]RD</sup> Jackson, A. 2003. "Peeper Samplers." Presented at the ITRC Fall Membership Meeting, Monterey, CA.). Peeper samplers can be constructed of LEXAN, acrylic, Teflon, stainless steel, or other millable material. Material selection is a function of site-specific characteristics (for example, target depth and chemicals of interest). Due to the wide range of peeper designs and sizes, individual peeper cell volumes can vary from less than 1 mL to more than 100 mL. Common peeper sampler structures can be divided into three categories: plate, cylinder, and bottle (Figure 5-14 and Table 5-3).

- Plate peepers range from approximately 5 to 100 cm long and approximately 1 to 3 cm thick. A typical plate peeper design resembles a box corer with individual cells milled into the sampler body at approximately 1-cm transects. Plate peeper cell volume ranges from approximately 1 to 20 mL per cell, depending on cell depth and length.
- Cylinder peeper designs have outer diameters ranging from approximately 1 cm to 7 cm and can be up to 4 m long. Similar to plate peepers, individual cell volume ranges from approximately 1 to 20 mL per cell, depending on peeper diameter and cell geometry. An example of common cylinder peeper sampler construction is an acrylic cylindrical rod with holes in the side that are fitted with membrane and/or mesh material.
- A typical bottle peeper design is a glass vial or polyethylene bottle with a membrane secured to the mouth of the bottle using the bottle cap. The bottle cap is perforated or cored to expose the membrane to the pore water. Bottle peeper sample volume is dependent upon the size and number of bottles used, but typically ranges from approximately 10 mL to 250 mL. Specialized modifications of the three traditional peeper designs (plate, cylinder, and bottle) have been developed to address specific needs, such as direct-drive (vs. down-well) deployment beyond near-surface sample depths (> 5 ft bgs), or to evaluate emerging contaminants with stringent sampling protocols (for example, PFAS).

A polysulfone membrane sampler (PsMS) is a modification of the bottle peeper sampler that was first implemented as part of a field demonstration of passive groundwater sampling devices performed at McClellan Air Force Base (AFB), near Sacramento, California ( Parsons 2004<sup>[993ENPDF]</sup> Parsons. 2004. "Final Work Plan for the Demonstration of Passive Groundwater Sampling Devices at Former McClellan Air Force Base."). The PsMS constructed for use in the McClellan AFB study consisted of a rigid 2-inch long, 2-inch OD section of PVC pipe covered on both ends with flexible 0.2- $\mu$ m polysulfone membrane ( Parsons 2005<sup>[IKZXKLEL]</sup> Parsons. 2005. "FINAL: Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California." F44650-9900005. [https://clu-in.org/download/char/passsamp/mcclellan\\_final\\_results\\_report.pdf](https://clu-in.org/download/char/passsamp/mcclellan_final_results_report.pdf)). The volume of each PsMS canister was approximately 108 mL ( Parsons 2005<sup>[IKZXKLEL]</sup> Parsons. 2005. "FINAL: Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California." F44650-9900005. [https://clu-in.org/download/char/passsamp/mcclellan\\_final\\_results\\_report.pdf](https://clu-in.org/download/char/passsamp/mcclellan_final_results_report.pdf)). Two canisters are typically deployed at each sample depth to provide adequate sample volume for standard laboratory analysis. The groundwater sample is transferred from the PsMS to the appropriate sample container by puncturing the membrane with a straw and pouring the contents from

the sampler into the container through the straw. Considerations regarding the orientation of peeper samplers led to the deployment of the PsMS in an orientation where the membrane is positioned horizontally ( Webster, Teasdale, and Grigg 1998<sup>[L4CH50FU]</sup> Webster, I.T., P.R. Teasdale, and N. Grigg. 1998. "Theoretical and Experimental Analysis of Peeper Equilibration Dynamics." *Environmental Science and Technology* 32:1727-33.).

The High-Resolution Passive Profiler (HRPP) is a modification of the cylindrical peeper sampler that was initially developed for direct-drive Geoprobe insertion into shallow (~30 ft bgs) aquifers to quantify chlorinated volatile organic compound (CVOC) concentrations, geochemical indicators, CVOC-degrading microorganisms/genes; and to perform compound-specific isotope analysis (CSIA) of CVOCs and estimate interstitial velocity at < 1 ft resolution ( Schneider et al. 2020<sup>[CW8YWUCD]</sup> Schneider, Haley A., W. Andrew Jackson, Paul B. Hatzinger, and Charles E. Schaefer. 2020. "High-Resolution Characterization of a Chlorinated Solvent Impacted Aquifer Using a Passive Profiler." *Groundwater Monitoring & Remediation* 40 (4): 27-43. <https://doi.org/10.1111/gwmr.12409>.) ( Garza-Rubalcava et al. 2022<sup>[6UQBTWYK]</sup> Garza-Rubalcava, Uriel, Paul B. Hatzinger, David Schanzle, Graig Lavorgna, Paul Hedman, and W. Andrew Jackson. 2022. "Improved Assessment and Performance Monitoring of a Biowall at a Chlorinated Solvent Site Using High-Resolution Passive Sampling." *Journal of Contaminant Hydrology* 246 (April):103962. <https://doi.org/10.1016/j.jconhyd.2022.103962>.) The HRPP design comprises 2.5-inch diameter, 4-foot-long stainless steel rods that can be coupled together to achieve the desired sample interval. The HRPP design consists of three cell types with individual functions that are repeated over the length of the HRPP ( Jackson and Hatzinger 2020<sup>[WLZ5MG5]</sup> Jackson, Dr. Andrew, and Dr. Paul B. Hatzinger. 2020. "High Resolution Delineation of Contaminant Concentrations, Biogeochemical Processes, and Microbial Communities in Saturated Subsurface Environments." SERDP Project ER-2419. [https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/project\\_documents/ER-2419\\_Final\\_Report.pdf](https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/project_documents/ER-2419_Final_Report.pdf).) The three different cell types and corresponding functionalities of the HRPP are:

- Equilibrium cells used to quantify contaminant concentrations and geochemical indicators (for example, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, Mn, Fe, SO<sub>4</sub><sup>2-</sup>). Equilibrium cells function similarly to traditional peeper sampling methods.
- Velocity cells used to measure multidirectional interstitial velocity (cm/d) based on mass transfer of a conservative tracer (for example, bromide). Velocity cells function similarly to equilibrium cells, but the velocity cells also incorporate varied ratios of cell volume to surface area that allow the HRPP cells to equilibrate with the pore water at different rates.
- Microbial/CSIA cells used to assess microbial community structure and CSIA of CVOCs. Microbial/CSIA cells are filled with Bio-Sep beads that perform a dual function by serving as a matrix for microbial colonization and subsequent quantitative polymerase chain reaction (qPCR) analysis, and by accumulating CVOCs for CSIA analysis through adsorption.

The sediment HRPP (sHRPP) is a modified HRPP design that is optimized for characterization of surface water sediments (vs. shallow aquifers). The sHRPP is a 3-ft-long, 5-inch-wide stainless steel modified plate peeper design that includes the same functionalities as the HRPP but has higher resolution of sample cells (< 1 inch resolution) than the HRPP, appropriate for shallow sediment characterization.

SPeeper and PFASsive are modified bottle peeper designs consisting of one or more 60-mL HDPE bottles capped with either polyethersulfone (SPeeper) or polycarbonate (PFASsive) membrane (Figure 5-18). SPeeper and PFASsive are distributed in ready-to-use sample packs and are intended for diverless deployment into shallow sediments for characterization of water-soluble compounds (SPeeper) and PFAS (PFASsive in sediment pore water) (Figure 5-19).



Figure 5-18. SPeeper modified bottle peepers are designed for diverless deployment in sediments.  
Source: SIREM, used with permission.

## PFASsive™ 3D Printed Housing for Peeper Samplers

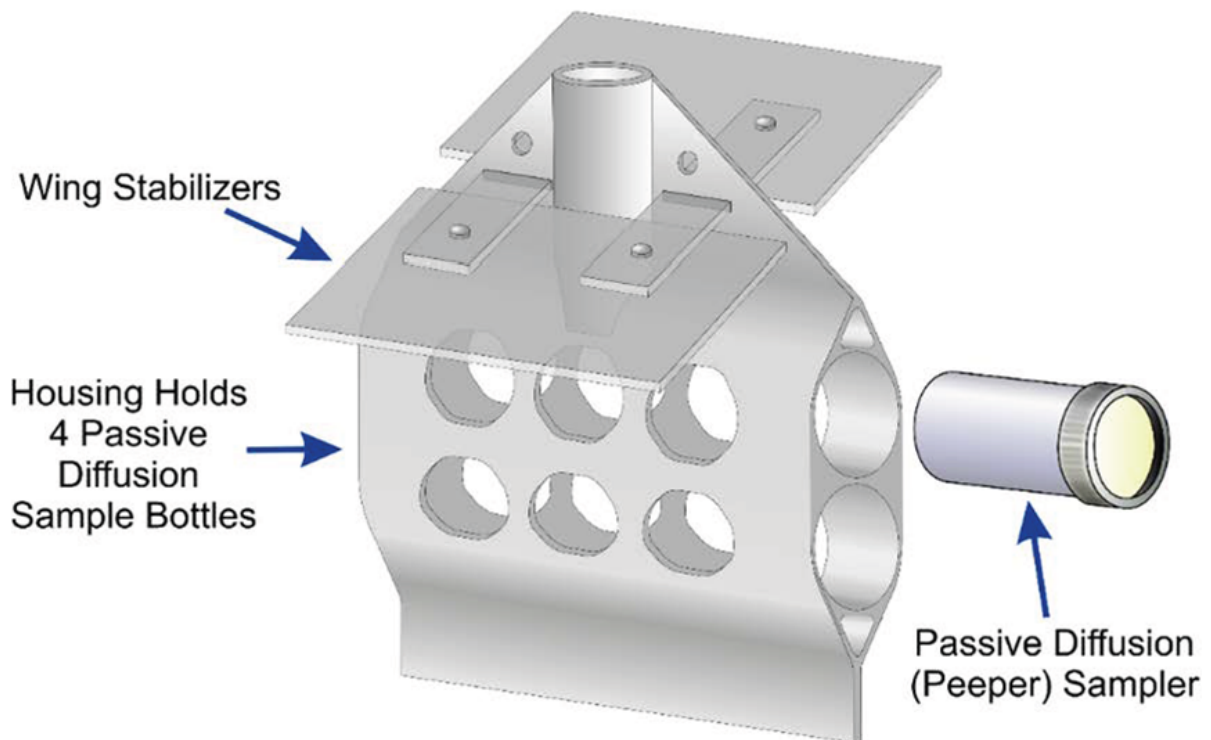


Figure 5-19. PFASsive sampler.

Source: NJDEP, figure used with permission.

### 5.2.4.3 Advantages

- Commercially available peepers are relatively low cost and user-friendly.
- Peeper types that are directly inserted into saturated soil/sediment are more representative of pore water concentrations than more active sampling methods.
- Peeper types that are intended to be deployed in monitoring wells can be deployed to great depths, and at multiple depth intervals. Deploying multiple peepers in a monitoring well can be a way to achieve more depth-discrete samples than traditional low-flow purging and sampling.
- The “skeleton” of peeper samplers is reusable if properly decontaminated.
- HRPP samplers can be a cost-effective alternative to installing groundwater monitoring wells.
- HRPP and sHRPP samplers offer higher vertical resolution than traditional sampling methods. High-resolution data are beneficial in refining conceptual site models and optimizing targeted monitoring/remediation, leading to long-term cost savings.

### 5.2.4.4 Limitation

- 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.
- The equilibration time for peeper samplers and PsMS 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 to allow chemicals 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 *Environmental Science & Technology* Webster, Teasdale, and Grigg ( Webster, Teasdale, and Grigg 1998<sup>[L4CH5QFU]</sup> Webster, I.T., P.R. Teasdale, and N. Grigg. 1998. “Theoretical and Experimental Analysis of Peeper Equilibration Dynamics.” *Environmental Science and Technology* 32:1727-33.).
- PsMS samplers are typically designed to fit into wells with a minimum inside diameter of 4 inches. The membrane orientation was demonstrated in only 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.
- HRPP and sHRPP sampler assembly, deployment, and sampling require training from experienced users.
- The cost to create a custom HRPP or sHRPP sampler can be over \$1,000. A more cost-effective solution is to rent prefabricated HRPP and sHRPP designs.
- Plate and cylinder peepers typically provide small sample volumes (~10 mL) at high depth resolution (cm intervals). Cells can be pooled to produce 100–300 ml per foot. Bottle peepers range in size but typically have a larger sample volume compared to plate peeper samplers.
- The inner membrane(s) cannot be reused.
- Samples withdrawn from wetlands or lacustrine environments, via piston or other coring devices, may be anoxic and would have to be kept anaerobic during transfer to the laboratory. Otherwise, follow normal shipping procedures specified by the intended laboratory.
- The sampler should be deoxygenated (both the receiving media and sampler body if PTFE or polycarbonate) to reduce introduction of oxygen into potentially reducing environments, especially for relatively short deployment times.

## 5.2.5 Regenerated Cellulose Dialysis Membrane Sampler (RCDM)

### 5.2.5.1 Description and Application

Regenerated cellulose dialysis membrane (RCDM) (Figure 5-20) samplers are equilibrium-based diffusion samplers, developed to sample dissolved inorganic and organic chemicals in groundwater, pore water, and surface water. RCDM samplers are disposable, so there is no need for field decontamination, and their use eliminates the possibility of cross contamination between wells from the sampling device.

The RCDM sampler consists of a tube, filled with DI water, which has two layers. A high-grade RCDM is contained within a protective layer of LDPE mesh. The RCDM used in previous studies by the USGS has a pore size of 0.0018  $\mu\text{m}$  and a molecular weight cutoff (MWCO) of 8,000 Daltons. Particulates from groundwater and surface water samples cannot pass through, and therefore, RCDM samplers collect only dissolved chemicals. RCDM samplers have been constructed using 31.8 mm (1.25 inches) and 63.7 mm (2.5 inches) filled-diameter membranes.

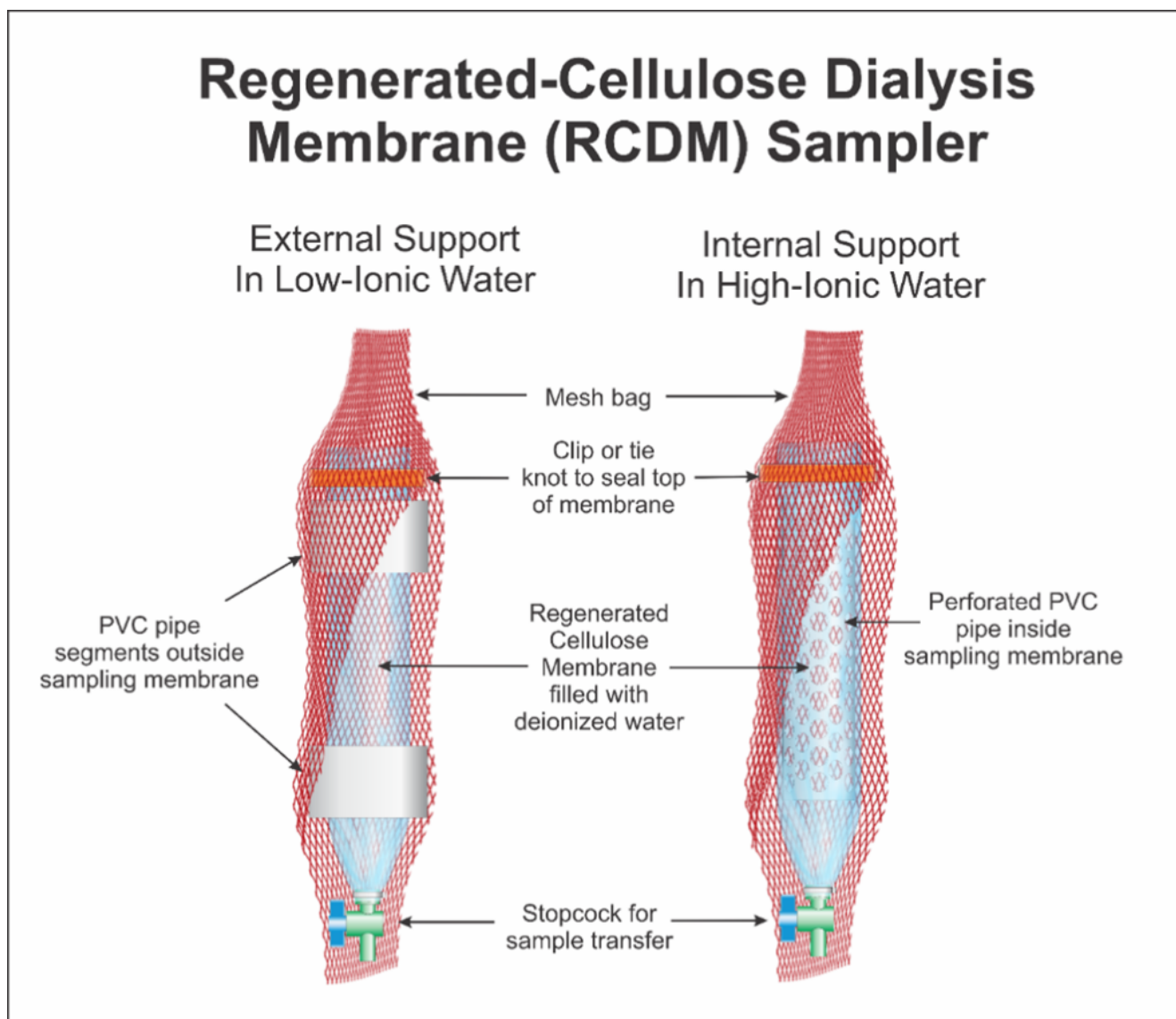


Figure 5-20. Regenerated Cellulose Dialysis Membrane sampler.

Source: NJDEP, figure used with permission.

Because the dialysis membrane is hydrophilic, water can diffuse through the membrane. The sampler may be constructed with or without PVC pipes external to the dialysis membrane in low-ionic strength waters. In high-ionic strength waters, an internal perforated PVC pipe to support the membrane should be used to help maintain water volume within the sampler. The sampler may have a stopcock at one end to facilitate filling with DI water and emptying the sample.

Fully constructed RCDM samplers are not currently available from any commercial vendors ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.) However, precleaned dialysis membranes can readily be purchased from several manufacturers. Because dry RCDMs may contain trace metals and sulfides, it is recommended that precleaned dialysis membrane material be purchased to construct RCDM samplers. The preservative that precleaned RCDM materials come in can easily be removed by rinsing the membranes with DI water several times.

The sampler is constructed from materials that can be purchased from vendors. The regenerated cellulose membrane can

be cut to the desired length based on the sample volume required. When constructing this sampler, it is important to have a source of DI water and the user should wear disposable gloves while handling the parts. The membrane needs to be rinsed thoroughly to remove the preservative the regenerated cellulose membrane is shipped in. The LDPE mesh slips around the sampler to protect the membrane during deployment.

Regenerated cellulose samplers have been successfully tested in the lab 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 hydrocarbon gases, sulfide, selected explosive compounds, perchlorate, MTBE, and some PFAS (

Imbrigiotta and Trotsky 2011<sup>[EKS36392]</sup> Imbrigiotta, Thomas E., and J.S. Trotsky. 2011. "Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Groundwater Quality and Remediation Progress at DoD Sites: Perchlorate and Ordnance Compounds." ER-200313. ESTCP.

<https://www.usgs.gov/publications/demonstration-and-validation-a-regenerated-cellulose-dialysis-membrane-diffusion-0.>)

RCDM samplers were unsuccessful in sampling for mercury, tin, and silver in the laboratory over a 4-week equilibration period ( Imbrigiotta, Trotsky, and Place 2007<sup>[NHT81688]</sup> Imbrigiotta, Thomas E., J.S. Trotsky, and M.C. Place. 2007.

"Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Groundwater Quality and Remediation Progress at DoD Sites." TR-2281-ENV. Technical Report. Naval Facilities Engineering Service. <https://pubs.usgs.gov/publication/70206138.>) These trace metals may form organic complexes that strongly sorb to the membrane.

### 5.2.5.2 Installation and Use

RCDM samplers are typically deployed in the saturated interval of the well screen or in the saturated open interval of an open borehole well at a desired sampling depth consistent with site DQOs. For deployment, the sampler is attached to a weighted suspension-tether and lowered to the intended depth, and the tether is secured at the top of the well ( Imbrigiotta, Trotsky, and Place 2008<sup>[UMSBJG68]</sup> Imbrigiotta, Thomas E., J.S. Trotsky, and M.C. Place. 2008. "Protocol for Use of Regenerated Cellulose Dialysis Membrane Diffusion Samplers (ER-0313): ESTCP." ESTCP Protocol Report for Project ER-0313.

<http://www.estcp.org/Technology/upload/ER-0313-Protocol.pdf.>; Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8.>) Multiple RCDMs can be deployed in a single well to sample at discrete intervals to vertically profile the water chemistry in the open interval.

After deployment, the RCDM sampler(s) must remain in the well for sufficient time (minimum residence time) for (1) hydraulic stabilization of the groundwater flow through the open interval of a well after the introduction of the sampler, and (2) chemical equilibration of the water inside the sampler membrane with the groundwater flowing past it outside the sampler membrane. Retrieve the dialysis sampler from the well after the appropriate equilibration time and transfer the samples to standard sample containers. The containers can be sent to the laboratory for direct analysis of water concentrations.

Laboratory equilibration testing has shown that RCDM samplers chemically equilibrate within the times below, not including the time it takes the well to restabilize hydraulically.

- 1-3 days for anions, silica, methane, dissolved organic carbon, and all VOCs on the USEPA 8260B list (including MTBE) ( Ehke, Imbrigiotta, and Dale 2004<sup>[80GB998Q]</sup> Ehke, T.A., T.E. Imbrigiotta, and J.M. Dale. 2004. "Laboratory Comparison of Polyethylene and Dialysis Membrane Diffusion Samplers." *Ground Water Monitoring and Remediation* 24 (1): 53-59.; Harter and Talozzi 2004; Imbrigiotta and Trotsky 2011<sup>[EKS36392]</sup> Imbrigiotta, Thomas E., and J.S. Trotsky. 2011. "Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Groundwater Quality and Remediation Progress at DoD Sites: Perchlorate and Ordnance Compounds." ER-200313. ESTCP. <https://www.usgs.gov/publications/demonstration-and-validation-a-regenerated-cellulose-dialysis-membrane-diffusion-0.>)
- 3-7 days for most cations and trace elements ( Vroblecky, Petkewich, and Campbell 2002<sup>[471YEXTP]</sup> Vroblecky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." *Water-Resources Investigations Report* 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wri02-4031.pdf.>; Imbrigiotta, Trotsky, and Place

2007<sup>[NHT816B8]</sup> Imbrigiotta, Thomas E., J.S. Trotsky, and M.C. Place. 2007. "Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Ground-Water Quality and Remediation Progress at DoD Sites." TR-2281-ENV. Technical Report. Naval Facilities Engineering Service. <https://pubs.usgs.gov/publication/70206138>.)

- 7-14 days for most explosive compounds and perchlorate ( LeBlanc 2003<sup>[NB6GALSH]</sup> LeBlanc, D.R. 2003. "Diffusion and Drive-Point Sampling to Detect Ordnance-Related Compounds in Shallow Groundwater beneath Snake Pond, Cape Cod." 03-4133. U.S. Geological Survey Water Resources Investigations. Cape Cod, Massachusetts.; Parker and Mulherin 2006<sup>[YFJ5ZNEU]</sup> Parker, L.V., and N.D. Mulherin. 2006. "Preliminary Studies of Alternative Passive Diffusion Devices for Sampling Explosives." In Proceedings of 2006 North American Environmental Field Conference and Exposition. Tampa, FL.; Imbrigiotta and Trotsky 2011<sup>[EKS36392]</sup> Imbrigiotta, Thomas E., and J.S. Trotsky. 2011. "Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Groundwater Quality and Remediation Progress at DoD Sites: Perchlorate and Ordnance Compounds." ER-200313. ESTCP. <https://www.usgs.gov/publications/demonstration-and-validation-a-regenerated-cellulose-dialysis-membrane-diffusion-0>.)
- Field equilibration testing has shown that RCDM samplers yield concentrations of VOCs similar to those yielded by PDBs and low-flow purging and sampling ( Vroblesky, Petkewich, and Campbell 2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-Resources Investigations Report 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>., 2; Vroblesky, Petkewich, and Campbell 2002<sup>[47IYEXTP]</sup> Vroblesky, Don A., Matthew D. Petkewich, and Ted R. Campbell. 2002. "Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone." Water-Resources Investigations Report 02-4031. U.S. Geological Survey. <https://pubs.usgs.gov/wri/wri024031/pdf/wrir02-4031.pdf>.; Parsons 2005<sup>[IKZXKLEL]</sup> Parsons. 2005. "FINAL: Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California." F44650-9900005. [https://clu-in.org/download/char/passsamp/mcclellan\\_final\\_results\\_report.pdf](https://clu-in.org/download/char/passsamp/mcclellan_final_results_report.pdf).; Vroblesky and Peterson 2004<sup>[55GWXGMZ]</sup> Vroblesky, Don A., and J.E. Peterson. 2004. "Flow-Meter and Passive Diffusion Bag Tests and Potential Influences on the Vertical Distribution of Contaminants in Wells at Galena Airport, Galena, Alaska, August to October 2002." U.S. Geological Survey Open-File Report 2004-124. USGS. [https://www.researchgate.net/publication/235060843\\_Flow-Meter\\_and\\_Passive\\_Diffusion\\_Bag\\_Tests\\_and\\_Potential\\_Influences\\_on\\_the\\_Vertical\\_Distribution\\_of\\_Contaminants\\_in\\_Wells\\_at\\_Galena\\_Airport\\_Galena\\_Alaska\\_August\\_to\\_October\\_2002](https://www.researchgate.net/publication/235060843_Flow-Meter_and_Passive_Diffusion_Bag_Tests_and_Potential_Influences_on_the_Vertical_Distribution_of_Contaminants_in_Wells_at_Galena_Airport_Galena_Alaska_August_to_October_2002).; Imbrigiotta et al. 2002<sup>[E2E8XZJ]</sup> Imbrigiotta, Thomas E., T. A. Ehlke, P. J. Lacombe, and J. M. Dale. 2002. "Comparison of Dialysis Membrane Diffusion Samplers and Two Purging Methods in Bedrock Wells." In , 195-206. <https://pubs.usgs.gov/publication/70023982>.; Vroblesky et al. 2003<sup>[2CU779MA]</sup> Vroblesky, D.A., J. Manish, J. Morrell, and J.E. Peterson. 2003. "Evaluation of Passive Diffusion Bag Samplers, Dialysis Samplers, and Nylon-Screen Samplers in Selected Wells at Andersen Air Force Base." 03-4157. Guam: U.S. Geological Survey Water Resources Investigations.; Imbrigiotta, Trotsky, and Place 2007<sup>[NHT816B8]</sup> Imbrigiotta, Thomas E., J.S. Trotsky, and M.C. Place. 2007. "Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Ground-Water Quality and Remediation Progress at DoD Sites." TR-2281-ENV. Technical Report. Naval Facilities Engineering Service. <https://pubs.usgs.gov/publication/70206138>.) Imbrigiotta and Trotsky ( Imbrigiotta and Trotsky 2011<sup>[EKS36392]</sup> Imbrigiotta, Thomas E., and J.S. Trotsky. 2011. "Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Groundwater Quality and Remediation Progress at DoD Sites: Perchlorate and Ordnance Compounds." ER-200313. ESTCP. <https://www.usgs.gov/publications/demonstration-and-validation-a-regenerated-cellulose-dialysis-membrane-diffusion-0>.) also showed that RCDM samplers yield concentrations of most inorganic chemicals, dissolved organic carbon, and most explosives similar to those collected by low-flow purging and sampling. There is also some preliminary evidence that RCDM samplers are able to recover concentrations of selected PFAS compounds, as well as low-flow purging does ( Imbrigiotta, Trotsky, and Place 2008<sup>[UMSBJG6B]</sup> Imbrigiotta, Thomas E., J.S. Trotsky, and M.C. Place. 2008. "Protocol for Use of Regenerated Cellulose Dialysis Membrane Diffusion Samplers (ER-0313): ESTCP." ESTCP Protocol Report for Project ER-0313. <http://www.estcp.org/Technology/upload/ER-0313-Protocol.pdf>.)

### 5.2.5.3 Advantages

- RCDM samplers provide a sample of dissolved chemicals, keeping out suspended particles.
- RCDM samplers have been lab- and field-tested for a wide range of commonly sampled organic and inorganic chemicals.
- RCDM sampler volume is dependent on diameter and length of sampler. The volume contained can be easily increased or decreased during construction, unlike some other equilibrium samplers that are volume-limited.

### 5.2.5.4 Limitations

- RCDM sampling devices are not commercially available, so they must be constructed by the user, and this requires some training. RCDMs are readily available for purchase from several vendors. The price per foot of regenerated cellulose membrane is more costly than polyethylene membrane, but PDBs cannot be used to sample for inorganics.
- RCDM samplers must be kept hydrated in DI water between construction and deployment to maintain the permeability, flexibility, and strength of the membrane.
- RCDMs can biodegrade within 4 weeks, depending on groundwater temperatures and bacterial populations, resulting in perforations and partial to total sample loss. However, all chemicals successfully sampled by RCDM samplers require equilibration times of only 2–3 weeks.
- RCDM samplers lose a small percentage of their water volume with time (<3% per week) due to the nature of the dialysis process ( Imbrigiotta, Trotsky, and Place 2007<sup>[NHT816BB]</sup> Imbrigiotta, Thomas E., J.S. Trotsky, and M.C. Place. 2007. “Demonstration and Validation of a Regenerated Cellulose Dialysis Membrane Diffusion Sampler for Monitoring Ground-Water Quality and Remediation Progress at DoD Sites.” TR-2281-ENV. Technical Report. Naval Facilities Engineering Service. <https://pubs.usgs.gov/publication/70206138>.). This is not a significant problem in fresh water when RCDM samplers are installed for less than 4 weeks. In saline waters, the water loss can be minimized by installing an internal support inside the dialysis membrane.

## 5.2.6 Rigid Porous Polyethylene Sampler (RPPS)

### 5.2.6.1 Description and Application

Rigid porous polyethylene samplers (RPPSs) (Figure 5-21) are diffusion-based samplers that were developed to sample for a broader range of chemicals than can be collected by the PDB sampler, including both organic and inorganic chemicals. The RPPS was specifically designed to collect groundwater samples from a discrete interval in monitoring or water wells. The RPPS can also be used to collect water from surface water and pore water.

# Rigid Porous Polyethylene Sampler (RPPS)

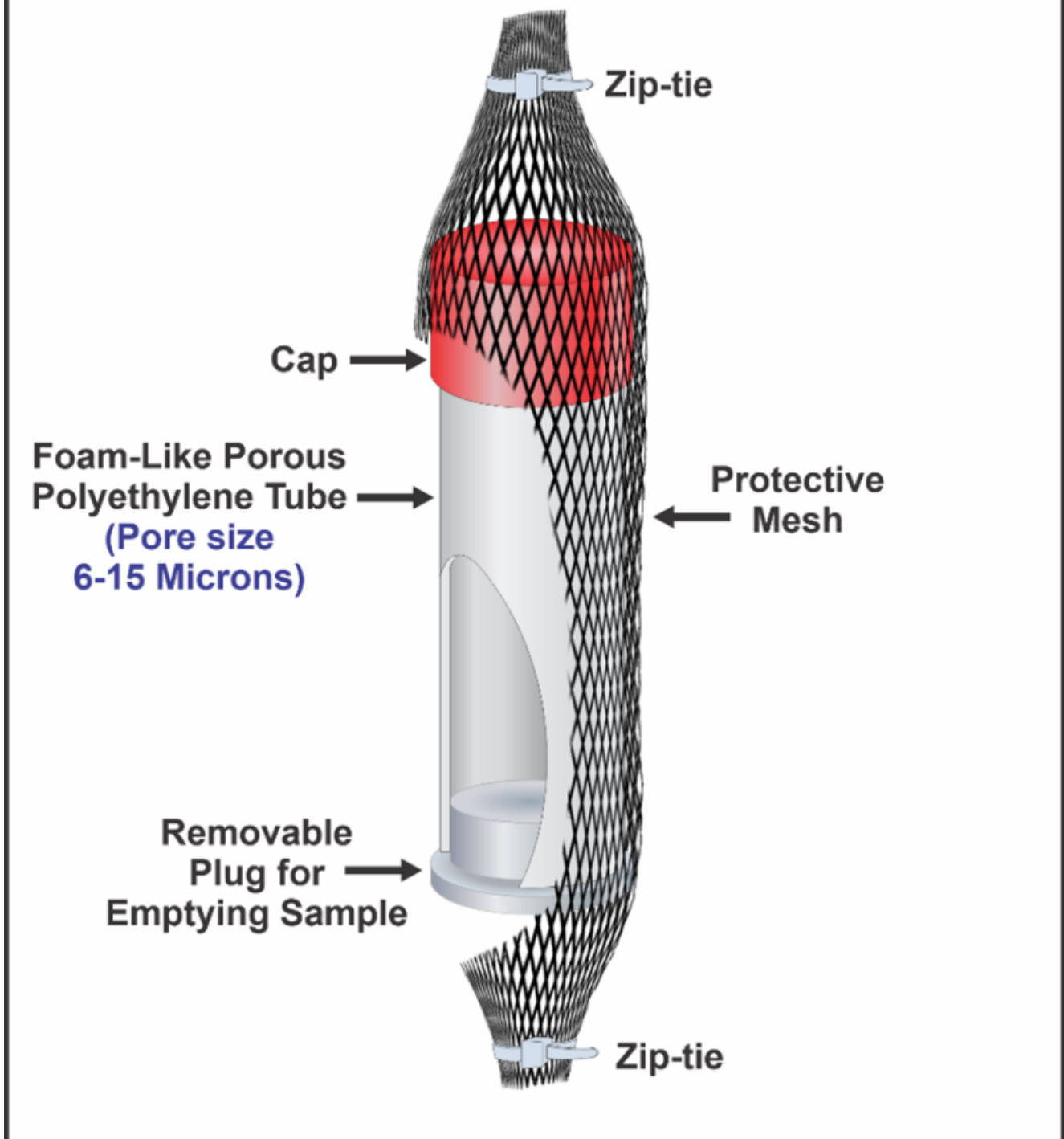


Figure 5-21. Rigid porous polyethylene sampler.

Source: NJDEP, figure used with permission.

The RPPS that is currently available commercially consists of a 1.5-inch OD, 6-inch-long, rigid porous polyethylene tube with a plug on one end and a cap on the other end ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.) The tube is constructed from thin sheets of foam-like porous polyethylene with pore sizes of 6-15  $\mu\text{m}$  ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive

Sampling of Groundwater Wells for Determination of Water Chemistry.” In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.). The sampler is filled with DI water and closed at both ends; additional water is added under pressure to overcome the hydrophobic nature of the material and saturate the pores. Using care in handling so the sampler will not lose water, the RPPS is inserted into a polyethylene mesh tube, attached to a weighted suspension tether using cable ties, and deployed in a well or surface water or sediment environment. Over time, chemicals diffuse through the water-filled pores of the porous polyethylene and equilibrate with the water inside the sampler. Upon retrieval, the plug is removed, and the contents of the sampler are poured into laboratory sample containers. The sampler may leak water upon retrieval due to the pore size of the polyethylene tubing. Although surface tension of the water can keep most of the sample within the sampler, the RPPS should be removed with care to avoid disturbing the surface tension within the sampler. Filtration may be required to achieve a dissolved-only groundwater sample for metal analysis.

The original, patented RPPS prototype consisted of a 1.5-inch-OD, 6- to 7-inch-long, 2-mm thick, rigid polyethylene tube with caps and valves at both ends ( Battelle 2010<sup>[257L2DVF]</sup> Battelle. 2010. “Department of the Navy Guidance for Planning and Optimizing Monitoring Strategies.” U.S. Department of Defense, Department of the Navy. <https://frtr.gov/matrix/documents/Monitored-Natural-Attenuation/2010-Guidance-for-Planning-and-Optimization-of-Remedial-Strategies.pdf>.). Upon retrieval the original prototype tended to leak sample water through the pores of the porous polyethylene material ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. “Passive Sampling of Groundwater Wells for Determination of Water Chemistry.” In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.). Subsequent designs of shorter lengths using a Delrin plug at the lower end have significantly reduced leakage. When VOCs are analytes of interest, an additional small plug is placed in the Delrin plug. Use of this smaller plug minimizes potential loss of VOCs by any vacuum that might be created when the plug is removed.

### 5.2.6.2 Installation and Use

RPPSs are shipped in a disposable DI-water-filled sleeve. The RPPS is deployed plug-end down in a predetermined interval in a groundwater well and left to equilibrate for at least 14 days (depending on target chemicals) or until the next sampling event. The maximum deployment period is unknown. The currently available RPPS must be deployed in a well with an inside diameter of at least 2 inches. When the RPPS is retrieved, it is inverted, the plug is removed, and the contents are poured into the sample bottles immediately. Compared to the original design, leakage is minimized and sample transfer into the bottles is much quicker.

The RPPS was specifically designed to collect groundwater samples from a discrete interval in monitoring or water wells. These samplers can monitor most compounds (both inorganic and organic) present in dissolved phases in the groundwater as the sampler volume allows.

Previous testing indicated 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 that overcomes the surface tension of the water at the pore interface, forcing water through any pores with more than about 6–7 inches of head ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. “Passive Sampling of Groundwater Wells for Determination of Water Chemistry.” In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.). The current 1.5-inch OD RPPS design contains approximately 110 mL. Larger volumes could be obtained by using a larger-diameter sampler, when the well diameter allows; however larger diameters are not currently commercially available. Larger sample volumes can be obtained by using multiple samplers attached end-to-end or side-by-side (if well diameter allows). The limited sample volume requires careful consideration of the total sample volume needed for each project. This may include coordination with the laboratory to address any sample volume limitations.

RPPS devices were included in a field demonstration of multiple passive groundwater sampling devices at the former McClellan Air Force Base (Sacramento, California) in 2004 ( Parsons 2005<sup>[IKZXKLEL]</sup> Parsons. 2005. “FINAL: Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California.” F44650-9900005. [https://clu-in.org/download/char/passsamp/mcclellan\\_final\\_results\\_report.pdf](https://clu-in.org/download/char/passsamp/mcclellan_final_results_report.pdf).). According to the field demonstration data, the RPPS performs well at monitoring for anions, metals, and hexavalent chromium. Although it performed similarly to the low-flow purge method for metals and inorganics, the RPPS did not provide results similar to low-flow purge for some VOCs, SVOCs, and other HOCs. It is suspected that such compounds with low recoveries sorbed to the polyethylene material and there was insufficient time to reach static equilibrium with the polyethylene material. Table 5-2 shows general applicability to chemicals of interest, as found in previous laboratory and field pilots. 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. This method would require special handling of prefilled samplers. However, when oxygenated water is used to fill the RPPS that is deployed in anaerobic water, the solution within the sampler becomes anaerobic over time by diffusion. Not enough work has been done yet to define when prefilling with anaerobic water is necessary or if there will be an effect on equilibration time.

### 5.2.6.3 Advantages

- RPPSs are applicable to inorganic and organic analytes.
- They are supplied field-ready.
- Decontamination of the RPPS is not needed because the device is disposable.

### 5.2.6.4 Limitations

- The cost of RPPS is at the high end for equilibration samplers.
- Multiple samplers may need to be deployed to obtain sufficient volume for laboratory analysis if testing for a wide range of chemicals. Coordination with the laboratory beforehand can avoid volume limitation as a concern.
- Additional testing may be necessary to understand possible chemical limitations for these samplers (in particular, hydrophobic VOCs and SVOCs).
- The samplers fit into wells with a minimum inner diameter of 2.0 inches.
- The porous polyethylene sampler pores often hold air even when submerged. Consequently, the oxygen entrained in the pore space must be removed by sparging with water and nitrogen prior to deployment.
- RPPSs should be deoxygenated (both the receiving media and sampler body if PTFE or polycarbonate) to reduce introduction of oxygen into potentially reducing environments, especially for relatively short deployment times.

## 5.2.7 Polymeric Sampling Devices

### 5.2.7.1 Description and Application

Polymeric sampling devices are diffusion-based samplers intended to sample surface water, groundwater, porewater, and air. Polymeric sampling devices consisting of LDPE, polydimethylsiloxane (PDMS)-coated glass fiber (that is, solid-phase microextraction [SPME] fiber), and/or polyoxymethylene (POM) are single-phase passive samplers that have been widely used in the United States to measure freely dissolved concentrations of various HOCs present in surface water, groundwater, and pore water ( Burgess et al. 2017<sup>[97]RK4GH</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://semsub.epa.gov/work/HQ/100000146.pdf>.) (Figure 5-22). The term "SPME" has been most often applied to the use of PDMS-coated glass fiber; however, POM and LDPE also essentially involve solid-phase extraction processes. Although a variety of polymeric materials, such as silicon rubbers, cyclodextrin (Tenax), and ethylene-octene copolymer, have been used for passive sampling, this section primarily focuses on LDPE, PDMS-coated glass fiber, and POM, given their prevalence and current use in the United States. More recently, advances in polymeric sampling have resulted in a shift to reliance on LDPE and PDMS-coated glass fiber ( Michalsen et al. 2018<sup>[IEVQDPQE]</sup> Michalsen, Mandy, Danny Reible, Adesewa Aribidara, Upal Ghosh, Mandar Bokare, Philip Gschwend, John MacFarlane, and Mingta Lin. 2018. "Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater." Standardized Method Memo ER-201735. ESTCP. <https://apps.dtic.mil/sti/pdfs/AD1084245.pdf>.)

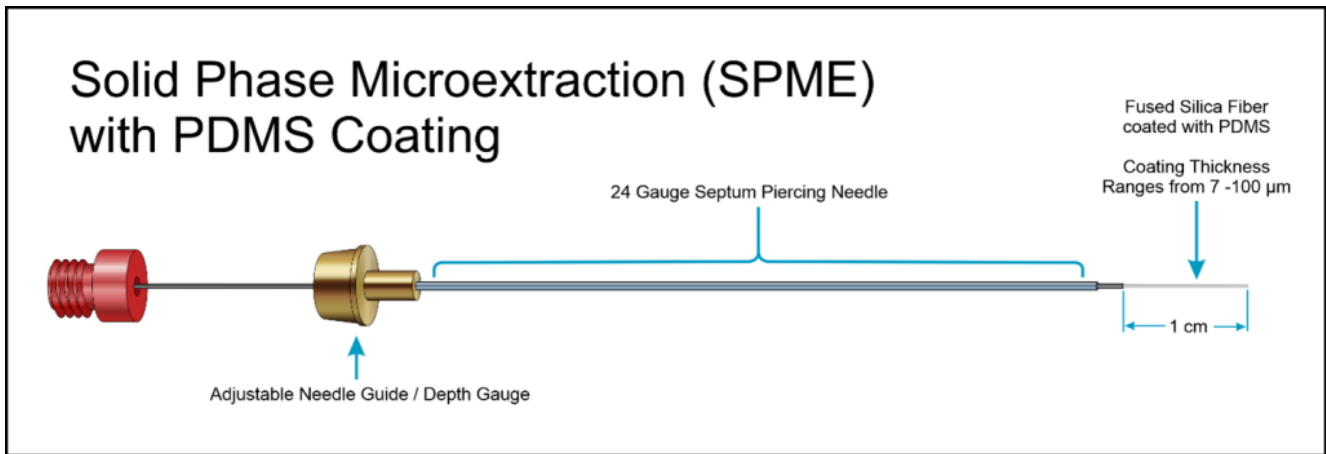


Figure 5-22. PDMS-coated solid-phase microextraction sampler.

Source: NJDEP, figure used with permission

These three polymers have similar, but not identical, sorption properties in different geometries or configurations. POM and LDPE are typically configured in thin bulk flat sheets from 10 to 100  $\mu\text{m}$  in thickness, while PDMS-coated glass fiber is cylindrical glass capillaries (100–1,000  $\mu\text{m}$  diameter) coated with a thin PDMS polymer (10–35  $\mu\text{m}$ ) ( Burgess et al.

2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP.

<https://semsub.epa.gov/work/HQ/10000146.pdf>). The most common thickness used for PDMS is 35  $\mu\text{m}$ . For PDMS-coated SPMEs, the PDMS coating the glass fiber SPME rods is generally around 30–100  $\mu\text{m}$  thick, with a typical thickness of 35  $\mu\text{m}$

(see Figure 5-22) ( Michalsen et al. 2018<sup>[IEVQDPQE]</sup> Michalsen, Mandy, Danny Reible, Adesewa Aribidara, Upal Ghosh, Mandar Bokare, Philip Gschwend, John MacFarlane, and Mingta Lin. 2018. "Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater." Standardized Method Memo ER-201735. ESTCP.

<https://apps.dtic.mil/sti/pdfs/AD1084245.pdf>).

When polymeric sampling devices are deployed in aqueous media, those can measure the freely dissolved concentrations, which can be used directly to assess chemical exposure and bioavailability without corrections on dissolved organic carbon or colloidal matter effect. The freely dissolved concentrations of HOCs are considered to be more representative as bioavailable concentrations of those chemicals. Polymeric sampling devices are also often used to measure gaseous

concentrations of various organic pollutants in air ( Khairy and Lohmann 2014<sup>[ZX9DHJSU]</sup> Khairy, Mohammed A., and Rainer Lohmann. 2014. "Field Calibration of Low Density Polyethylene Passive Samplers for Gaseous POPs." Environmental Science. Processes & Impacts 16 (3): 414–21. <https://doi.org/10.1039/c3em00493g>.) and to monitor long-term personal exposures (

Samon et al. 2022<sup>[ZD3GYDYS]</sup> Samon, Samantha M., Stephanie C. Hammel, Heather M. Stapleton, and Kim A. Anderson. 2022. "Silicone Wristbands as Personal Passive Sampling Devices: Current Knowledge, Recommendations for Use, and Future Directions." Environment International 169 (November):107339. <https://doi.org/10.1016/j.envint.2022.107339>., O'Connell,

Kincl, and Anderson 2014<sup>[YDD93BAF]</sup> O'Connell, Steven G., Laurel D. Kincl, and Kim A. Anderson. 2014. "Silicone Wristbands as Personal Passive Samplers." Environmental Science & Technology 48 (6): 3327–35. <https://doi.org/10.1021/es405022f>).

Polymeric sampling devices rely on the equilibrium partitioning of a contaminant of interest between the sampler and water or via diffusion. The use of polymeric passive samplers enables the determination of time-weighted averaged concentrations of HOCs at low detection levels without the need for high-volume media collection.

After retrieval, target chemicals are extracted from a polymeric sampling device and their concentrations are determined. Subsequently, the concentrations in the sampling devices are converted to concentrations in water or air by applying the polymer-water or polymer-air partitioning coefficients. For example, the freely dissolved concentration of a target chemical in aqueous media can be estimated from the measured concentration in a polymeric sampling device and a polymer-water

partition coefficient as shown in Equation 2 ( Mayer et al. 2003<sup>[NXMH6HGA]</sup> Mayer, Philipp, Johannes Tolls, Joop L. M. Hermens, and Donald Mackay. 2003. "Peer Reviewed: Equilibrium Sampling Devices." Environmental Science & Technology 37 (9): 184A-191A. <https://doi.org/10.1021/es032433i>).

The partition coefficient of a target chemical between a polymer and water or air are available in the scientific literature for LDPE, PDMS, and POM ( Mayer et al. 2003<sup>[NXMH6HGA]</sup> Mayer, Philipp, Johannes

## Equation 2

$$C_w = \frac{C_p}{K_{p-w}}$$

Where:

$C_w$  = freely dissolved concentration in water (ng/L)

$C_p$  = concentration in polymer (ng/kg)

$K_{p-w}$  = polymer-water partitioning coefficient (L/kg)

\*partition coefficient will depend on type of polymer used

Polymeric sampling devices need to be deployed in a target media long enough to allow the chemical partitioning to fully or partially reach equilibrium to accurately determine concentrations of target chemicals. Multiple factors influence the time required to reach equilibrium, including chemicals of interest, types and dimensions of polymer used, flow conditions, temperature, and other environmental factors. If equilibrium is not achieved during the deployment time, disequilibrium must be corrected to determine the concentrations of target chemicals. PRCs are commonly spiked into the polymeric sampling devices to allow the estimation of the fraction of equilibrium during deployment ( Huckins et al. 2002<sup>[DN3HJ22M]</sup> Huckins, James N., Jimmie D. Petty, Jon A. Lebo, Fernanda V. Almeida, Kees Booij, David A. Alvarez, Walter L. Cranor, Randal C. Clark, and Betty B. Mogensen. 2002. "Development of the Permeability/Performance Reference Compound Approach for in Situ Calibration of Semipermeable Membrane Devices." *Environmental Science & Technology* 36 (1): 85-91. <https://doi.org/10.1021/es010991w>.) PRCs are analytically noninterfering chemicals that are spiked in the polymeric sampling devices prior to deployment. Because both the uptake and the dissipation of HOCs are governed by thermodynamically regulated chemical partitioning, the dissipation rate of PRCs during deployment reflects the uptake rate of a target chemical ( Burgess et al. 2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://sempub.epa.gov/work/HQ/100000146.pdf>.) PRCs commonly used are isotope-labeled (for example, <sup>13</sup>C), or deuterated forms of the target chemicals of interest, (for example, PAHs, <sup>13</sup>C-labeled PCBs, and <sup>13</sup>C-labeled dioxin). PCB congeners rarely found in the environment can also be used as PRCs. These PRCs are preloaded into a polymeric sampling device, and the loss of PRCs during deployment is then quantified and used to correct the concentration when equilibrium is not achieved during the deployment period ( Burgess et al. 2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://sempub.epa.gov/work/HQ/100000146.pdf>.)

As discussed in Section 2.2.3, polymeric sampling devices can be deployed in the field (in situ) or in the laboratory (ex situ) to determine freely dissolved concentrations of hydrophobic organic compounds in sediment pore water. In ex situ deployment, sediment samples collected from the field site are shipped on ice in a cooler to the laboratory. Polymeric sampling devices are added to the sediment jars and equilibrated with sediment pore water by either "active" (continuously mixed) or "static" (no mixing) exposures in the laboratory for a duration sufficient to reach equilibrium among the polymeric sampling device, bulk sediment, and sediment pore water. There are several factors to consider when selecting between the ex situ and in situ approaches, and those are summarized well elsewhere ( Ghosh et al. 2014<sup>[TB8HY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." *Integrated Environmental Assessment and Management* 10 (2): 210-23. <https://doi.org/10.1002/ieam.1507>.) When PDMS-coated glass fibers are deployed in situ, perforated stainless steel rods, perforated cylindrical copper housing, or similar enclosures are typically used to ensure the samplers are protected while maintaining contact with the surrounding media. LDPE is often enclosed in a stainless steel mesh sleeve or protected by a metal frame. Deployment times can vary depending on sampling

conditions, in situ versus ex situ exposure parameters, and the target analytes being measured. Both LDPE and PDMS-coated glass fiber typically require 30 days of deployment to measure most HOCs ex situ. However, more hydrophobic compounds, such as PCBs and dioxin/furans, typically require the minimum residence time, along with potential corrections to account for analytes that do not achieve equilibrium relative to less hydrophobic compounds, such as PAHs.

Numerous guidance documents and tools have been developed to support application of these types of passive samplers in multiple phases of site investigation and monitoring. The USEPA published a 2017 user's manual along with calculator tools for data analysis available on the USEPA's website. Regulatory acceptance of integrating passive samplers into site characterization and monitoring has increased in recent years. Although no published standard methods are currently available for polymeric passive samplers, numerous studies have been conducted to standardize the preparation and analysis (Jonker et al. 2018<sup>[UFDMH7LV]</sup> Jonker, Michiel T. O., Stephan A. van der Heijden, Dave Adelman, Jennifer N. Apell, Robert M. Burgess, Yongju Choi, Loretta A. Fernandez, et al. 2018. "Advancing the Use of Passive Sampling in Risk Assessment and Management of Sediments Contaminated with Hydrophobic Organic Chemicals: Results of an International Ex Situ Passive Sampling Interlaboratory Comparison." *Environmental Science & Technology* 52 (6): 3574-82.

<https://doi.org/10.1021/acs.est.7b05752>.; Lotufo et al. 2022<sup>[BM8MW6FA]</sup> Lotufo, Guilherme R., Mandy M. Michalsen, Danny D. Reible, Philip M. Gschwend, Upal Ghosh, Alan J. Kennedy, Kristen M. Kerns, et al. 2022. "Interlaboratory Study of Polyethylene and Polydimethylsiloxane Polymeric Samplers for Ex Situ Measurement of Freely Dissolved Hydrophobic Organic Compounds in Sediment Porewater." *Environmental Toxicology and Chemistry* 41 (8): 1885-1902. <https://doi.org/10.1002/etc.5356>.)

The LDPE pore water samplers (Figure 5-23) consist of a clean, uncoated sheet of LDPE, which can vary in thickness but is generally from 13 to 76  $\mu\text{m}$  (Figure 5-23) (Burgess et al. 2017<sup>[97JRK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://sempub.epa.gov/work/HQ/100000146.pdf>.) The dimensions of the LDPE can be developed to meet specific project conditions and deployment requirements. These samplers are most typically deployed within an open frame or a metal mesh envelope.

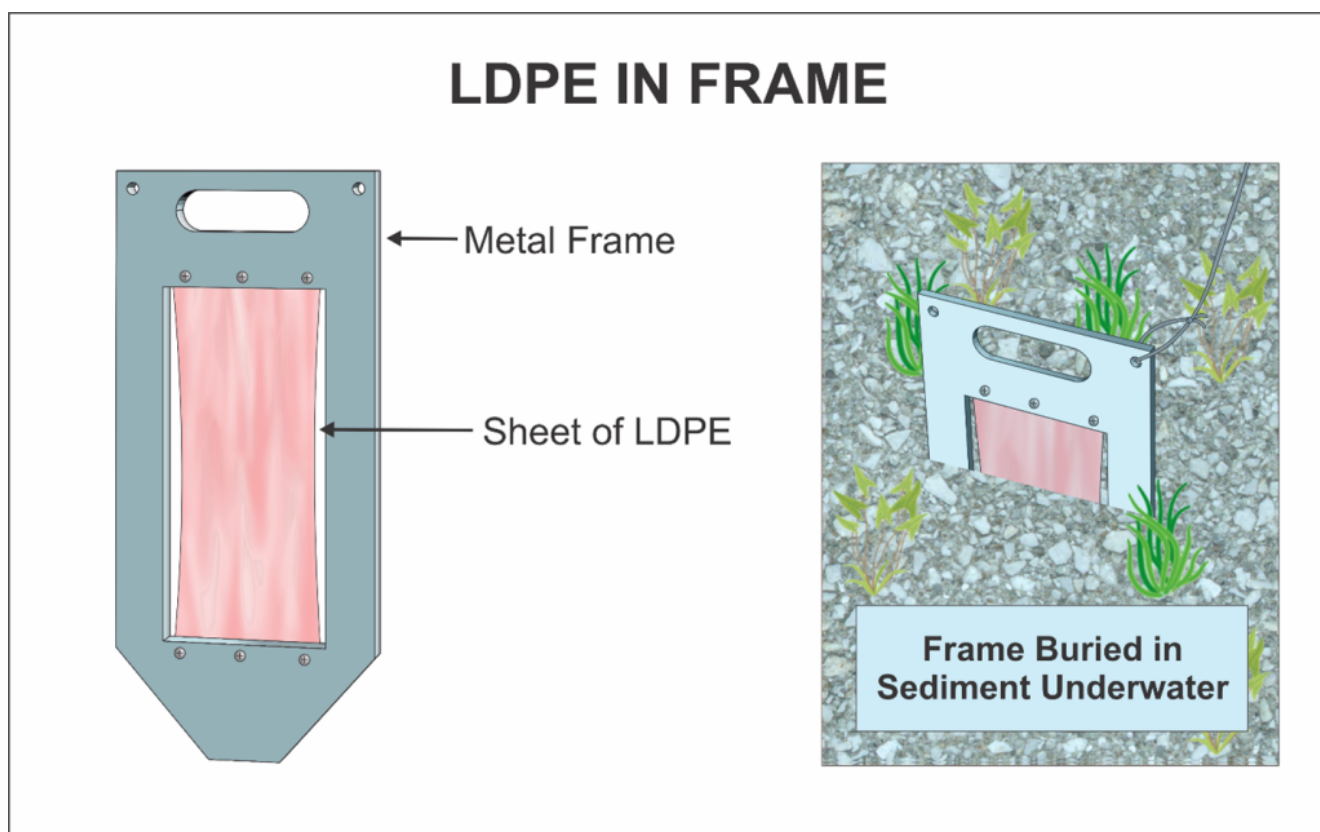


Figure 5-23. Low-density polyethylene sampler.  
Source: NJDEP, figure used with permission.

The polyurethane foam passive air sampler (PUF-PAS) is a device used to monitor the presence, distribution, and

concentration of airborne chemicals over a long-term deployment period without actively pumping the air. PUF-PAS passively collects airborne chemicals onto a PUF disk, which absorbs chemicals transported by advection and diffusion ( Moeckel et al. 2009<sup>[6QW9AHVA]</sup> Moeckel, Claudia, Tom Harner, Luca Nizzetto, Bo Strandberg, Andres Lindroth, and Kevin C. Jones. 2009. "Use of Depuration Compounds in Passive Air Samplers: Results from Active Sampling-Supported Field Deployment, Potential Uses, and Recommendations | Environmental Science & Technology." Environ. Sci. Technol 43 (9): 3227-32. <https://pubs.acs.org/doi/10.1021/es802897x>.) The PUF disk is uniformly porous and has a large surface area to allow gaseous chemicals to diffuse and absorb. The PUF disk also filters chemicals associated with particulates ( Klánová et al. 2008<sup>[QR58D68B]</sup> Klánová, Jana, Pavel Èupr, Jiří Kohoutek, and Tom Harner. 2008. "Assessing the Influence of Meteorological Parameters on the Performance of Polyurethane Foam-Based Passive Air Samplers." Environmental Science & Technology 42 (2): 550-55. <https://doi.org/10.1021/es072098o>.; Chaemfa et al. 2009<sup>[DE6HQ489]</sup> Chaemfa, Chakra, Edward Wild, Brian Davison, Jonathan L. Barber, and Kevin C. Jones. 2009. "A Study of Aerosol Entrapment and the Influence of Wind Speed, Chamber Design and Foam Density on Polyurethane Foam Passive Air Samplers Used for Persistent Organic Pollutants." Journal of Environmental Monitoring 11 (6): 1135-39. <https://doi.org/10.1039/B823016A>.; Bohlin, Jones, and Strandberg 2010<sup>[6ANIG7G]</sup> Bohlin, Pernilla, Kevin C. Jones, and Bo Strandberg. 2010. "Field Evaluation of Polyurethane Foam Passive Air Samplers to Assess Airborne PAHs in Occupational Environments." Environmental Science & Technology 44 (2): 749-54. <https://doi.org/10.1021/es902318g>.)

The PUF disk is usually housed in a protective stainless steel casing that shields it from direct sunlight, precipitation, the deposition of other particles, and physical damage while acting to buffer the air flow and allowing air to gently flow around the PUF disk. Target organic chemicals in gaseous phase diffuse and partition into PUF. Similar to the LDPE and PDMS polymeric devices, the PUF-air partition coefficients (KPUF-A) predict the partitioning of target chemicals between PUF and the gaseous phase at partition equilibrium ( Shoeib and Harner 2002<sup>[MI632BXE]</sup> Shoeib, Mahiba, and Tom Harner. 2002. "Characterization and Comparison of Three Passive Air Samplers for Persistent Organic Pollutants." Environmental Science & Technology 36 (19): 4142-51. <https://doi.org/10.1021/es020635t>.) Because the PUF disk used in PUF-PAS has an extremely large sorption capacity for persistent organic pollutants (POPs), most POPs do not reach partition equilibrium within a reasonable deployment time (weeks or months). Target chemical concentrations in the air are often calculated from the sampling rate and deployment time at the linear uptake regime (Equation 3).

### Equation 3

$$C_{air} = M_{PUF} / V_{eff}$$

Where:

$C_{air}$  = concentration in air

$M_{PUF}$  = mass of the target compound

$V_{eff}$  = effective sampling volume

### 5.2.7.2 Installation and Use

Polymeric passive samplers are typically deployed within a protective metal mesh sleeve, frame, or perforated metal rod. Samplers deployed within a sediment bed can be segmented and analyzed upon retrieval to obtain stratified discrete concentration results. Samplers can also be deployed into the sediment bed to also capture the near-bottom surface water.

These passive samplers can be used for both ex situ and in situ sampling of sediment pore water, surface water, and groundwater. Under in situ conditions, samplers are deployed in the field and retrieved after the required deployment timeframe. For ex situ sampling, the media of interest is collected, brought back to a laboratory setting, and the samplers are deployed into the collected media. There are advantages and disadvantages to both in situ and ex situ sampling methods. For in situ, environmental conditions for the exposure period are maintained and any confounding factors introduced by moving to the laboratory are eliminated. However, there are logistic challenges that accompany in situ deployments, including loss of samplers. For ex situ sampling, exposure conditions can be controlled and time to equilibrium can be accelerated through mixing or agitation of the media in a laboratory setting. However, site-specific environmental factors that could influence the concentrations of analytes could be altered and thus influence results.

For sediment pore water characterization, deployment and retrieval of polymeric passive samplers is most easily performed in shallow or intertidal environments when done in situ. Samplers can also be deployed in deeper water, but typically require the use of a dive team to assist in deployment and retrieval. Ex situ sampling only requires the collection of sediment using a core or grab.

The components necessary to assemble PUF-PAS, such as PUF disks and protective stainless steel housings, are commercially available from several suppliers. Prior to field deployment, the PUF disks need to be precleaned to remove any background contaminants, which is typically done using Soxhlet extraction. Precleaned PUF disks can be obtained from suppliers. PUF disks are sometimes spiked with PRCs such as isotope-labeled chemicals or congeners rarely found in the environment to help quantify the fraction of equilibrium at different sampling locations ( Huckins et al. 2002<sup>[DN3HJ22M]</sup> Huckins, James N., Jimmie D. Petty, Jon A. Lebo, Fernanda V. Almeida, Kees Booij, David A. Alvarez, Walter L. Cranor, Randal C. Clark, and Betty B. Mogensen. 2002. "Development of the Permeability/Performance Reference Compound Approach for in Situ Calibration of Semipermeable Membrane Devices." *Environmental Science & Technology* 36 (1): 85-91. <https://doi.org/10.1021/es010991w>.) Unexposed PUF-PAS should be used for QA/QC to assess background contamination introduced during the precleaning processes, transport, and deployment/retrieval. The PUF disk is usually housed in a protective stainless steel casing, and there are different casing designs available ( Melymuk et al. 2021<sup>[M2BMRBJC]</sup> Melymuk, Lisa, Pernilla Bohlin Nizzetto, Tom Harner, Kevin B. White, Xianyu Wang, Maria Yumiko Tominaga, Jun He, et al. 2021. "Global Intercomparison of Polyurethane Foam Passive Air Samplers Evaluating Sources of Variability in SVOC Measurements." *Environmental Science & Policy* 125 (November):1-9. <https://doi.org/10.1016/j.envsci.2021.08.003>.) PUF-PAS for air sampling are often mounted on poles, tripods, or other structures to position PUF-PAS at an optimum height (usually 1.5-2.0 m from the ground) to avoid influence from the ground. After the predetermined deployment period (usually weeks to months), PUF-PAS are retrieved from the sampling site, and PUF disks are carefully removed from the protective housing using a gloved hand and tweezers and sent for analysis. Prior to chemical extraction, PUF disks are spiked with a recovery standard to assess the integrity of the samples. Then PUF disks are extracted in a Soxhlet apparatus for 24 hours using a solvent.

The five polymeric sampling devices discussed all have different sampling capabilities (Table 5-4). The laboratory should always be contacted with questions prior to sampling.

Table 5-4: Polymeric sampler applications

Polymeric Sampler	Application	Chemical Constituents
POM	Water	PAH and PCB

Polymeric Sampler	Application	Chemical Constituents
PUF-PAS	Air	<p>Some SVOCs, including PAHs ( Cheng et al. 2013<sup>[SKMG77W6]</sup> Cheng, Hairong, Zongming Deng, Paromita Chakraborty, Di Liu, Ruijie Zhang, Yue Xu, Chunlin Luo, Gan Zhang, and Jun Li. 2013. "A Comparison Study of Atmospheric Polycyclic Aromatic Hydrocarbons in Three Indian Cities Using PUF Disk Passive Air Samplers." <i>Atmospheric Environment</i> 73 (July):16-21. <a href="https://doi.org/10.1016/j.atmosenv.2013.03.001">https://doi.org/10.1016/j.atmosenv.2013.03.001</a>.; Harner et al. 2013), PCBs, flame retardants ( Hazrati and Harrad 2007<sup>[OS2NNY4K]</sup> Hazrati, Sadegh, and Stuart Harrad. 2007. "Calibration of Polyurethane Foam (PUF) Disk Passive Air Samplers for Quantitative Measurement of Polychlorinated Biphenyls (PCBs) and Polybrominated Diphenyl Ethers (PBDEs): Factors Influencing Sampling Rates." <i>Chemosphere</i> 67 (3): 448-55. <a href="https://doi.org/10.1016/j.chemosphere.2006.09.091">https://doi.org/10.1016/j.chemosphere.2006.09.091</a>.; Okeme et al. 2018<sup>[IVCVCLAZA]</sup> Okeme, Joseph O., Congqiao Yang, Atousa Abdollahi, Suman Dhal, Shelley A. Harris, Liisa M. Jantunen, Dina Tsirlin, and Miriam L. Diamond. 2018. "Passive Air Sampling of Flame Retardants and Plasticizers in Canadian Homes Using PDMS, XAD-Coated PDMS and PUF Samplers." <i>Environmental Pollution (Barking, Essex: 1987)</i> 239 (August):109-17. <a href="https://doi.org/10.1016/j.envpol.2018.03.103">https://doi.org/10.1016/j.envpol.2018.03.103</a>.), dioxin/furan ( Mari et al. 2008<sup>[BLSAW68L]</sup> Mari, Montse, Marta Schuhmacher, Joan Feliubadaló, and José L. Domingo. 2008. "Air Concentrations of PCDD/Fs, PCBs and PCNs Using Active and Passive Air Samplers." <i>Chemosphere</i> 70 (9): 1637-43. <a href="https://doi.org/10.1016/j.chemosphere.2007.07.076">https://doi.org/10.1016/j.chemosphere.2007.07.076</a>.), and PFAS ( Ahrens et al. 2013<sup>[4W5GZIM4]</sup> Ahrens, Lutz, Tom Harner, Mahiba Shoeib, Martina Koblizkova, and Eric J. Reiner. 2013. "Characterization of Two Passive Air Samplers for Per- and Polyfluoroalkyl Substances." <i>Environmental Science &amp; Technology</i> 47 (24): 14024-33. <a href="https://doi.org/10.1021/es4048945">https://doi.org/10.1021/es4048945</a>.; Karásková et al. 2018<sup>[9ALWFY7S]</sup> Karásková, Pavlína, Garry Codling, Lisa Melymuk, and Jana Klánová. 2018. "A Critical Assessment of Passive Air Samplers for Per- and Polyfluoroalkyl Substances." <i>Atmospheric Environment</i> 185 (July):186-95. <a href="https://doi.org/10.1016/j.atmosenv.2018.05.030">https://doi.org/10.1016/j.atmosenv.2018.05.030</a>.)</p>
SPME	Water and Air	VOCs and SVOCs
LDPE	Water	PAH, PCBs, and other HOCs
PDMS	Water	PAH, PCBs, and other HOCs

### 5.2.7.3 Advantages

Applicable to POM, SPME, LDPE, and PDMS samplers:

- These samplers measure the bioavailable fraction of organic chemicals, providing a more accurate representation of the fraction of contaminant available for uptake by benthic and aquatic organisms.
- They can be performed in situ or ex situ.
- Use of PRCs allows for correction to equilibrium for more hydrophobic contaminants or time-constricted deployments.
- These samplers combine water sampling, extraction, and concentration.
- They measure time-averaged concentrations.
- There are low detection limits for more hydrophobic compounds.
- They cause minimal impact on sampling matrix and interferences with dissolved organic matter.
- They allow high resolution profiling of sediment pore water concentrations.

Applicable to PUF-PAS sampler:

- The components necessary to assemble PUF-PAS are commercially available.
- A standard PUF or modified PUF can be used to collect a wide range of SVOCs and POPs.

- PUF-PAS can also accumulate chemicals associated with particulates over time.

#### 5.2.7.4 Limitations

Applicable to POM, SPME, LDPE, and PDMS samplers:

- These samplers are limited to hydrophobic contaminants.
- No published standard method is currently available, but numerous studies have been conducted to standardize methods.
- POM requires extended equilibration time.
- These samplers are commercially available, but on a limited basis. Several academic institutions produce and analyze passive samplers, and commercial availability is anticipated to grow.

Applicable to PUF-PAS sampler:

- The sampling rates for target chemicals at different sites may vary due to the influence of temperature and wind speed. The sampling rates need to be calibrated under specific site conditions to ensure accurate quantitative data.
- Airborne particulates can cause significant differences in estimating air concentration of target organic chemicals in gaseous phase.

### 5.2.8 Passive In Situ Concentration Extraction Sampler (PISCES)

#### 5.2.8.1 Description and Application

The passive in situ concentration extraction sampler (PISCES) (Figure 5-24) is intended to sample nonpolar or HOCs in surface water ( Belluomini et al. 2008<sup>[HM25Q6CJ]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency. [https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf).) The sampler relies on diffusion and absorption to accumulate the target chemicals in the sampling medium ( Belluomini et al. 2008<sup>[HM25Q6CJ]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency. [https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf).) The residence period is compound-specific and can range from one day to one month. The rugged construction allows the sampler to be deployed for extended periods of time.

# Passive In-situ Concentration Extraction Sampler (PISCES)

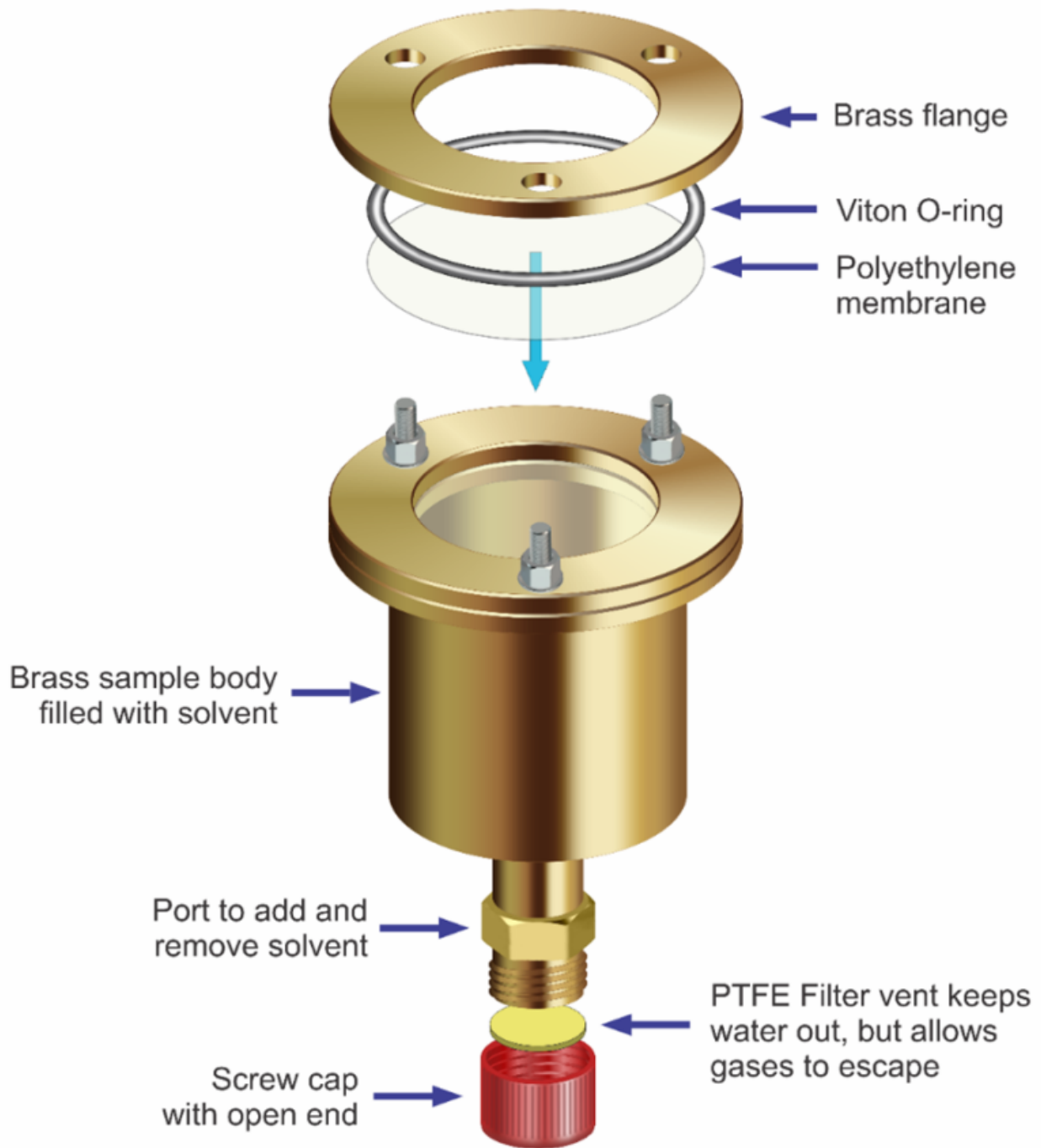


Figure 5-24. Passive in situ concentration extraction sampler (PISCES).

Source: NJDEP, figure used with permission.

PISCES consist of a membrane, typically LDPE, covering one end of a metal container filled with an organic solvent, typically hexane or isooctane (2,2,4-trimethylpentane) ( Belluomini et al. 2008<sup>[HM2506C]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency. [https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf)).

Other solvents such as alcohols (methanol, ethanol, propanol) were evaluated for use in this technology. Chemical uptake is propelled by the preferential partitioning of nonionic organic chemicals from water to the solvent ( Belluomini et al.

2008<sup>[HM2506CJ]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. "Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations." California Environmental Protection Agency.

[https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf)).

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. 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.

LDPE membranes typically are between 150 and 700  $\mu\text{m}$  thick. The solvents pass through the membrane at an appreciable rate if the membrane is properly mounted and not damaged. Sampling rate does not differ between hexane or isooctane. 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 chemicals such as xylenes are to be analyzed.

PISCES are reusable and allow the easy addition and retrieval of the selected organic solvent, which is placed in the brass body (see Figure 5-24). The top cap of the sampler is fitted with a flange and Viton O-ring to retain the LDPE membrane. A port with a screw cap is at the other end to allow addition and removal of solvent. The PTFE vent filter on the top cap prevents the migration of the sample media from entering the sampler but allows gases that may accumulate during deployment to escape. PISCES are manufactured in two sizes: a 7.6-cm (3-inch) flange diameter (has a membrane area of 21  $\text{cm}^2$  and can hold 100 mL of solvent), and a 10-cm (4-inch) flange diameter (has a membrane area of 50  $\text{cm}^2$  and can hold 200 mL of solvent). Both samplers are approximately 9.5 cm (3.75 inches) long.

### 5.2.8.2 Installation and Use

The PISCES device is 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.

At the end of the deployment, solvent is decanted from the sampler into the laboratory-supplied container 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.

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 aqueous media where the water can be considered a source of chemical concentrations.

The uptake of compounds by PISCES is characterized by the sampling rate. The sampling rate is the volume of water that is cleared of chemical 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, more than 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 1-liter water sample.

### 5.2.8.3 Advantages

- PISCES samplers can be redeployed without decontamination to the same sample location.
- They are lightweight.
- They are reusable.
- They have improved laboratory detection limits.

- PISCES allow easy addition and retrieval of solvent.

#### 5.2.8.4 Limitations

- PISCES samplers are expensive.
- Samplers must remain submerged during deployment.
- Deployment to moving bodies of surface water requires careful consideration to avoid damage.
- Samplers may contain solvent that potentially could be released to sampled media.
- Some hazardous shipping and handling requirements may apply.
- Many laboratories do not accept these samplers for analysis.

### 5.2.9 Ceramic Diffusion Sampler/Ceramic Dosimeter

#### 5.2.9.1 Description and Application

The ceramic diffusion sampler consists of a porous ceramic cup filled with reagent water with a PTFE or stainless steel cap. Target chemicals in the bulk water phase diffuse into the sampler through micropores (that is, a few microns pore size) in the ceramic cup and equilibrate with the water inside the sampler over time. Therefore, the ceramic diffusion sampler (Figure 5-25) is an equilibrium-type passive sampler and works the same as other equilibrium-type passive samplers such as the rigid porous polyethylene sampler. The sampler can be used to measure SVOCs and hydrophobic organic compounds such as PAHs in groundwater, surface water, and pore water ( Gefell et al. 2018<sup>[TZJNM6RC]</sup> Gefell, M.J., M. Kanematsu, D. Vlassopoulos, and D.S. Lipson. 2018. "Aqueous-Phase Sampling with NAPL Exclusion Using Ceramic Porous Cups." *Groundwater* 56:847-51.). The ceramic cup is inert, water-wet (hydrophilic), and does not adsorb or swell target chemicals. A major advantage of the ceramic diffusion sampler is that it allows the collection of aqueous media while excluding NAPL ( Gefell et al. 2018<sup>[TZJNM6RC]</sup> Gefell, M.J., M. Kanematsu, D. Vlassopoulos, and D.S. Lipson. 2018. "Aqueous-Phase Sampling with NAPL Exclusion Using Ceramic Porous Cups." *Groundwater* 56:847-51.). Aqueous-phase sampling can be complicated when NAPL is present in aqueous media. NAPL contained in water samples biases the interpreted aqueous concentrations unrealistically high. NAPLs also preferentially coat and foul polymeric sampling devices and complicates the determination of freely dissolved concentrations ( Ghosh et al. 2014<sup>[T8GHY3EM]</sup> Ghosh, Upal, Susan Kane Driscoll, Robert M Burgess, Michiel TO Jonker, Danny Reible, Frank Gobas, Yongju Choi, et al. 2014. "Passive Sampling Methods for Contaminated Sediments: Practical Guidance for Selection, Calibration, and Implementation." *Integrated Environmental Assessment and Management* 10 (2): 210-23. <https://doi.org/10.1002/ieam.1507>.). The porous ceramic cup is permeable to allow water to diffuse into the sampler but also resistant to NAPL entry and acts as a capillary barrier to exclude NAPL.

# Ceramic Diffusion Sampler

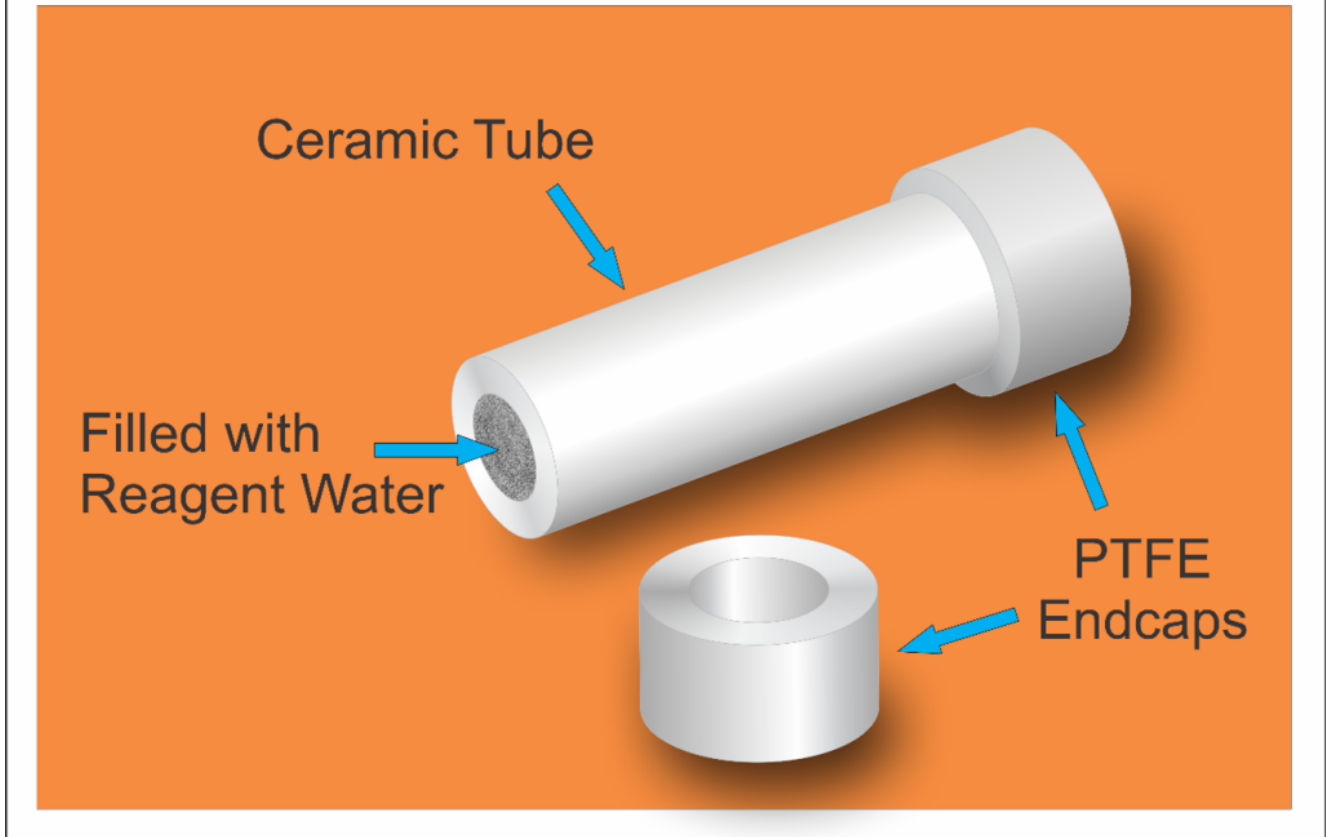


Figure 5-25. Ceramic diffusion sampler.

Source: NJDEP, figure used with permission.

The ceramic dosimeter (Figure 5-26) is similar to the ceramic diffusion sampler but functions differently. The ceramic dosimeter is made of a porous ceramic tube and solid adsorbent beads or resins enclosed in the ceramic tube ( Martin, Patterson, and Davis 2003<sup>[Q4MV5B7J]</sup> Martin, H., B.M. Patterson, and G.B. Davis. 2003. "Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling." *Environmental Science and Technology* 37:1360-64.

<https://pdfslide.net/documents/field-trial-of-contaminant-groundwater-monitoring-comparing-time-integrating.html?page=1.>)

The ceramic dosimeter is used to measure VOCs, PAHs, and other organic chemicals in groundwater, surface water, and pore water ( Martin, Patterson, and Davis 2003<sup>[Q4MV5B7J]</sup> Martin, H., B.M. Patterson, and G.B. Davis. 2003. "Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling." *Environmental Science and Technology* 37:1360-64.

<https://pdfslide.net/documents/field-trial-of-contaminant-groundwater-monitoring-comparing-time-integrating.html?page=1.>

Bopp, Hansjorg, and Schirmer 2005<sup>[RWJTD3C2]</sup> Bopp, S., W. Hansjorg, and K. Schirmer. 2005. "Time-Integrated Monitoring of Polycyclic Aromatic Hydrocarbons (PAHs) in Groundwater Using the Ceramic Dosimeter Passive Sampling Device." *Journal of Chromatography A* 1072:137-47.; Bopp, Mclachlan, and Schirmer 2007<sup>[EGPHZ7J]</sup> Bopp, S., M.S. Mclachlan, and K. Schirmer. 2007. "Passive Sampler for Combined Chemical and Toxicological Long-Term Monitoring of Groundwater: The Ceramic

Toximeter." *Environmental Science and Technology* 41:6868-76.; Bonifacio et al. 2017<sup>[LQ5BK3YL]</sup> Bonifacio, R.G., G.-U. Nam, Y.-S. Hong, and I-Y Eom. 2017. "Development of Solid Ceramic Dosimeters for the Time-Integrative Passive Sampling of Volatile Organic Compounds in Waters." *Environmental Science and Technology* 51:12557-65.). A ceramic tube acts as diffusive-controlling layer for target chemicals, and the enclosed solid adsorbents or resins adsorb target chemicals. PTFE caps are used to close a ceramic tube to minimize sorption of target chemicals, and those caps are fixed in a stainless steel holder (

Martin, Patterson, and Davis 2003<sup>[Q4MV5B7J]</sup> Martin, H., B.M. Patterson, and G.B. Davis. 2003. "Field Trial of Contaminant

Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling.”  
Environmental Science and Technology 37:1360-64.

<https://pdfslide.net/documents/field-trial-of-contaminant-groundwater-monitoring-comparing-time-integrating.html?page=1.>) The solid adsorbents or resins concentrate target organic chemicals diffused through the ceramic tube over time and eventually saturate if deployed for an extended period. The ceramic dosimeter works only at the kinetic regime, where the uptake rates of a target chemical to the sampler are linearly proportional to the difference between the chemical activity of the chemical in the bulk phase and that in the sampler. Therefore, the ceramic dosimeter is an accumulation-type sampler, whereas the ceramic diffusion sampler is an equilibrium-type sampler.

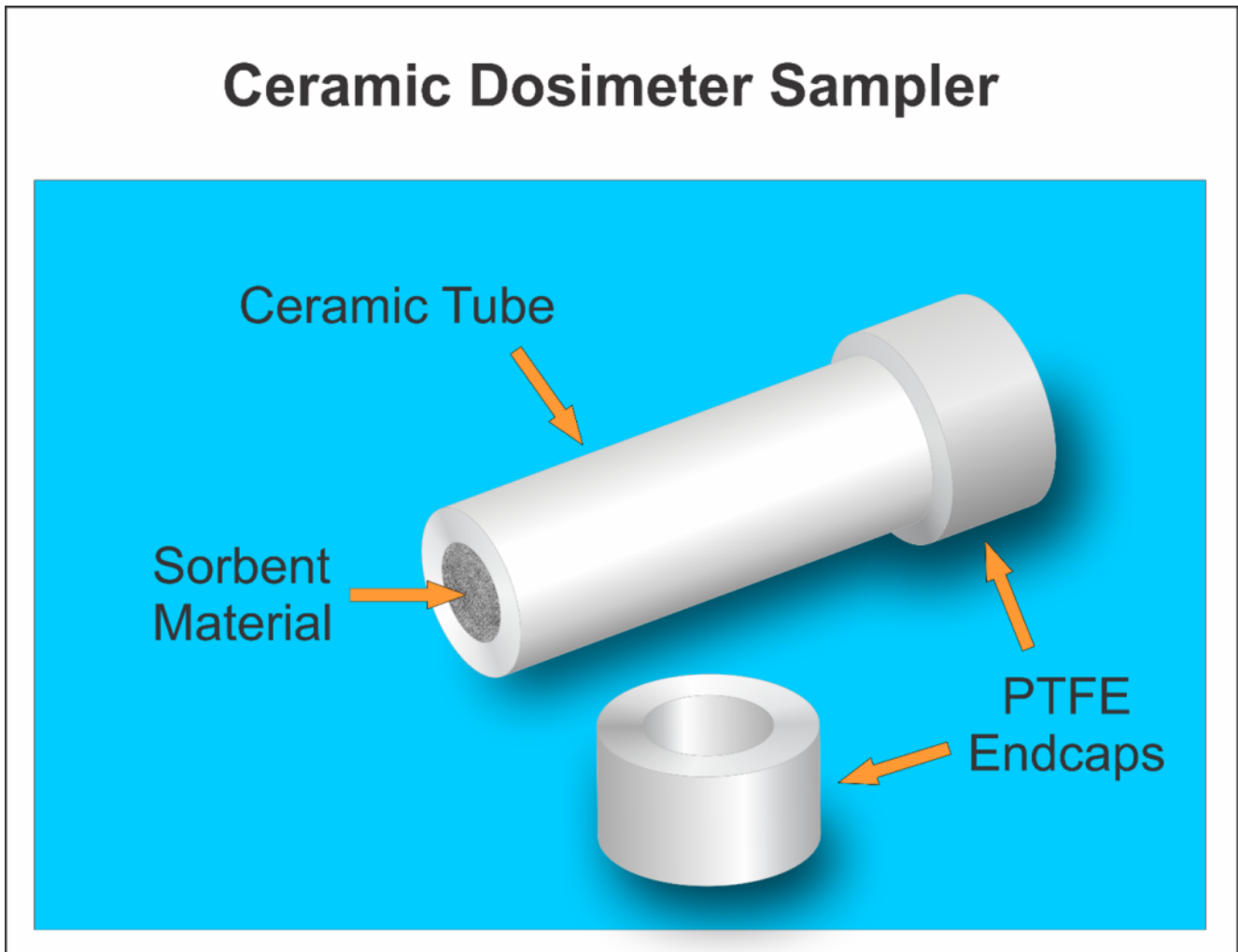


Figure 5-26. Ceramic dosimeter sampler.

Source: NJDEP, figure used with permission.

Martin, Patterson, and Davis ( Martin, Patterson, and Davis 2003<sup>[04MV5B7J]</sup> Martin, H., B.M. Patterson, and G.B. Davis. 2003. “Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling.” Environmental Science and Technology 37:1360-64. <https://pdfslide.net/documents/field-trial-of-contaminant-groundwater-monitoring-comparing-time-integrating.html?page=1.>) showed that the relationship between the time-weighted average concentration of a target chemical and the accumulated mass on the solid adsorbent beads is based on Fick’s first law as follows (Equation 4):

#### Equation 4

$$M = F \cdot A \cdot t = D_e \frac{\Delta C}{\Delta x} \cdot A \cdot t \approx D_e \frac{C_w}{l} \cdot A \cdot t$$

where:

$M$  = accumulated mass of a target chemical [M]

$F$  = mass flux of a target chemical through the ceramic tube [ $M t^{-1} L^{-2}$ ]

$A$  = ceramic tube surface area [ $L^2$ ]

$t$  = deployment time [t]

$D_e$  = effective diffusion coefficient of a target chemical [ $L^2 t^{-1}$ ]

$\Delta C / \Delta x$  = concentration gradient across the ceramic tube [ $ML^{-4}$ ]

$C_w$  = average concentration of a target chemical in water [ $ML^{-3}$ ]

$l$  = ceramic tube thickness [L]

Maintaining the concentration of the solute inside the sampler as close to zero as possible will allow a time-weighted concentration to be calculated from the accumulated mass. This is accomplished through the addition of high-capacity adsorbent beads inside the tube. These beads ensure the linear uptake of the target compound during the entire deployment time. Comparison between the concentrations derived from ceramic dosimeters and average concentrations determined by frequent conventional snapshot active sampling showed that ceramic dosimeters perform well over up to 90 days of deployment in a contaminated aquifer ( Martin, Patterson, and Davis 2003<sup>[O4MV5B7J]</sup> Martin, H., B.M. Patterson, and G.B. Davis. 2003. "Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling." *Environmental Science and Technology* 37:1360-64. <https://pdfslide.net/documents/field-trial-of-contaminant-groundwater-monitoring-comparing-time-integrating.html?page=1>).

In a recent study, Kaserzon et al. ( Kaserzon et al. 2019<sup>[75EEAA35]</sup> Kaserzon, Sarit L., Soumini Vijayasarathy, Jennifer Bräunig, Linus Mueller, Darryl W. Hawker, Kevin V. Thomas, and Jochen F. Mueller. 2019. "Calibration and Validation of a Novel Passive Sampling Device for the Time Integrative Monitoring of Per- and Polyfluoroalkyl Substances (PFASs) and Precursors in Contaminated Groundwater." *Journal of Hazardous Materials* 366 (March):423-31. <https://doi.org/10.1016/j.jhazmat.2018.12.010>.) used a microporous polyethylene tube instead of using a porous ceramic tube as a diffusion-controlling layer to enclose an anion exchange resin (Strata X-AW) to measure per- and polyfluoroalkyl substances (PFAS) in aqueous media. The use of ceramic materials for PFAS may be problematic due to the adsorption of PFAS on ceramics, but polyethylene materials are suitable to measure PFAS ( Kaserzon et al. 2019<sup>[75EEAA35]</sup> Kaserzon, Sarit L., Soumini Vijayasarathy, Jennifer Bräunig, Linus Mueller, Darryl W. Hawker, Kevin V. Thomas, and Jochen F. Mueller. 2019. "Calibration and Validation of a Novel Passive Sampling Device for the Time Integrative Monitoring of Per- and Polyfluoroalkyl Substances (PFASs) and Precursors in Contaminated Groundwater." *Journal of Hazardous Materials* 366 (March):423-31. <https://doi.org/10.1016/j.jhazmat.2018.12.010>).

#### 5.2.9.2 Installation and Use

As described above, the ceramic diffusion sampler can be placed in NAPL-contaminated aqueous media to equilibrate by diffusion to measure SVOCs and PAHs while excluding NAPL. This is a unique feature of this technology as NAPL exclusion is quite difficult for other passive samplers. It takes approximately 30 days for PAHs to reach equilibrium between the water inside the sampler and the surrounding aqueous phase under a static condition ( Gefell et al. 2018<sup>[T2JNM6RC]</sup> Gefell, M.J., M. Kanematsu, D. Vlassopoulos, and D.S. Lipson. 2018. "Aqueous-Phase Sampling with NAPL Exclusion Using Ceramic Porous Cups." *Groundwater* 56:847-51.).

Different solid adsorbent beads have been used in ceramic dosimeters to measure a variety of organic compounds, such as VOCs, PAHs, dioxins, flame retardants, and pharmaceutical compounds ( Addeck et al. 2012<sup>[MVIQABXJ]</sup> Addeck, A., K. Croes, K. Langenhove, M. Denison, M. Elskens, and W. Baeyens. 2012. "Dioxin Analysis in Water by Using a Passive Sampler and CALUX Bioassay." *Talanta* 88:73-78.; Franquet-Griell et al. 2017<sup>[L4EY5QC9]</sup> Franquet-Griell, H., V. Pueyo, J. Silva, V.M. Orera, and

S. Lacorte. 2017. "Development of a Macroporous Ceramic Passive Sampler for the Monitoring of Cytostatic Drugs in Water." *Chemosphere* 182:681–90.; Cristale et al. 2013<sup>[ACH7B6J]</sup> Cristale, J., A. Katsoyiannis, C. Chen, K.C. Jones, and S. Lacorte. 2013. "Assessment of Flame Retardants in River Water Using a Ceramic Dosimeter Passive Sampler." *Environmental Pollution* 172:163–69.; Kaserzon et al. 2019<sup>[75EEA35]</sup> Kaserzon, Sarit L., Soumini Vijayasarathy, Jennifer Bräunig, Linus Mueller, Darryl W. Hawker, Kevin V. Thomas, and Jochen F. Mueller. 2019. "Calibration and Validation of a Novel Passive Sampling Device for the Time Integrative Monitoring of Per- and Polyfluoroalkyl Substances (PFASs) and Precursors in Contaminated Groundwater." *Journal of Hazardous Materials* 366 (March):423–31. <https://doi.org/10.1016/j.jhazmat.2018.12.010>). The ceramic dosimeters are deployed in aqueous media for a few weeks or months to uptake target chemicals, and the deployment duration may vary depending on target chemicals. Solid adsorbent beads are extracted a few times with organic solvents such as acetone after retrieval to determine the accumulated mass of a target compound. Once adsorbed, certain chemicals do not significantly degrade, desorb, or diffuse out of the ceramic dosimeter ( Martin, Patterson, and Davis 2003<sup>[Q4MV5B7J]</sup> Martin, H., B.M. Patterson, and G.B. Davis. 2003. "Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling." *Environmental Science and Technology* 37:1360–64. <https://pdfslide.net/documents/field-trial-of-contaminant-groundwater-monitoring-comparing-time-integrating.html?page=1>). The ceramic dosimeter can be combined with bioassay and biomonitoring by using a unique solid adsorbent material; this technique is called a ceramic toximeter ( Bopp, Mclachlan, and Schirmer 2007<sup>[EGPHZ7J]</sup> Bopp, S., M.S. Mclachlan, and K. Schirmer. 2007. "Passive Sampler for Combined Chemical and Toxicological Long-Term Monitoring of Groundwater: The Ceramic Toximeter." *Environmental Science and Technology* 41:6868–76.; Addeck et al. 2012<sup>[MVIQABXJ]</sup> Addeck, A., K. Croes, K. Langenhove, M. Denison, M. Elskens, and W. Baeyens. 2012. "Dioxin Analysis in Water by Using a Passive Sampler and CALUX Bioassay." *Talanta* 88:73–78.). Bonifacio et al. ( Bonifacio et al. 2017<sup>[LQ5BK3YL]</sup> Bonifacio, R.G., G.-U. Nam, Y.-S. Hong, and I-Y Eom. 2017. "Development of Solid Ceramic Dosimeters for the Time-Integrative Passive Sampling of Volatile Organic Compounds in Waters." *Environmental Science and Technology* 51:12557–65.) used a nonporous ceramic tube that excluded the permeation of water but allowed only gas-phase diffusion of VOCs to the dry resin inside the ceramic tube and showed its effectiveness to measure VOC concentrations in water.

### 5.2.9.3 Advantages

- Ceramic materials can exclude NAPL from water samples.
- A ceramic dosimeter can achieve better detection limits for VOCs compared to grab- and equilibrium-based passive samplers because of the accumulation of those compounds on solid adsorbent beads.
- A wide range of organic compounds may be measured by using different solid adsorbent beads inside the ceramic dosimeter.

### 5.2.9.4 Limitations

- The ceramic diffusion sampler and ceramic dosimeter are not commercially available. However, users can construct these samplers using commercially available porous ceramic cups/tubes and other parts.
- Ceramic dosimeters and ceramic equilibrium samplers cannot be used for inorganic compounds and PFAS because of the uptake of those chemicals by ceramic materials.
- The ceramic dosimeter is still in the development phase and requires extra steps to determine aqueous phase concentrations compared to grab or equilibrium passive samplers.
- PTFE parts may contain PFAS, which should be considered based on project DQOs.

## 5.3 Accumulation Sampling Technologies

Accumulation (integrative) devices function in liquid and gas media where molecules freely move about within the medium under naturally occurring conditions of molecular motion, thermal convection, and flow. They concentrate the target chemical on a selective collecting medium such as an adsorbent or absorbent solid, a solvent, or chemical reagent (ITRC 2022).

The collecting medium may be in direct contact with the sampled medium. For example, ambient air being sampled may be in direct contact with the adsorptive granular solid material, such as granular activated carbon, in the device. Alternatively,

the collecting medium may be contained within a semipermeable membrane so that only certain molecules can diffuse from the sampled medium, through the membrane, and into contact with the collecting medium. For example, an absorbent gel may be contained within a hydrophobic membrane so that when immersed in water the membrane prevents water molecules from coming in direct contact with the collecting gel but it allows diffusion of specific contaminant molecules through the membrane so they can be absorbed by the gel.

Target molecules that come in contact with the collecting medium accumulate on the collecting medium during the exposure period, at compound-specific uptake rates that are influenced by environmental conditions (including temperature, pressure, flow rate past the sampler, and turbulence of the sampled environment), depending on the medium sampled. The target molecules will continue to accumulate on the collecting medium until the medium reaches saturation; therefore, the collecting medium needs to be of sufficient mass so that a concentration equilibration with the surrounding medium does not occur. If the target medium becomes saturated before removal and analysis, the calculation of concentration will be biased low.

After the sampler has been recovered, the target molecules are desorbed from the collecting medium at a lab to produce a result of mass of accumulated target molecules. The resulting sample chemical mass is used to calculate a time-weighted average concentration of target chemicals over the exposure period ( Huckins, Petty, and Booji 2006<sup>[6V87RUVQ]</sup> Huckins, James N., Jimmie D. Petty, and Kees Booji. 2006. *Monitors of Organic Chemicals in the Environment Semipermeable Membrane Devices*. Springer eBooks. <https://doi.org/10.1007/0-387-35414-x>; Taylor et al. 2021). Previously calculated uptake rates for the individual compounds are needed to calculate the mass accumulated to a time-weighted average concentration ( $\mu\text{g}/\text{m}^3$ ). Uptake rates are not flow rates and may have units of volume/time but are dependent on media for specific calculation. The longer the sampling duration, the more of the medium that is sampled and, therefore, the lower the reporting limit.

Time-weighted average concentrations of VOCs are collected over days or weeks on accumulation samplers to provide time-integrated measurements and average measurements over an extended sampling period. No pumps or vacuums are used, so the reported measurement represents a concentration under ambient conditions. The sampling protocols are simpler than traditional sampling methods, which reduces the cost of sampling and risk of operator error.

These longer, time-integrated samples are a preferred approach for determining both short-term and long-term average exposure levels. As noted in the USEPA Office of Solid Waste and Emergency Response (OSWER) Vapor Intrusion Guidance says, "All else being equal, a longer collection period for each individual sample would be expected to yield a more reliable basis for estimating long-term [and short-term], time-average exposure than would a one-day sample collection period" ( USEPA 2015<sup>[ZH2YKUR7]</sup> USEPA. 2015. "OSWER Technical Guide For Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air." USEPA, Office of Solid Waste and Emergency Response. <https://www.epa.gov/sites/default/files/2015-09/documents/oswer-vapor-intrusion-technical-guide-final.pdf>). Passive samplers have the additional benefit of being small, lightweight, easy to ship, and easy to use with simple sampling protocols not requiring specialized training.

As part of the data evaluation of a passive sample collected over an extended time period, inferences can be made of what the highest concentration may have been for any shorter time period within the total sampling time. As an example, a trichloroethene (TCE) measurement of  $1.0 \mu\text{g}/\text{m}^3$  recorded over a 10-day sampling period also means that the highest 2-day (48 hour) average concentration could not have exceeded  $5 \mu\text{g}/\text{m}^3$  or the highest 1-day (24 hour) average concentration could not have exceeded  $10 \mu\text{g}/\text{m}^3$ .

Although this document mentions several passive accumulation samplers by name, it should be noted that there are other companies providing sorbent samplers for the collection of soil gas and/or indoor/outdoor air samples. Typically, these samplers consist of a sorbent material held in either a stainless steel or glass tube or within a "housing." The adsorbent materials in these tubes are chosen based on the target analytes and the analytical extraction method to be used (for example, thermal desorption or solvent extraction). Frequently used adsorbents include, but are not limited to Anasorbs, Carbosieves, Carbo-pack X, Carbograph, Carboxens, Chromosorbs, Tenax TA, XADs, and silica gels. These sorbent tubes, depending on the sorbent material and target chemicals, can be analyzed by USEPA Methods TO-17 or 325A. When using passive sampling methods for the collection of air and/or soil gas samples, be sure to consider all of the different samplers and sorbent options that may be applicable for sampling the target chemicals.

Table 5-5, adapted from USGS's Table 4 ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020.

“Passive Sampling of Groundwater Wells for Determination of Water Chemistry.” In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.), below lists chemical families that can be analyzed using the noted passive sampling technologies. Always check with your state agency, sampler manufacturer, and laboratory to confirm that the selected technology meets your DQOs.

<b>Passive Accumulation Sampling Technologies</b>	<b>AGI</b>	<b>POCIS</b>	<b>Sentinel</b>	<b>SPMD</b>	<b>DGT</b>	<b>Min-Trap</b>	<b>Radiello</b>	<b>Waterloo</b>	<b>Beacon</b>	<b>Dart</b>	<b>Fossil Fuel</b>	<b>Bio-Trap</b>
<b>Chemical constituents and characteristics</b>												
<b>Field physiochemical characteristics</b> (Temp, pH, SC, DO, ORP)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>Major cations and anions</b> (Ca, Mg, Na, K, HCO <sub>3</sub> , Cl, SO <sub>4</sub> , F, Br)	N/A	N/A	N/A	N/A	Some	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>Nutrients</b> (NO <sub>3</sub> , NO <sub>2</sub> , NH <sub>4</sub> , PO <sub>4</sub> )	N/A	N/A	N/A	N/A	Some (NO <sub>3</sub> , PO <sub>4</sub> )	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>Trace elements (metals)</b> (Fe, Mn, Al, Ag, Zn and others)	N/A	N/A	N/A	N/A	ALL	N/A	N/A	Some (Hg)	Hg	N/A	N/A	N/A
<b>Perchlorate</b> (ClO <sub>4</sub> )	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>Organic carbon</b> (dissolved or total)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	petrogenic CO <sub>2</sub> in soil (via measurements of total and modern (based on <sup>14</sup> C))	N/A
<b>Dissolved hydrocarbon gases</b> (Methane, ethane, ethene)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>Volatile organic compounds</b> (Chlorinated solvents, BTEX)	Some	N/A	N/A	N/A	N/A	N/A	Some	Some	Most	N/A	N/A	N/A
<b>Semivolatile organics</b> (1,4-dioxane, BN, phenols, PAH, PCB, dioxins, furans)	Some	N/A	N/A	Some		N/A	N/A	Some	Some	Some (PAH)	N/A	N/A
<b>Pesticides, herbicides, and fungicides</b> (organoCl, organoPO <sub>4</sub> )	Some	ALL	N/A	Some	Some (Organic PO <sub>4</sub> )	N/A	N/A	N/A	Some	N/A	N/A	N/A

<b>Passive Accumulation Sampling Technologies</b>	<b>AGI</b>	<b>POCIS</b>	<b>Sentinel</b>	<b>SPMD</b>	<b>DGT</b>	<b>Min-Trap</b>	<b>Radiello</b>	<b>Waterloo</b>	<b>Beacon</b>	<b>Dart</b>	<b>Fossil Fuel</b>	<b>Bio-Trap</b>
<b>Explosive compounds</b> (RDX, HMX, TNT)	Some	N/A	N/A	NT	NT	N/A	N/A	N/A	Some	N/A	N/A	N/A
<b>Poly- and perfluoroalkyl substances</b> (PFASs)	NT	Some	Some	NT	Some	N/A	N/A	N/A	Some	N/A	N/A	N/A
<b>Pharmaceuticals</b> (Drugs, fragrances, hormones)	N/A	ALL	N/A	Some	Some	N/A	N/A	N/A	NT	N/A	N/A	N/A
<b>Minerals</b> (pyrite, mackinawite, iron compounds)	N/A	N/A	N/A	N/A	N/A	ALL	N/A	N/A	N/A	N/A	N/A	N/A
<b>Microbial population sampling</b> (e.g., Dehalococcoides)	N/A	N/A	N/A	N/A	N/A	Some	N/A	N/A	N/A	N/A	N/A	ALL

**Table 5-5 Key**

Most	Most compounds are compatible with the sampler
Some	Some compounds are compatible with the sampler
NT	Not tested (no study to support)
N/A	Not applicable to this sampler

**Table 5-5 Acronym Key**

[Temp, temperature; SC, specific conductivity; DO, dissolved oxygen; ORP, oxidation-reduction potential; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO<sub>3</sub>, bicarbonate; Cl, chloride; SO<sub>4</sub>, sulfate; F, fluoride; Br, bromide; NO<sub>3</sub>, nitrate, NO<sub>2</sub>, nitrite; NH<sub>4</sub>, ammonium; PO<sub>4</sub>, phosphate; Fe, iron; Mn, manganese; Al, aluminum; Ag, silver; Zn, zinc; ClO<sub>4</sub>, perchlorate; BTEX, benzene, toluene, ethylbenzene and xylene; BN, base-neutral organics; PAH, polycyclic aromatic hydrocarbons; PCB, polychlorinated biphenyls; organoCl, organochlorine; organoPO<sub>4</sub>, organophosphate; RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane; TNT, trinitrotoluene; TOC, total organic carbon; Hg, mercury; CO<sub>2</sub>, carbon dioxide]

### 5.3.1 AGI Universal Sampler (Formerly the Gore Sorber)

#### 5.3.1.1 Description and Applications

The Amplified Geochemical Imaging (AGI) Universal Sampler (Figure 5-27) is a device that relies on diffusion and adsorption to accumulate chemicals on the “passive sorbent collection units (‘sorbent’)” contained within the sampler (or module). These modules yield a chemical mass that reportedly can then be correlated with concentrations of said chemicals in water or air. This device can be used to sample soil gas in the vadose zone, indoor/outdoor air for vapor intrusion studies, and dissolved organic chemicals in either saturated soils or groundwater monitoring wells. AGI samplers can be used in both fresh and saltwater environments, including marsh sediments, streams, river embankments, and coastal settings (

Belluomini et al. 2008<sup>[HM25Q6C]</sup> Belluomini, Steve, Kathleen Considine, Bill Owen, and John Woodling. 2008. “Representative Sampling of Groundwater for Hazardous Substances: Guidance Manual for Groundwater Investigations.” California

Environmental Protection Agency.

[https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative\\_Sampling\\_of\\_GW\\_for\\_Haz\\_Subst.pdf](https://dtsc.cdev.sites.ca.gov/wp-content/uploads/sites/112/2018/09/Representative_Sampling_of_GW_for_Haz_Subst.pdf)).

Each module is approximately ¼ inch in diameter, 13 inches in length, and consists of a polytetrafluoroethylene (PTFE Gore-Tex) membrane tube that contains four connected sorber pockets holding engineered sorbent material. The PTFE Gore-Tex membrane is microporous, expandable, and relatively chemically inert ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.) A typical sorber pocket is about 25 mm in length, 3 mm in diameter, and contains a PTFE rod embedded with granular adsorbent material that is chosen based on the specific target compounds. Hydrophobic carbonaceous and polymeric resins are used for VOCs and SVOCs, but the adsorbent material can be custom designed for other chemicals. Organic compounds dissolved in water partition to the vapor phase (Henry's Law) and move across the membrane to the sorbent ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>.) The end of the module has a loop with a unique serial number label.

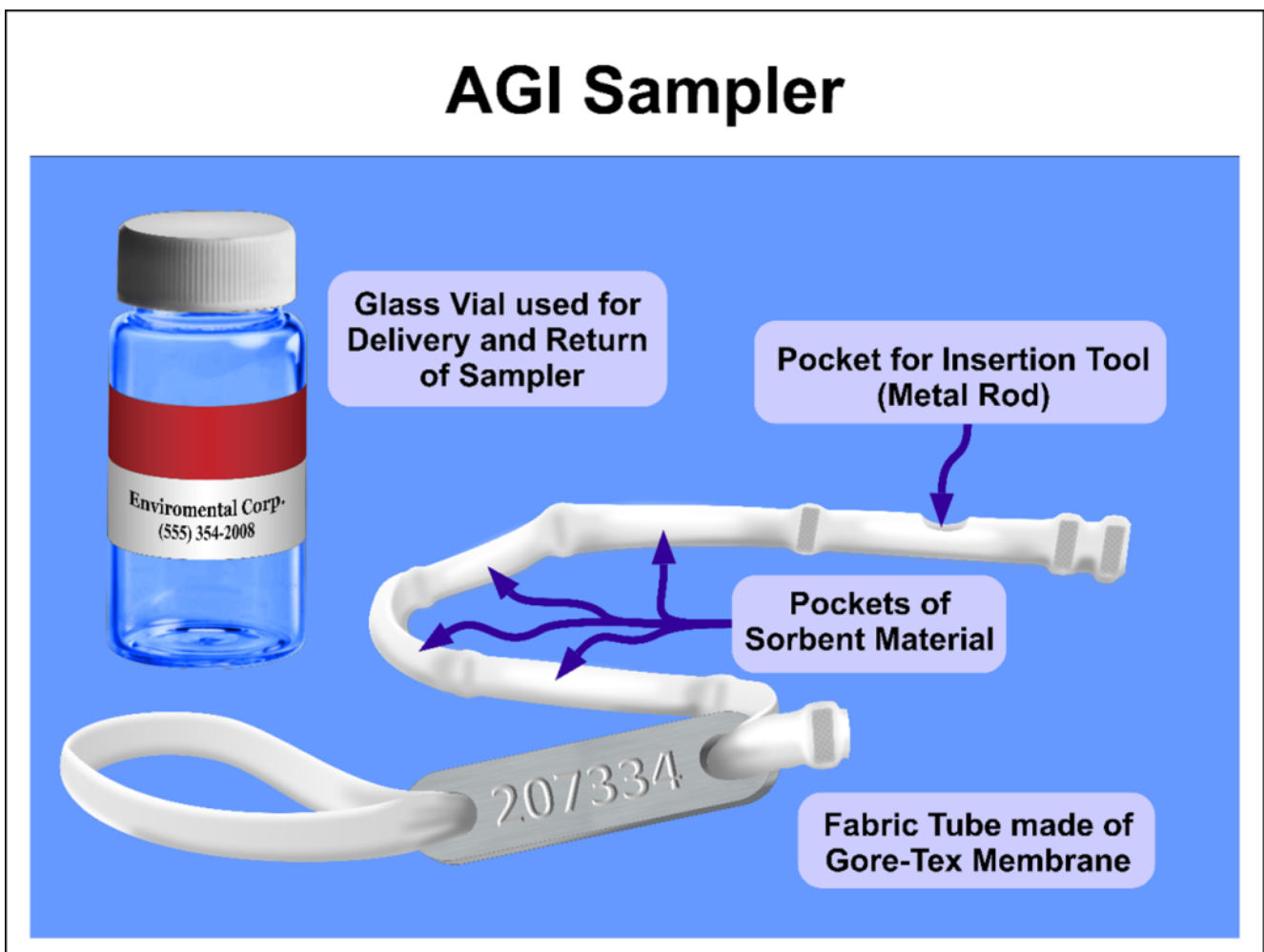


Figure 5-27. Amplified Geochemical Imaging Universal Sampler.

Source: NJDEP, figure used with permission.

### 5.3.1.2 Installation and Use

The AGI Universal Sampler (Figure 5-28 to 5-30) can be used to sample vadose zone soil gas, indoor/ outdoor air, and dissolved gases in groundwater. The modules arrive clean and contained in a sealed glass vial from the manufacturer. The samplers are provided as part of a sampling kit that includes additional installation supplies (see photos below), such as corks, string, stainless steel insertion rods, and chains of custody. Medium-specific installation and use is as follows:

#### Soil Gas Sampling

Field personnel advance a vertical boring using a slide hammer, rotary hammer drill, metal drive rod and hammer, or direct

push drill rig. The standard soil gas survey kit provided by AGI is designed for a 36-inch vertical hole of 1/2-inch diameter. Should a project's DQOs require deeper samples, AGI should be consulted during the planning phase of the investigation. Once the boring is advanced, the field personnel cut a 72-inch length of string (provided) and loop it through the eyelet of the cork. The AGI passive sampler is then removed from the glass vial, the string is threaded through the looped end, and a knot is tied to secure it. One of the stainless steel insertion rods (see Figure 5-28) is placed in the pocket of the sampler and both the rod and sampler are inserted into the boring. Note that the insertion rod is used only to assist in the sampler insertion process, providing rigidity to the otherwise flexible sampler. Using the insertion rod, the sampler is then pushed down to the target depth interval and the rod is detached (ideally by twisting it) and removed from the boring. Once the sampler is placed at the target depth interval, the cork, to which the string is attached, is used to seal/plug the boring. Once the sampler is deployed and the installation date and time are recorded, the samplers are left to passively collect for 7-10 days.

To retrieve, the field personnel remove the cork (by hand or with a screwdriver) and remove the sampler from the ground using the attached string. Once removed, the string is cut and the sampler is wiped clean using a clean cloth rag or paper towel and returned to the corresponding glass vial. All collected samples are then logged on to the chain of custody and shipped to AGI's laboratory for analysis. AGI's internal research has determined that, for all media sampled, the modules do not have to be kept cold for shipment (AGI 2016<sup>[EPIA/EYWH]</sup> AGI. 2016. "Guidelines for Storage, Installation, and Retrieval of Air Sampling." Amplified Geochemical Imaging LLC. <https://agisurveys.net/wp-content/uploads/2020/04/Technical-pdf-7.1.pdf>). Therefore, the modules can be kept in glass vials (without refrigeration) until they are analyzed by the laboratory (typically within 4-7 days).



AGI Survey Kit



Numbered vials



Corks



Insertion rods

Figure 5-28. AGI sampler kit and components.  
Source: AGI, used with permission.



Slide hammer and tile probe



Rotary hammer drill and 36 in (1 m) long, 0.5 in (1 cm) diameter carbide-tipped bit



Hammer and 36 in (1 m) long, narrow diameter steel rod

Figure 5-29. AGI sampler installation.

Source: AGI, used with permission.



Figure 5-30. AGI sampler deployment and retrieval.

Source: AGI, used with permission.

### **Indoor/Outdoor Sampling**

When using this device to collect indoor/outdoor air (Figure 5-31), the field personnel should decide on the appropriate method for installing the samplers in their desired locations and have the appropriate supplies (that is, pre-cut pieces of string, nails, or pushpins) ready prior to the sampling event. On the day of sample deployment, the first step is selecting which samplers will be treated as trip blanks. These samplers are left in the kit unopened. Next, at each location, remove the sampler from its jar and re-seal the empty jar. The sampler is then attached to the sample location using the predetermined method. If string is used, tie the string to the sampler loop and then affix to the location. Once deployed, the sampler's serial number, along with the date and time of installation, are recorded on the sampling log. Following the installation of all samplers, store the sample box that contains the trip blanks in a clean place, free from potential sources of organic vapors. After the samplers are allowed to passively collect for the desired time (which can range from several days to multiple months), each sampler is retrieved, the retrieval date and time are recorded, the attachment material is disposed of, and the samplers are returned to their appropriate vials. The vials are placed back into the sample box, the samples are logged on the chain of custody, and the box is shipped to AGI's laboratory for analysis.



Residential basement



Manufacturing warehouse



Office conference room



Residential crawlspace



Commercial building basement, two AGI Universal Samplers Suspended, Summa can on floor; heating oil tank and workbench

Figure 5-31. AGI samplers being used for indoor/outdoor air sampling.

Source: AGI, used with permission.

### **Groundwater Sampling**

After removing the module from the vial, a line is attached to the module as described above and a weight is added to the end of the module to keep the module suspended in groundwater at the desired depth (typically in the screened interval). If warranted by a project's DQOs, several modules can be placed at varying depths within a single well's screened interval. After an exposure period of 15 minutes to 4 hours, the module is retrieved and returned to its glass vial, which is then placed in the shipping container. The glass vials containing the exposed modules, quality control samples (that is, trip blanks, equipment blanks, and/or duplicates), and chain of custody forms are shipped to AGI's laboratory, typically via overnight courier for analysis ( AGI 2016<sup>[EPIAEYWH]</sup> AGI. 2016. "Guidelines for Storage, Installation, and Retrieval of Air Sampling." Amplified Geochemical Imaging LLC. <https://agisurveys.net/wp-content/uploads/2020/04/Technical-pdf-7.1.pdf>).

### **Deployment Time**

The recommended exposure period for AGI passive adsorbents will depend on the matrix to which they are exposed and the adsorbent that is used. The adsorbents have different uptake rates, and they will reach equilibrium with their surroundings at different intervals. For instance, if the AGI passive adsorbents are used for indoor air sampling, they will reach equilibrium within a few hours (recommended exposure would be 3-4 hours). If they are placed in a monitoring well for detection of dissolved constituents, they will reach equilibrium within an hour or two. While in the vadose zone, detecting soil gases, equilibrium can be reached at either 3-5 days or 7-10 days, depending on the adsorbent.

#### **5.3.1.3 Advantages**

- When sampling groundwater, no purge water is generated.
- AGI passive samplers are applicable to a wide range of VOC and SVOC compounds.
- They can be placed in NAPL to sample.
- They are sensitive to parts per trillion levels.
- AGI passive samplers can be used in small-diameter piezometers or monitoring wells, sediments, surface water, springs, and other aqueous settings, regardless of their flow or turbidity.

- They have minimal shipping requirements (do not require ice or coolers) and reduced shipping costs.
- They have a short residence period for groundwater.
- Modules contain duplicate samples.

#### 5.3.1.4 Limitations

- When used to measure dissolved gases in groundwater, data are reported in total mass desorbed, thereby requiring calibration with concentration measurements from standard groundwater samples in wells.
- The sampler contains a small amount of adsorbent that makes it prone to sorbent saturation when high concentrations are present.
- The melting point of PTFE is lower than the upper temperature limit of carbonaceous adsorbents, which may result in inefficient desorption of all compounds adsorbed (that is, irreversible adsorption).
- AGI passive samplers have a single source supplier and analysis laboratory.
- This technology cannot be used to measure field parameters.
- This technology cannot be used for inorganics.
- Compound detection is limited by vapor pressure.
- AGI passive samplers are not particularly feasible for vertical delineation in soil gas.
- Soil gas data may not be accepted for risk assessment purposes in most states.
- Some components of this sampler may contain PFAS, which should be considered based on project DQOs.

### 5.3.2 Polar Organic Chemical Integrative Sampler

#### 5.3.2.1 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 chemicals. 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 such as dissolved oxygen levels, water quality, and high concentrations of toxic pollutants that affect biomonitoring organisms. The POCIS also concentrates trace organic chemicals for toxicity assessments and toxicity identification evaluation approaches.

The standard POCIS consists of a solid material (sorbent) contained between two microporous polyethersulfone (PES) membranes. The membranes have a pore size of 0.1  $\mu\text{m}$ , which allows water and dissolved chemicals to pass through to the sorbent where the chemicals are trapped ( MacKeown et al. 2022<sup>[HYI8DJZB]</sup> MacKeown, Henry, Emanuele Magi, Marina Di Carro, and Barbara Benedetti. 2022. "Unravelling the Role of Membrane Pore Size in Polar Organic Chemical Integrative Samplers (POCIS) to Broaden the Polarity Range of Sampled Analytes." *Analytical and Bioanalytical Chemistry* 414 (5): 1963–72. <https://doi.org/10.1007/s00216-021-03832-4>.) Larger materials, such as sediment and particulate matter, do not pass through the membrane ( Alvarez and Huckins 2004<sup>[VK9IPYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>.) The buildup of biofilms can be a rate-limiting step in the accumulation of chemicals by many membrane-based sampling devices. The PES membranes used in the POCIS have an inherent resistance to the buildup of biofilms, thereby reducing this potential impediment to uptake. Specific chemicals and chemical classes can be targeted by using different sorbent types. A standard POCIS has a sampling surface area (surface area of exposed membrane) to sorbent mass ratio of about 180  $\text{cm}^2/\text{g}$  ( Alvarez and Huckins 2004<sup>[VK9IPYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>.) Typically when deployed, POCIS can effectively sample a surface area of 41  $\text{cm}^2$  ( Alvarez and Huckins 2004<sup>[VK9IPYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>.) Figure 5-32 depicts an exploded view of a single POCIS disk. The PES membranes must be secured with a compression ring system to prevent loss of sorbent because they are not compatible with standard sealing techniques (that is, heat sealing). Compression rings are typically constructed from stainless steel or another rigid inert material. 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.

The most common sorbent used in the POCIS is Oasis HLB (Waters, Milford, MA). Depending on the chemicals of interest to be sampled, it may be desirable to use a different sorbent inside the POCIS. Weak anion exchange and molecularly imprinted polymers have been used in POCIS as the sequestration medium for specific applications.

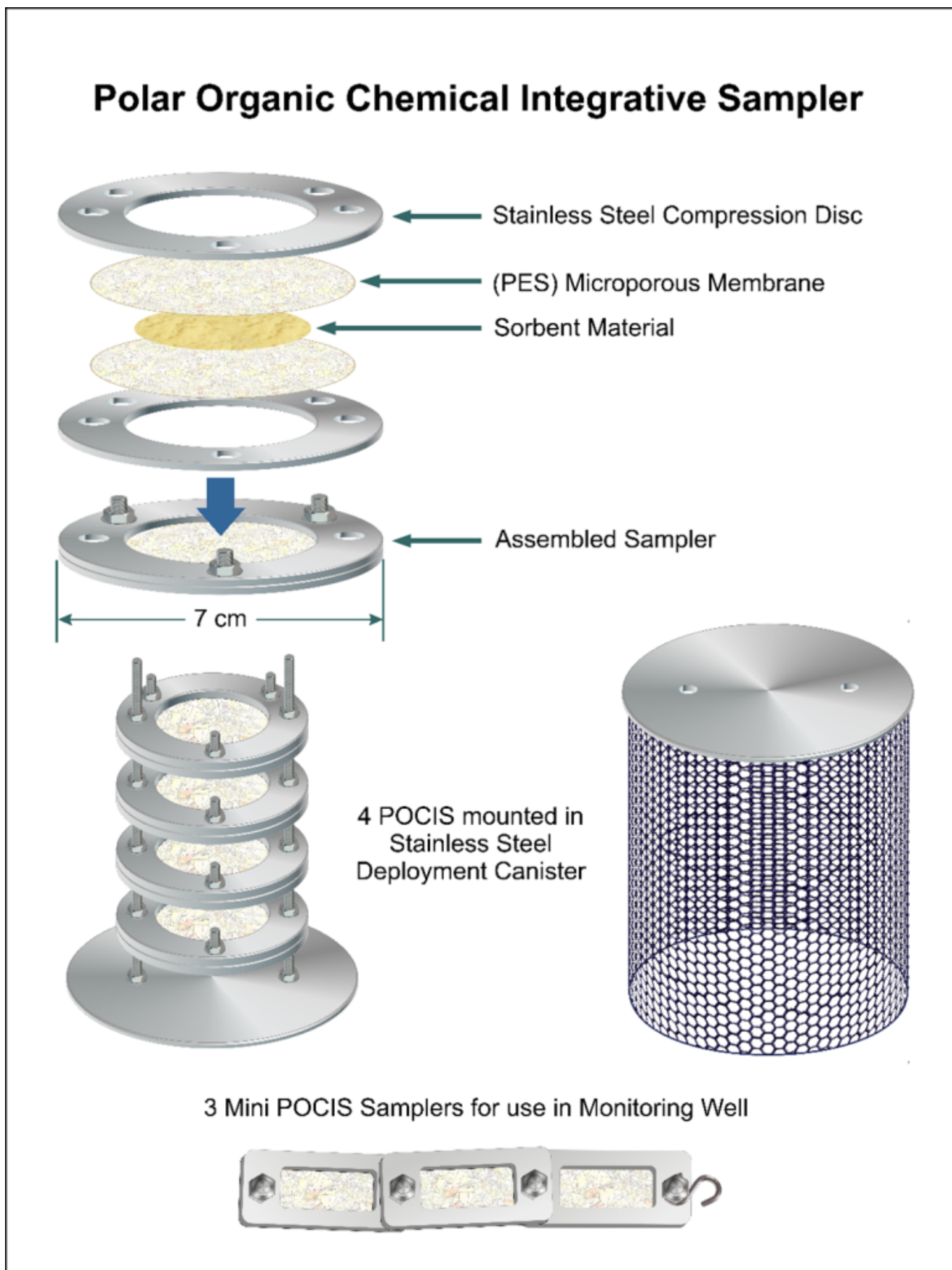


Figure 5-32. Polar Organic Chemical Integrative Sampler.

Source: NJDEP, used with permission.

### 5.3.2.2 Installation and Use

Deployment time for POCIS is typically one month but can range from weeks to months depending on the study design ( Alvarez and Huckins 2004<sup>[VK91PYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>). Deployment equipment can vary depending on the site and target media but generally will require deployment hardware (cable and clamps, floats, tie-down anchor) and tools for device assembly ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>). The device, secured at the desired location in the water column, must remain submerged for the entire deployment period, but not buried in the sediment, to achieve data representative of the target media ( Alvarez and Huckins 2004<sup>[VK91PYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>). If the device is exposed to air, there can be potential loss of chemicals with higher volatility from the POCIS and accumulation of chemicals from the air, resulting in measurements of nontarget media. Deployment methods can vary depending on the site and target media, but some common examples are tying the device to a fixed point on the shore (tree, boulder, fence post, etc.), hanging the device in open water (buoy, pier, floating platform), or suspending at the bottom with anchors and floats ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>). During the deployment period, considerations must be made for the effects of accumulation of suspended sediments or biofouling on the membrane surface over prolonged water exposure, protection from vandalism or external events, etc. ( Alvarez and Huckins 2004<sup>[VK91PYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>). After retrieval, the sorbent is transferred to a chromatography column for sample recovery. Using an organic solvent optimized for the specific sorbent and target chemicals, the sampled chemicals are recovered.

POCIS extracts have been analyzed by various instrumental techniques, including high performance liquid chromatography (HPLC), gas chromatography (GC), GC/ (mass spectrometry (MS), and liquid chromatograph/mass spectrometer (LC/MS) ( Alvarez and Huckins 2004<sup>[VK91PYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>). Additionally, bioindicator tests, such as Microtox and the Yeast Estrogen Screen, have been tested to determine the toxicological significance of the complex mixture of chemicals sampled by POCIS. POCIS can sample moderately polar to polar organic chemicals from water under almost any environmental conditions. The samplers have been successfully used in fresh, estuarine, and marine waters ( Alvarez and Huckins 2004<sup>[VK91PYIJ]</sup> Alvarez, David, and Jim Huckins. 2004. "Polar Organic Chemical Integrative Sampler (POCIS)." USGS. <https://www.cerc.usgs.gov/pubs/center/pdfdocs/pocis.pdf>).

### 5.3.2.3 Advantages

- POCIS are easily deployable to a variety of water bodies.
- POCIS can be used to sample hydrophilic organic compounds.

### 5.3.2.4 Limitations

- Samplers must remain submerged during deployment.
- Estimation of time-weighted average water concentrations from POCIS measurements requires the availability of experimentally derived sampling rates that may not be available for all chemicals of interest.

## 5.3.3 Sentinel PFAS Passive Sampler

### 5.3.3.1 Description and Application

The Sentinel passive sampler is a time-integrative passive sampler specifically designed to measure PFAS in various environmental waters, including groundwater, surface water, and pore water at concentrations ranging from low nanograms per liter (ng/L) to high micrograms per liter (µg/L). It was developed with U.S. Department of Defense funding under Strategic Environmental Research and Development Project ER20-1127.

The Sentinel passive sampler body (Figure 5-33) is a thin tag-like shape (approximately 2.5 cm wide by 5.0 cm long) constructed of either HDPE for water sampling or stainless steel for sediment pore water sampling, with a 1-cm diameter through-hole to contain sorbent resin. The sorbent resin consists of a modified organosilica (Osorb) infused with cross-linked polyethyleneimine and copper ions to optimize PFAS sorption across a range of chain lengths ( Edmiston et al. 2023<sup>[WFMXVRA]</sup> Edmiston, Paul L., Erika Carter, Kevin Toth, Riley Hershberger, Noah Hill, Patrick Versluis, Patrick Hollinden, and Craig Divine. 2023. "Field Evaluation of the Sentinel™ Integrative Passive Sampler for the Measurement of Perfluoroalkyl and Polyfluoroalkyl Substances in Water Using a Modified Organosilica Adsorbent." *Groundwater Monitoring & Remediation* 43 (4): 38-54. <https://doi.org/10.1111/gwmr.12574>.) The resin is emplaced between HDPE mesh screens and is in direct contact with the environmental water being sampled. The sorbent comes prewetted with glycerol from the manufacturer, which allows the samplers to be placed directly into the environmental water without pretreatment steps ( "FAQ: Sentinel™ PFAS Passive Samplers," n.d.<sup>[77UF7LCY]</sup> "FAQ: Sentinel™ PFAS Passive Samplers." n.d. Aquanex Technologies, LLC. Accessed February 12, 2024. <https://aquanex.tech.com/pages/faq-sentinel%e2%84%a2-passive-sampler>.) The sampler has two attachment points (at either end), with one end sized and tapered to fit into a standard 50 mL centrifuge tube, which reduces handling during sample collection, transport, and analysis. A small stainless steel weight is included with the sampler.

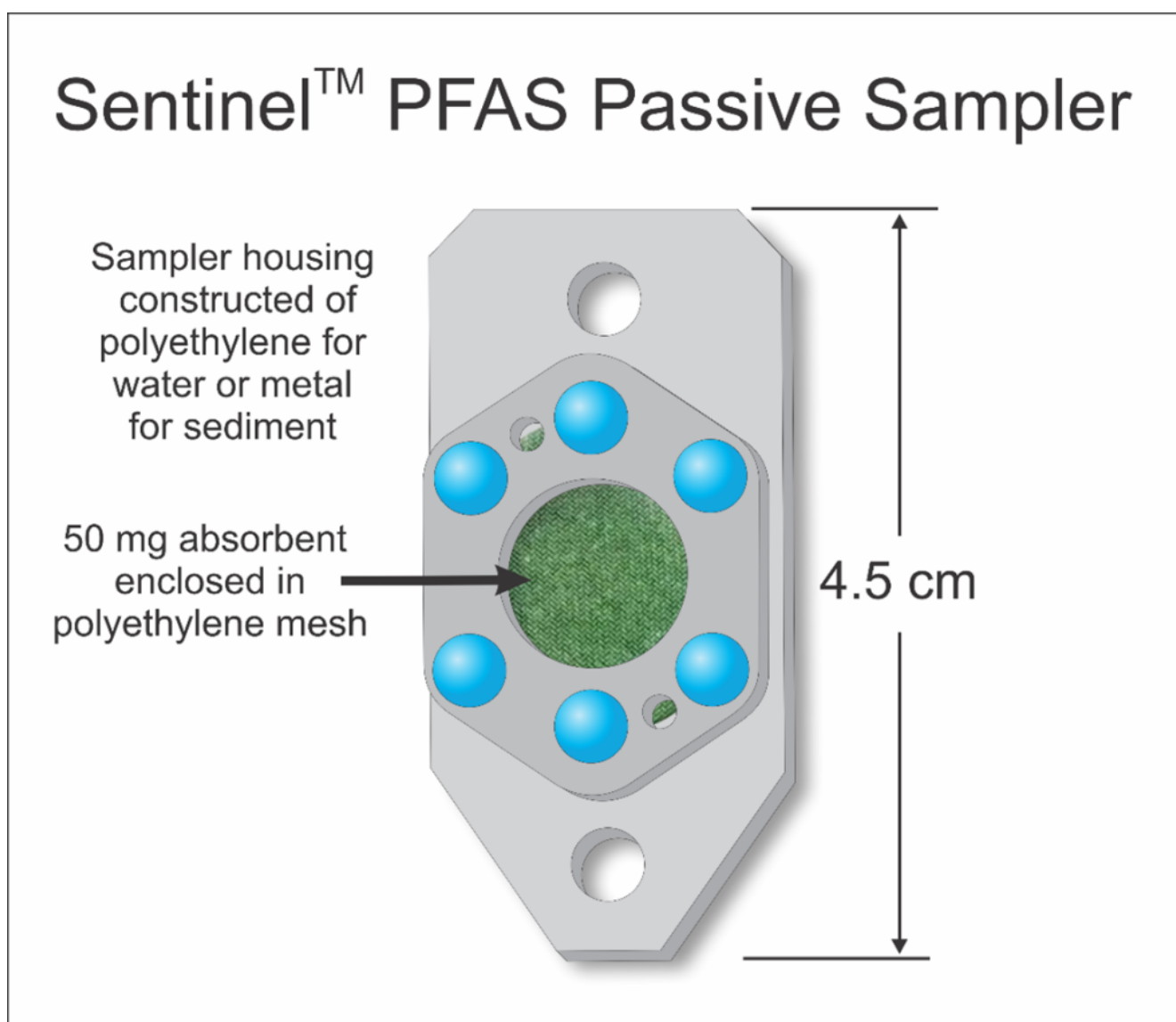


Figure 5-33. Sentinel PFAS sampler.  
Source: NJDEP, figure used with permission.

During the deployment period, PFAS compounds accumulate on/in the sorbent. Following retrieval, PFAS compounds are extracted from the sampler in the laboratory, and the compound mass accumulated on the passive sampler is measured and converted to the average concentration in the water during the period of deployment. The samplers may be analyzed using

modified versions of standard PFAS methods, including USEPA Method 537.1 or USEPA Method 1633.

The accumulated mass (ng) recovered from the Sentinel passive sampler is converted to the aqueous phase concentration,  $C_w$  (ng/L), using Equation 5 (Edmiston et al. 2023<sup>[WFMXVRA]</sup> Edmiston, Paul L., Erika Carter, Kevin Toth, Riley Hershberger, Noah Hill, Patrick Versluis, Patrick Hollinden, and Craig Divine. 2023. "Field Evaluation of the Sentinel™ Integrative Passive Sampler for the Measurement of Perfluoroalkyl and Polyfluoroalkyl Substances in Water Using a Modified Organosilica Adsorbent." *Groundwater Monitoring & Remediation* 43 (4): 38–54. <https://doi.org/10.1111/gwmr.12574>.):

#### Equation 5

$$C_w = \text{accumulated mass} / (R_s \times t)$$

where:

$C_w$  = aqueous phase concentration

$R_s$  = sampling rate (L/day)

$t$  = sampling time (days)

Sampling rates ( $R_s$ ) are experimentally determined in bench-scale measurements for each PFAS analyte and vary according to flow rate and temperature. Recorded field temperature and flow rate category (groundwater versus surface water) are incorporated in the laboratory calculation of the PFAS concentration in the water.  $R_s$  values have been determined for all 40 of the compounds included in USEPA Method 1633. As of the publication date of this report, several commercial laboratories offer analysis of the Sentinel passive sampler.

Experiments have shown that passive sampler uptake rates are relatively constant, even under a range of temperature, pH, ionic strength, and natural organic matter concentrations, which suggests potential applicability to a wide range of environmental water types (Hartmann et al. 2021<sup>[Y5HC6KRL]</sup> Hartmann, Heather, Claire Hefner, Erika Carter, David Liles, Craig Divine, and Paul L. Edmiston. 2021. "Passive Sampler Designed for Per- and Polyfluoroalkyl Substances Using Polymer-Modified Organosilica Adsorbent." *AWWA Water Science* 3 (4): e1237. <https://doi.org/10.1002/aws2.1237>.). A user may conduct site-specific calibration of  $R_s$  if needed to improve comparability between passive and conventional sampling results based on observed field conditions. The Sentinel passive sampler was demonstrated in the field at deployment durations of several days to several weeks (Edmiston et al. 2023<sup>[WFMXVRA]</sup> Edmiston, Paul L., Erika Carter, Kevin Toth, Riley Hershberger, Noah Hill, Patrick Versluis, Patrick Hollinden, and Craig Divine. 2023. "Field Evaluation of the Sentinel™ Integrative Passive Sampler for the Measurement of Perfluoroalkyl and Polyfluoroalkyl Substances in Water Using a Modified Organosilica Adsorbent." *Groundwater Monitoring & Remediation* 43 (4): 38–54. <https://doi.org/10.1111/gwmr.12574>.). Laboratory studies found that deployment duration should generally be limited to a maximum of 45 days due to the potential for short-chain PFAS to approach equilibrium at longer deployment times (Edmiston et al. 2023<sup>[WFMXVRA]</sup> Edmiston, Paul L., Erika Carter, Kevin Toth, Riley Hershberger, Noah Hill, Patrick Versluis, Patrick Hollinden, and Craig Divine. 2023. "Field Evaluation of the Sentinel™ Integrative Passive Sampler for the Measurement of Perfluoroalkyl and Polyfluoroalkyl Substances in Water Using a Modified Organosilica Adsorbent." *Groundwater Monitoring & Remediation* 43 (4): 38–54. <https://doi.org/10.1111/gwmr.12574>.).

#### 5.3.3.2 Installation and Use

The small size of the Sentinel passive sampler permits a variety of attachment configurations. Most importantly, the Sentinel passive sampler needs to remain submerged within the water column being sampled during the duration of deployment and should not rest within sediment (except for sediment pore water applications). Guidance for groundwater and surface water field applications is available from the SERDP project website (Divine et al. 2023<sup>[JCP2UFFR]</sup> Divine, Craig, Shandra Justicia-León, Jennifer M. Tilton, Erika Carter, Erik Zardouzian, Katherine Clark, and Dora Taggart. 2023. "Field Methods and Example Applications for the Min-Trap® Mineral Sampler." *Remediation Journal* 33 (3): 209–16. <https://doi.org/10.1002/rem.21752>.; Divine and Edmiston 2022<sup>[BAK8T9JS]</sup> Divine, Craig, and Paul Edmiston. 2022. "Technology Guidance for Sentinel™ Passive PFAS Samplers: Osorb® Media Use in PFAS Passive Samplers." SERDP Technical Guidance ER20-1127. SERDP. <https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/2023-12/ER20-1127%20Technical%20Guidance.pdf>

f?VersionId=34bFzHz68\_uzd\_vzGAfTnyxHHH5sZoRx.). For groundwater applications, the passive sampler may be attached to a deployment line (for example, nylon or polypropylene) using cable ties or wire, weighted using the included stainless steel weight, and suspended from the well cap. If additional weight is needed (to overcome buoyancy of deployment line), it should be attached directly to the deployment line. For surface water applications, the passive sampler attachment point (for example, driven stake, concrete block) should be submerged below the water surface and in a zone of flowing water (if surface water is flowing). Specific guidelines for sediment applications have not been published to date but are the subject of current research ( "Osorb Passive Sampler for Determination of PFAS in Sediment Porewater," n.d.<sup>[G8CXRWVC]</sup> "Osorb Passive Sampler for Determination of PFAS in Sediment Porewater." n.d. SERDP/ESTCP. Accessed May 3, 2024.

<https://serdp-estcp.mil/projects/details/e35f142d-31d4-468d-bfe0-619a83e9abfc.>; Lotufo et al. 2022<sup>[BM8MW6FA]</sup> Lotufo, Guilherme R., Mandy M. Michalsen, Danny D. Reible, Philip M. Gschwend, Upal Ghosh, Alan J. Kennedy, Kristen M. Kerns, et al. 2022. "Interlaboratory Study of Polyethylene and Polydimethylsiloxane Polymeric Samplers for Ex Situ Measurement of Freely Dissolved Hydrophobic Organic Compounds in Sediment Porewater." *Environmental Toxicology and Chemistry* 41 (8): 1885-1902. [https://doi.org/10.1002/etc.5356.](https://doi.org/10.1002/etc.5356))

The passive sampler is shipped inside a 50 mL centrifuge tube. This tube should be retained in a clean sealable bag for shipping the sampler to the laboratory following retrieval. At retrieval, the sampler should be detached from its attachment point. If passive sampler housing/weight contains gross sediment, shake manually, and gently rinse with PFAS-free DI water. Return the passive sampler (and weight) to the laboratory in the clean, labeled centrifuge tube. Samplers should be packed on ice for shipment to the laboratory. The field team must record the date/time of deployment, date/time of retrieval, water temperature, and flow category (groundwater, surface water, sediment) on the chain of custody form to permit calculation of PFAS concentrations.

### 5.3.3.3 Advantages

- The Sentinel passive sampler is small, easy to use, and commercially available.
- The single-use device limits potential for cross contamination.
- The time-integrative sampler provides average concentration over the entire period of deployment, capturing both spikes and low concentrations.
- The Sentinel passive sampler has a broad operating range over ng/L to µg/L in PFAS concentrations. Low detection limits can be achieved by accumulating PFAS on the sampler over days to weeks.
- Method minimizes sample handling, investigation-derived waste generation, and shipping costs.

### 5.3.3.4 Limitations

- The Sentinel passive sampler is new to the market in 2023 and therefore not yet in widespread use; several commercial laboratories perform analysis.
- Estimation of time-weighted average water concentrations from Sentinel passive sampler measurements require the availability of experimentally derived sampling rates that may not be available for all PFAS chemicals of interest. (To date, sampling rates are available for 40 PFAS listed in USEPA Method 1633.)
- Samplers must remain submerged during deployment.

## 5.3.4 Semipermeable Membrane Devices (SPMDs)

### 5.3.4.1 Description and Applications

Semipermeable membrane devices (SPMDs) (Figure 5-34) were developed in the mid-1990s by personnel at the USGS Columbia Environmental Research Center and designed to sample HOCs in surface water, mimicking the accumulation of HOCs and pesticides into the fatty tissues of organisms ( Huckins, Petty, and Booji 2006<sup>[6V87RUVQ]</sup> Huckins, James N., Jimmie D. Petty, and Kees Booji. 2006. *Monitors of Organic Chemicals in the Environment Semipermeable Membrane Devices*. Springer eBooks. [https://doi.org/10.1007/0-387-35414-x.](https://doi.org/10.1007/0-387-35414-x)) Although SPMDs have been used for sampling both water and air, they are primarily used in surface water monitoring. SPMDs have also been adapted to sample HOCs in groundwater in wells ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. [https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf.](https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf)) SPMDs have been used to determine freely dissolved (bioavailable)

concentrations of HOCs with log octanol-water partition coefficients (log KOW) greater than 3, such as PAHs and PCBs. Extracts from SPMDs can also be screened by in vitro and in vivo bioindicator tests to determine the potential effects on biota from exposure to the complex mixtures of chemicals present at a site ( Imbrigiotta and Harte 2020<sup>[9LSVPE48]</sup> Imbrigiotta, Thomas, and Philip Harte. 2020. "Passive Sampling of Groundwater Wells for Determination of Water Chemistry." In U.S. Geological Survey Techniques and Methods. <https://doi.org/10.3133/tm1d8>).

The SPMD is an integrative sampler that accumulates chemical mass over a deployment period that typically ranges from days to months. The SPMD consists of a high-purity lipid such as triolein, which serves as a representation of the fatty tissues of aquatic organisms, and a thin-walled (50-100 µm) nonporous lay-flat polyethylene membrane tube (Figures 5-34 and 5-35). The tube allows the nonpolar chemicals to pass through to the lipid where the chemicals are concentrated. The tube excludes larger molecules (> 600 Daltons) and materials such as particulate matter and microorganisms.

SPMDs use the PRC approach to account for site-specific environmental factors that can affect the sampling rates such as water flow, temperature, and the buildup of a biofilm on the sampler's surface ( Tertuliani et al. 2008<sup>[VWQ5933]</sup> Tertuliani, J.S., D.A. Alvarez, E.T. Furlong, M.T. Meyer, S.D. Zaugg, and G.F. Koltun. 2008. "Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed and Two Other Tributaries to the Cuyahoga River, Northeast Ohio." Scientific Investigations Report 2008-5173. U.S. Geological Survey. <https://pubs.usgs.gov/sir/2008/5173/pdf/sir20085173.pdf>). The calculated amount of PRC lost during deployment (Figure 5-37) is used to adjust the laboratory sampling rates at each sampling location.

Chemicals sampled by SPMDs include HOCs (with log KOW) greater than 3, such as PCBs, PAHs, organochlorine pesticides, dioxins and furans, selected organophosphate and pyrethroid pesticides, and many other nonpolar organic chemicals.

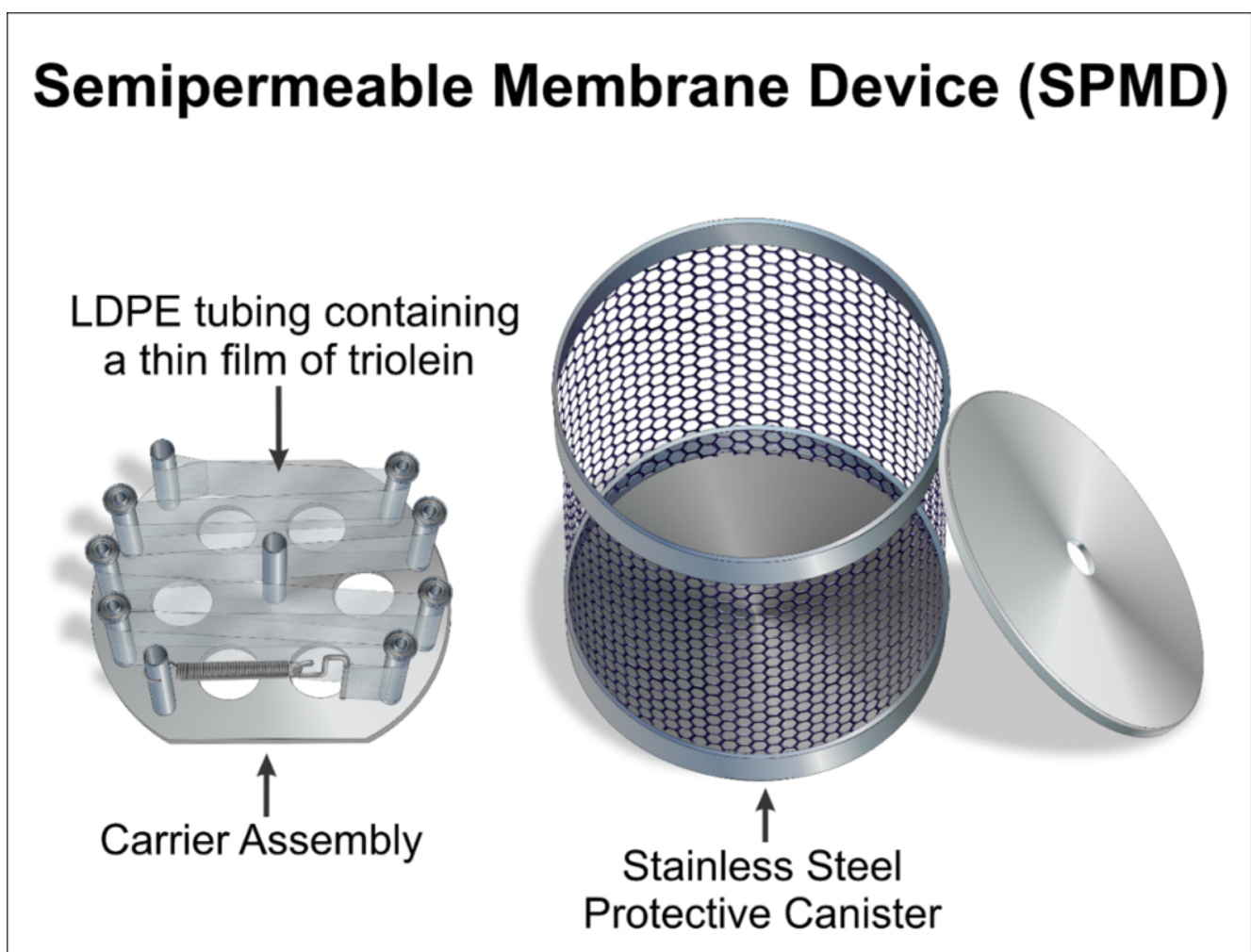


Figure 5-34. Semipermeable membrane device (SPMD) sampler.  
Source: NJDEP, used with permission.



Figure 5-35. SPMD carrier assembly and triolein film.  
Source: Anchor QEA, used with permission.



Figure 5-36. SPMD carrier assembly inside the protective canister.  
Source: Anchor QEA, used with permission.



Figure 5-37. A semipermeable membrane device assembled prior to deployment.  
Source: Anchor QEA, used with permission.

### 5.3.4.2 Installation and Use

SPMDs come from the commercial vendor as intact samplers, with the triolein film sealed in the PE tube and the requested PRCs added, and are dependent on the needs of the user (Figure 5-37). For example, the SPMDs may be preloaded onto carrier racks and shipped in cleaned airtight metal cans, ready to be loaded into protective deployment canisters in the field (Figure 5-36). Or if the user has deployment hardware, the SPMDs may be shipped loose in small cleaned airtight metal cans ready to attach to the deployment apparatus in the field. Two sizes of deployment canisters are commercially available (capable of holding between 2 and 5 SPMDs), but custom ones can be created and used provided they meet specific criteria (Figure 5-37) ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>).

Deployment equipment can vary depending on the site and target media but generally will require deployment hardware (cable and clamps, floats, tie-down anchor) and tools for device assembly ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>). The device, secured at the desired location in the water column, must remain submerged for the entire deployment period, but not buried in the sediment, to achieve data representative of the target media. If the device is exposed to air, there can be a potential loss of chemicals with higher volatility from the SPMD and accumulation of chemicals from the air, resulting in measurements of nontarget media. It is important to keep SPMDs shaded to prevent the photodegradation of some light-sensitive chemicals such as PAHs. Deployment methods can vary depending on the site and target media, but some common examples are tying the device to a fixed point on the shore (tree, boulder, fence post, etc.), hanging the device in open water (buoy, pier, floating platform), or suspending at the bottom with anchors and floats ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>). During the deployment period, considerations must be made for the effects of biofouling over prolonged water exposure, protection from vandalism or

external events, etc.

Once the deployment period has been achieved, the device is removed from the water, SPMDs are placed in air-tight shipping containers and returned to the laboratory on ice. To conduct SPMD dialysis, remove each device from the storage container/support rack and clean to remove surficial particulate matter and biofilm ( Alvarez et al. 2008<sup>[DIQJYMEN]</sup> Alvarez, David A., Walter L. Cranor, Stephanie D. Perkins, Randal C. Clark, and Steven B. Smith. 2008. "Chemical and Toxicologic Assessment of Organic Contaminants in Surface Water Using Passive Samplers." *Journal of Environmental Quality* 37 (3): 1024-33. <https://doi.org/10.2134/jeq2006.0463>.) Sampled chemicals are recovered from the SPMDs using a two-step dialysis method into hexane following a surficial cleaning to remove adhered particulate matter and biofilm. Dialysis times may vary depending on target chemicals. Extended dialysis periods (over three 24-hour periods) may result in an increased amount of coextracted matrix components in the sample ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>.) Following dialysis, additional cleanup and fractionation of the samples is dependent on the target analytes but typically involves size exclusion chromatography and other sorbent-based chromatographic methods ( Alvarez et al. 2008<sup>[DIQJYMEN]</sup> Alvarez, David A., Walter L. Cranor, Stephanie D. Perkins, Randal C. Clark, and Steven B. Smith. 2008. "Chemical and Toxicologic Assessment of Organic Contaminants in Surface Water Using Passive Samplers." *Journal of Environmental Quality* 37 (3): 1024-33. <https://doi.org/10.2134/jeq2006.0463>.; Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>.)

#### 5.3.4.3 Advantages

- SPMDs provide data as a time-weighted average concentration of a chemical within the whole deployment period ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>.)
- Low detection limits can be achieved for HOCs because SPMDs can concentrate HOCs during the period of deployment.
- The concentrations of HOCs measured by SPMDs represent freely dissolved (bioavailable) concentrations.

#### 5.3.4.4 Limitations

- Surface water sampling for HOCs can be done by other commonly used passive samplers such as LDPE samplers, which are readily available. In contrast, the sole commercial vendor of SPMDs in North America is Environmental Sampling Technologies, Inc. (St. Joseph, Missouri). They can also provide standard operating procedures for completing the extractions of SPMD matrix for laboratory processing and analysis.
- Long deployments can result in a substantial buildup of a biofilm, which can inhibit the ability of the sampler to accumulate chemicals. The use of PRC can improve quantitation of the target chemicals.
- Short deployments will yield smaller volumes of sampled water, which limits some of the advantages of using a passive sampler ( Alvarez 2010<sup>[DE6V4FIB]</sup> Alvarez, David A. 2010. "Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies." In , 38. U.S. Geological Survey. <https://pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf>.)

### 5.3.5 Diffusive Gradient in Thin Films (DGT)

#### 5.3.5.1 Description and Application

Diffusive gradient in thin films (DGT) (Figure 5-38) has been used to sample dissolved inorganic and organic chemicals in aqueous environments, including pore water, surface water, and groundwater ( Zhang and Davison 2015<sup>[862YQQBI]</sup> Zhang, Hao, and William Davison. 2015. "Use of Diffusive Gradients in Thin-Films for Studies of Chemical Speciation and Bioavailability." *Environmental Chemistry* 12 (January). <https://doi.org/10.1071/EN14105>.) Since the first development by researchers at Lancaster University in 1994 ( Davison and Zhang 1994<sup>[5WSRXFN4]</sup> Davison, W., and H. Zhang. 1994. "In Situ Speciation

Measurements of Trace Components in Natural Waters Using Thin-Film Gels." *Nature* 367 (6463): 546-48. <https://doi.org/10.1038/367546a0>.), the DGT technique has been predominantly used to measure inorganic chemicals in aqueous media. In the last few decades, the DGT technique has been improved and expanded to measure a large number of inorganic chemicals, including heavy metals, inorganic nutrients, oxyanions, and radionuclides ( Marrugo-Madrid et al. 2021<sup>[UG6L9JW9]</sup> Marrugo-Madrid, Siday, Marta Turull, Hao Zhang, and Sergi Díez. 2021. "Diffusive Gradients in Thin Films for the Measurement of Labile Metal Species in Water and Soils: A Review | *Environmental Chemistry Letters*." *Environmental Chemistry Letters* 19:3761-88. <https://link.springer.com/article/10.1007/s10311-021-01246-3>.). In addition, DGT has recently been modified and adapted to sample a variety of organic compounds, such as pharmaceuticals ( Challis, Hanson, and Wong 2016<sup>[K23QPDVR]</sup> Challis, Jonathan K., Mark L. Hanson, and Charles S. Wong. 2016. "Development and Calibration of an Organic-Diffusive Gradients in Thin Films Aquatic Passive Sampler for a Diverse Suite of Polar Organic Contaminants." *Analytical Chemistry* 88 (21): 10583-91. <https://doi.org/10.1021/acs.analchem.6b02749>.; Fang et al. 2019<sup>[NBPJGSH8]</sup> Fang, Zhou, Li Kexin, Yuan Li, Hao Zhang, Kevin C Jones, Xinyu Liu, Shengyu Liu, Lena Q Ma, and Jun Luo. 2019. "Development and Application of the Diffusive Gradients in Thin-Films Technique for Measuring Psychiatric Pharmaceuticals in Natural Waters - PubMed." *Environ Sci Technol* 53 (19): 11223-31. <https://doi.org/10.1021/acs.est.9b03166>.), antibiotics ( Cheng et al. 2013<sup>[SKMG77W6]</sup> Cheng, Hairong, Zongming Deng, Paromita Chakraborty, Di Liu, Ruijie Zhang, Yue Xu, Chunlin Luo, Gan Zhang, and Jun Li. 2013. "A Comparison Study of Atmospheric Polycyclic Aromatic Hydrocarbons in Three Indian Cities Using PUF Disk Passive Air Samplers." *Atmospheric Environment* 73 (July):16-21. <https://doi.org/10.1016/j.atmosenv.2013.03.001>.; Xie et al. 2018<sup>[97PQFZYR]</sup> Xie, Huaijun, Jingwen Chen, Qining Chen, Chang-Er L. Chen, Juan Du, Feng Tan, and Chengzhi Zhou. 2018. "Development and Evaluation of Diffusive Gradients in Thin Films Technique for Measuring Antibiotics in Seawater." *The Science of the Total Environment* 618 (March):1605-12. <https://doi.org/10.1016/j.scitotenv.2017.09.330>.), and PFAS ( Wang et al. 2021<sup>[P9JILGTP]</sup> Wang, Po, Jonathan K. Challis, Kim H. Luong, Trisha C. Vera, and Charles S. Wong. 2021. "Calibration of Organic-Diffusive Gradients in Thin Films (o-DGT) Passive Samplers for Perfluorinated Alkyl Acids in Water." *Chemosphere* 263 (January):128325. <https://doi.org/10.1016/j.chemosphere.2020.128325>.; Fang et al. 2021<sup>[Q6Q5GZQY]</sup> Fang, Zhou, Yuan Li, Yanying Li, Danxing Yang, Hao Zhang, Kevin C. Jones, Cheng Gu, and Jun Luo. 2021. "Development and Applications of Novel DGT Passive Samplers for Measuring 12 Per- and Polyfluoroalkyl Substances in Natural Waters and Wastewaters." *Environmental Science & Technology* 55 (14): 9548-56. <https://doi.org/10.1021/acs.est.0c08092>.), although future studies may be needed to fill several gaps and limitations to apply DGT for organic chemicals ( Ji, Challis, and Brinkmann 2022<sup>[LS64NE8X]</sup> Ji, Xiaowen, Jonathan K. Challis, and Markus Brinkmann. 2022. "A Critical Review of Diffusive Gradients in Thin Films Technique for Measuring Organic Pollutants: Potential Limitations, Application to Solid Phases, and Combination with Bioassays." *Chemosphere* 287 (January):132352. <https://doi.org/10.1016/j.chemosphere.2021.132352>).

# Diffusive Gradients in Thin Films (DGT)

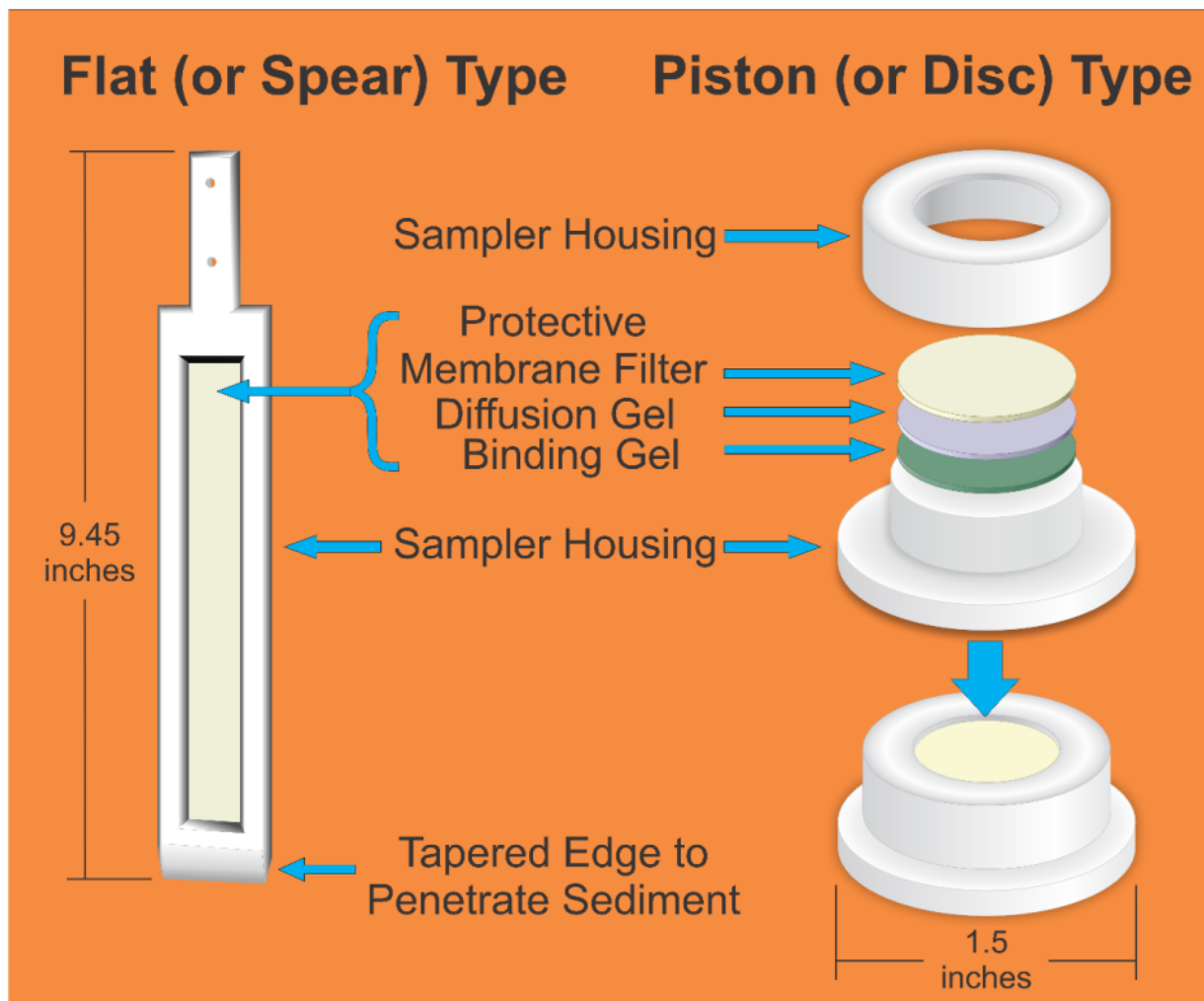


Figure 5-38. Diffusive gradient in thin films (DGT) sampler.

Source: NJDEP, figure used with permission.

DGT usually comprises three successive layers of material held together by a plastic housing. The outer protective layer is typically a filter membrane with  $0.45 \mu\text{m}$  pore size that permits only dissolved species to interact with the underlying gels, protects the gels from physical damages, and prevents the influence of surrounding hydrodynamic fluctuations. Below the protective membrane filter is a diffusion hydrogel with a known thickness. Dissolved chemicals diffuse through the diffusion hydrogel layer, and the diffusion kinetics in the diffusion hydrogel are well known and established for many chemicals. Below the diffusion gel is a binding gel that reacts with dissolved species diffused through the diffusion gel and serves as a chemical sink. Because DGT is an accumulation-type sampler, it works at the linear accumulation regime (or kinetic regime), where the chemical uptake is linearly correlated with time ( Wang et al. 2021<sup>[P9JLGT<sup>P</sup>]</sup> Wang, Po, Jonathan K. Challis, Kim H. Luong, Trisha C. Vera, and Charles S. Wong. 2021. "Calibration of Organic-Diffusive Gradients in Thin Films (o-DGT) Passive Samplers for Perfluorinated Alkyl Acids in Water." *Chemosphere* 263 (January):128325. <https://doi.org/10.1016/j.chemosphere.2020.128325>.) Because the binding gel accumulates a target chemical over time, DGT can achieve better detection limits after longer deployment times. However, once the binding gel is saturated with a target chemical, the DGT sampler is no longer useful to quantitatively determine its dissolved concentration.

Because the diffusion kinetics in the diffusion hydrogel are well established for many chemicals, a concentration of a target chemical at the surface of DGT can be calculated from the mass of the chemical accumulated to the binding gel ( Zhang and

Davison 2015<sup>[862YQ08I]</sup> Zhang, Hao, and William Davison. 2015. "Use of Diffusive Gradients in Thin-Films for Studies of Chemical Speciation and Bioavailability." *Environmental Chemistry* 12 (January). <https://doi.org/10.1071/EN14105>. Both the membrane filter and the hydrogel effectively exclude target chemicals associated with larger molecules such as aqueous complexes, colloids, and humic substances. Therefore, DGT is a suitable technique for in situ evaluation of labile fractions and, by approximation, bioavailability of a target chemical in aqueous media, although some chemicals associated with dissolved organic matters can be sampled by DGT ( Davison and Zhang 1994<sup>[5W5RXFN4]</sup> Davison, W., and H. Zhang. 1994. "In Situ Speciation Measurements of Trace Components in Natural Waters Using Thin-Film Gels." *Nature* 367 (6463): 546–48. <https://doi.org/10.1038/367546a0>.; Zhang 2004<sup>[WM9DK8U4]</sup> Zhang, Hao. 2004. "In-Situ Speciation of Ni and Zn in Freshwaters: Comparison between DGT Measurements and Speciation Models | *Environmental Science & Technology*." *Environ. Sci. Technol* 38 (5): 1421–27. <https://doi.org/10.1021/es034654u>.; Warnken, Davison, and Zhang 2008<sup>[K99QIG4Y]</sup> Warnken, Kent W., William Davison, and Hao Zhang. 2008. "Interpretation of in Situ Speciation Measurements of Inorganic and Organically Complexed Trace Metals in Freshwater by DGT." *Environmental Science & Technology* 42 (18): 6903–9. <https://doi.org/10.1021/es800359n>).

### 5.3.5.2 Installation and Use

The piston-type (or disk-type) and flat-type (also known as "spear-type") samplers shown in Figure 5-38 are two common configurations for DGT. Selection of the DGT configuration depends on sampling media and objectives. The flat-type DGT can be deployed into sediments or soils to measure vertical concentration profiles of target chemicals in pore water ( Teasdale, Hayward, and Davison 1999<sup>[X8FZJWMF]</sup> Teasdale, P R, S Hayward, and W Davison. 1999. "In Situ, High-Resolution Measurement of Dissolved Sulfide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry - PubMed." *Anal Chem* 71 (11): 2186–96. <https://doi.org/10.1021/ac981329u>.; Wei et al. 2022<sup>[Y6NFRJZG]</sup> Wei, Tian-Jiao, Dong-Xing Guan, Xi-Yuan Li, Yi-Long Hao, Henry Teng, Ji-Feng Yang, Yao-Yang Xu, and Gang Li. 2022. "Analysis of Studies on Environmental Measurements Using Diffusive Gradients in Thin-Films (DGT) from 1994 to 2020." *Journal of Soils and Sediments* 22 (April). <https://doi.org/10.1007/s11368-022-03168-1>.). When the flat-type DGT is deployed and positioned in surface sediment, the DGT can measure dissolved concentrations in both pore water and overlying surface water at the same time. Carefully insert the flat-type DGT by hand into sediment or soil so as not to alter physical characteristics of sediment or soil such as density, which may result in biased results ( Li et al. 2019<sup>[QNRWN4I7]</sup> Li, Cai, Shiming Ding, Liyuan Yang, Yan Wang, Mingyi Ren, Musong Chen, Xianfang Fan, and Eric Lichtfouse. 2019. "Diffusive Gradients in Thin Films: Devices, Materials and Applications." *Environmental Chemistry Letters* 17 (2): 801–31. <https://doi.org/10.1007/s10311-018-00839-9>., Li et al. 2012<sup>[X9GF3GG2]</sup> Li, Yingming, Dawei Geng, Fubin Liu, Thanh Wang, Pu Wang, Qinghua Zhang, and Guibin Jiang. 2012. "Study of PCBs and PBDEs in King George Island, Antarctica, Using PUF Passive Air Sampling." *Atmospheric Environment* 51 (May):140–45. <https://doi.org/10.1016/j.atmosenv.2012.01.034>.). The piston-type DGT can be used to measure dissolved concentrations of target chemicals in aqueous media or placed on the sediment surface to measure chemical flux at the sediment–surface water interface.

It should be noted that DGT needs to be deoxygenated prior to use because dissolved oxygen in the diffusion hydrogel and binding gel can influence the speciation of redox-sensitive chemicals. For example, dissolved sulfide measurement in sediment pore water by the DGT technique has been shown to be very effective ( Teasdale, Hayward, and Davison 1999<sup>[X8FZJWMF]</sup> Teasdale, P R, S Hayward, and W Davison. 1999. "In Situ, High-Resolution Measurement of Dissolved Sulfide Using Diffusive Gradients in Thin Films with Computer-Imaging Densitometry - PubMed." *Anal Chem* 71 (11): 2186–96. <https://doi.org/10.1021/ac981329u>.), but dissolved sulfide is very sensitive to dissolved oxygen. DGT can be deoxygenated by submerging in 0.03 molar NaCl solution (or other solutions with different solutes or ionic strengths) gently bubbled with nitrogen or argon gas for more than 24 hours. After deoxygenation, DGT should be carefully shipped in sealed oxygen-barrier bags on ice in a cooler to the field site. DGT should be deployed as soon as possible after taking out from oxygen-barrier bags to minimize the introduction of oxygen into DGT.

The DGT deployment time should be carefully determined considering a few different factors. It should be sufficiently long to accumulate target chemicals in the binding gel but short enough to avoid the saturation of the binding gel. As noted above, the DGT deployment should be conducted to maintain the linear accumulation regime (or the kinetic regime) to accurately measure dissolved concentrations of target chemicals. Although a deployment time of ~24 hours has been recommended for DGT ( Burgess et al. 2017<sup>[97]RK4GH]</sup> Burgess, R.M., S.B. Kane Driscoll, A. Burton, P.M. Gschwend, U. Ghosh, D. Reible, S. Ahn, and T. Thompson. 2017. "Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of

Contaminated Sediments: User's Manual." User's Manual EPA/600/R-16/357. Washington, DC: USEPA and SERDP-ESTCP. <https://semsub.epa.gov/work/HQ/100000146.pdf>), it can vary depending on target chemicals and their concentrations in the sampling media. The DGT binding gel can be saturated when deployed for a prolonged duration, which does not allow use of the linear diffusion assumption. Once the DGT binding gel is saturated, it is no longer used for quantitative sample. It may be necessary to deploy a few replicates to find an optimum deployment time. A prolonged DGT deployment time in soil or sediment may also cause the depletion of target chemicals in pore water ( Ernstberger et al. 2005<sup>[TMB74A7L]</sup> Ernstberger, H., H. Zhang, A. Tye, S. Young, and W. Davison. 2005. "Desorption Kinetics of Cd, Zn, and Ni Measured in Soils by DGT." *Environmental Science & Technology* 39 (6): 1591-97. <https://doi.org/10.1021/es048534d>.) Therefore, the uptake mass of the target chemical should be small enough not to alter the initial concentration of the target chemical.

The DGT deployment time, temperature, pH, and salinity in aqueous media need to be recorded during deployment and retrieval. The diffusion coefficients of target chemicals in the diffusion hydrogel vary depending on temperature. The water quality parameters may be necessary to calculate the distribution of aqueous species of inorganics.

DGT should be carefully deployed, positioned, and secured to measure dissolved concentrations of target chemicals in pore water. When the flat-type DGT is used, the depth of penetration should be recorded. DGT should be tied with a weight to submerge under the water surface when deployed in surface water or groundwater.

### 5.3.5.3 Advantages

- DGT can be purchased as assembled units from a manufacturer, or selected components can be purchased so that users can assemble custom-made units.
- Better detection limits can be achieved with a longer deployment time because the DGT binding gel accumulates target chemicals over time.
- DGT allows in situ evaluation of labile fractions of target chemicals, and by approximation, bioavailability in aqueous environments.
- A spear-type DGT can be inserted into the sediment or soil vertically to assess the vertical profile of a target chemical with submillimeter high resolution.

### 5.3.5.4 Limitations

- A longer deployment time may cause the saturation of the DGT binding gel and the depletion of target chemicals in pore water, which may result in biased results.
- The diffusion kinetics of a target chemical can be influenced by several factors, such as temperature, competing chemicals, and biofilm development after longer deployment.
- Although DGT can be used to sample many different organic chemicals, future studies may be needed to further refine the sampler to overcome some limitations, such as lag times introduced by the filter membranes and storage of DGT ( Ji, Challis, and Brinkmann 2022<sup>[LS64NE8X]</sup> Ji, Xiaowen, Jonathan K. Challis, and Markus Brinkmann. 2022. "A Critical Review of Diffusive Gradients in Thin Films Technique for Measuring Organic Pollutants: Potential Limitations, Application to Solid Phases, and Combination with Bioassays." *Chemosphere* 287 (January):132352. <https://doi.org/10.1016/j.chemosphere.2021.132352>.)
- DGT should be deoxygenated to reduce introduction of oxygen into reducing environments.

## 5.3.6 Mineral Sampler (Min-Traps)

### 5.3.6.1 Description and Application

The Min-Trap (Figure 5-39) is a passive sampling device that is deployed within a conventional monitoring well and allowed to incubate to collect mineral samples for analysis. It consists of a nonreactive medium (for example, silica sand), a reactive medium (for example, iron oxide sand or site soil), or a combination of both, contained within a water-permeable mesh, which is housed within a 1.5-inch diameter, 18-inch-long 0.010 inch slotted polyvinyl chloride (PVC) casing. The standard Min-Trap has a nonreactive medium that provides a carrier substrate where target minerals can form passively ( Tilton and Gentile 2019<sup>[THUZSYL]</sup> Tilton, Jennifer Martin, and Margaret Gentile. 2019. "Strategic Approaches to Address the Unique Challenges of Groundwater Remediation at Coal Ash Facilities." <https://uknowledge.uky.edu/cgi/viewcontent.cgi?article=1526&context=woca>.) Alternatively, the Min-Trap can be

configured with reactive media to provide a substrate for mineral transformation processes taking place under the natural or engineered geochemical conditions in the aquifer. Groundwater flow modeling results indicate that the hydraulics of the Min-Trap are approximately representative of flux through an equivalent width of the aquifer ( Ulrich et al. 2021<sup>[66YF5YT4]</sup> Ulrich, Shannon, Jennifer Martin Tilton, Shandra Justicia-Leon, David Liles, Robert Prigge, Erika Carter, Craig Divine, Dora Taggart, and Katherine Clark. 2021. "Laboratory and Initial Field Testing of the Min-Trap<sup>TM</sup> for Tracking Reactive Iron Sulfide Mineral Formation during in Situ Remediation." *Remediation Journal* 31 (3): 35–48. <https://doi.org/10.1002/rem.21681>.). The minerals accumulating in a Min-Trap are representative of minerals forming in the subsurface. Because Min-Traps are designed to measure minerals that are actively forming, they are not intended to assess background mineralogy of an aquifer. Min-Traps were demonstrated for use at chlorinated solvent sites in an ESTCP project (ER19-5190). The final report highlights an advantage of Min-Traps being that laboratory analysis (for example, chemical, microscopic, and spectroscopic) of Min-Trap samples provides direct evidence of mineral formation, dissolution, and/or transformation processes while avoiding challenges associated with traditional sampling methods (typically, drilling) ( Divine 2022<sup>[84A4BIPA]</sup> Divine, Criag. 2022. "Demonstration of Mineral Traps to Passively Evaluate and Monitor In-Situ Reactive Minerals for Chlorinated Solvent Treatment." Final Report ER19-5190. Department of Defense Environmental Security Technology Certification Program (ESTCP). [https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/2023-05/ER19-5190%20Final%20Report.pdf?VersionId=6J.vmN6\\_wLLM3jjoXV3xErmmY\\_9iYm3u](https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/2023-05/ER19-5190%20Final%20Report.pdf?VersionId=6J.vmN6_wLLM3jjoXV3xErmmY_9iYm3u)).

# Min-Trap<sup>®</sup> Sampler

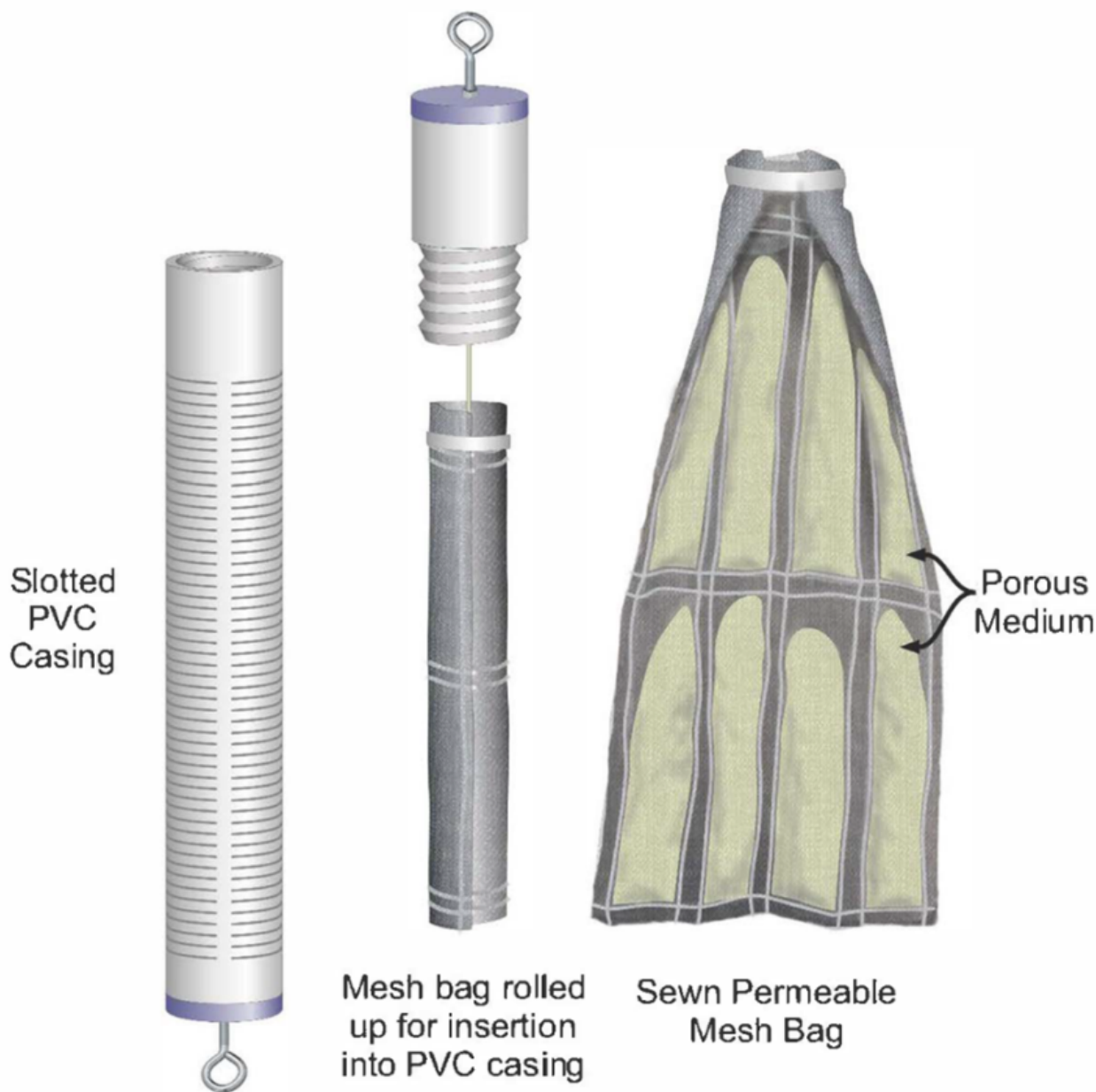


Figure 5-39. Min-Trap sampler.

Source: NJDEP, used with permission.

## 5.3.6.2 Installation and Use

Virtually any in situ remediation strategy that results in the precipitation, dissolution, or transformation of a mineral species can be validated, monitored, and assessed with Min-Traps. The Min-Trap approach is particularly applicable to identifying and quantifying the formation of reactive iron minerals for the treatment of CVOCs, which is often a target mechanism for in situ chemical reduction and enhanced reductive dichlorination strategies.

Min-Traps are attached to a suspension line and deployed within the target monitoring well screen zone (often at the center of the saturated interval). For wells with long screens, baffles at the top and bottom of the Min-Trap can be used to reduce the potential for in-well vertical mixing effects. Eyebolts at the top and bottom of the Min-Trap allow multiple samplers to be

connected in series, if desired. It is recommended in Divine et al. ( Divine et al. 2023<sup>[CP2UFR]</sup> Divine, Craig, Shandra Justicia-León, Jennifer M. Tilton, Erika Carter, Erik Zardouzian, Katherine Clark, and Dora Taggart. 2023. "Field Methods and Example Applications for the Min-Trap® Mineral Sampler." Remediation Journal 33 (3): 209-16. <https://doi.org/10.1002/rem.21752>., Divine et al. 2023<sup>[SM2FU9X8]</sup> Divine, Craig, Shandra Justicia-León, Jennifer Martin Tilton, David Liles, Erika Carter, Erik Zardouzian, Katherine Clark, et al. 2023. "Min-Trap® Samplers to Passively Monitor In-Situ Iron Sulfide Mineral Formation for Chlorinated Solvent Treatment." Groundwater Monitoring & Remediation 43 (3): 57-69. <https://doi.org/10.1111/gwmmr.12595>.) that Min-Traps be deployed for at least 30 days to ensure recovery of detectable amounts of mineral mass; however, they can be deployed for longer periods depending on project objectives (zotpress items="{4889498:JCP2UFR}" style="chicago-author-date"); Divine et al. 2023<sup>[SM2FU9X8]</sup> Divine, Craig, Shandra Justicia-León, Jennifer Martin Tilton, David Liles, Erika Carter, Erik Zardouzian, Katherine Clark, et al. 2023. "Min-Trap® Samplers to Passively Monitor In-Situ Iron Sulfide Mineral Formation for Chlorinated Solvent Treatment." Groundwater Monitoring & Remediation 43 (3): 57-69. <https://doi.org/10.1111/gwmmr.12595>.)

At the conclusion of the deployment period, the Min-Trap is retrieved from the well, the housing is opened, and the media "pillows" are unrolled for logging and photo documentation. Care should be taken to process Min-Trap samples as quickly as possible (within minutes of removal from the well) to minimize exposure to the atmosphere. The media pillows may be separated with a cutting tool to provide the needed solid sample mass for desired laboratory analyses. Unused pillows can be placed back into the Min-Trap housing and redeployed for future sampling, if desired. The media pillow samples are double-sealed in a manner to minimize oxygen exposure (for example, vacuum sealing with a household vacuum sealer). The sealed samples are shipped on ice to the analytical laboratory. Further detailed descriptions of field deployment, sampling, and preservation procedures are presented in Divine et al. ( Divine et al. 2023<sup>[CP2UFR]</sup> Divine, Craig, Shandra Justicia-León, Jennifer M. Tilton, Erika Carter, Erik Zardouzian, Katherine Clark, and Dora Taggart. 2023. "Field Methods and Example Applications for the Min-Trap® Mineral Sampler." Remediation Journal 33 (3): 209-16.

<https://doi.org/10.1002/rem.21752>.) ( Divine et al. 2023<sup>[CP2UFR]</sup> Divine, Craig, Shandra Justicia-León, Jennifer M. Tilton, Erika Carter, Erik Zardouzian, Katherine Clark, and Dora Taggart. 2023. "Field Methods and Example Applications for the Min-Trap® Mineral Sampler." Remediation Journal 33 (3): 209-16. <https://doi.org/10.1002/rem.21752>.)

Min-Trap samples are analyzed using laboratory methods appropriate for soils. Some relevant analyses include extraction for total metals or characterization of iron sulfide (FeS, FeS<sub>2</sub>) minerals using the Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) suite ( Kennedy, Everett, and Gonzales 2004<sup>[NXHF26RV]</sup> Kennedy, L., J.W. Everett, and J. Gonzales. 2004. "Aqueous and Mineral Intrinsic Bioremediation Assessment: Natural Attenuation." Journal of Environmental Engineering 130 (9): 942-50.), and spectroscopic analyses such as scanning electron microscopy with energy dispersive spectral analysis (SEM-EDS) and x-ray diffraction (XRD) for mineralogical characterization. The applicability of XRD analysis may be limited due to the relatively high quantity of mineral precipitates required for detection (typically greater than 1 percent by weight).

### 5.3.6.3 Advantages

- Min-Traps provide a reliable and cost-effective method for measuring the formation of reactive minerals in the subsurface.
- The Min-Trap sampling approach can be adapted to monitor the performance of essentially any treatment remedy where minerals are formed, dissolved, or transformed, providing direct evidence of treatment without additional drilling.
- For CVOC sites, confirmation of the formation of reactive, reduced iron minerals (for example, FeS, FeS<sub>2</sub>) in situ can be a key line of evidence to evaluate the synergy between biological and abiotic processes, support remedy optimization by indicating the need to increase or decrease injection frequency, and provide a basis for the transition from active treatment to a monitored natural attenuation approach.
- For sites where metals treatment via precipitation is the remedy, such as enhanced precipitation of hexavalent chromium or uranium, data collected from Min-Traps provide direct confirmation that the target precipitation activity is occurring. Min-Trap data can also be used to proactively evaluate the ongoing stability of mineral precipitates once formed without the need for repeated drilling events.

### 5.3.6.4 Limitations

- The failure to detect minerals that are forming in the aquifer in the Min-Traps (that is, “false negative”) is the most likely limitation and could be the result of inadequate deployment times and/or elevated mineral detection limits (for example, typically >1 percent by weight for XRD).
- Degradation of reactive minerals by oxygen during sampling, transport, and analysis may result in lost or misrepresentative data; however, this limitation can be addressed by using the recommended sample preservation protocol that includes steps to minimize oxygen exposure during transport. Field testing of this protocol indicated minor loss of target minerals (that is, iron sulfides) during sampling and short-term storage (Ulrich et al. 2021<sup>[66YF5YT4]</sup> Ulrich, Shannon, Jennifer Martin Tilton, Shandra Justicia-Leon, David Liles, Robert Prigge, Erika Carter, Craig Divine, Dora Taggart, and Katherine Clark. 2021. “Laboratory and Initial Field Testing of the Min-Trap™ for Tracking Reactive Iron Sulfide Mineral Formation during in Situ Remediation.” *Remediation Journal* 31 (3): 35–48. <https://doi.org/10.1002/rem.21681>).

## 5.3.7 Radiello Sampler

### 5.3.7.1 Description and Application

Radiello (Figure 5-40) is a trade name of cylindrical, concentration gradient-reliant samplers originally developed by Fondazione Salvatore Maugeri (Padova, Italy) and distributed by Millipore Sigma (Burlington, MA, U.S.), primarily for indoor air quality monitoring. As a diffusive sampler, this device takes in compounds from the surrounding media without the forced movement of air, such as would involve a pump.

In addition to indoor air, these samplers can be used to monitor personal breathing zones, industrial workplace air, and outdoor ambient air. The core parts of the Radiello sampling system consist of a sorbent-filled tube (adsorbent cartridge) inserted into a protective housing that allows for air diffusion (diffusive body). Several different adsorbent cartridges are available for different classes of compounds. Compounds that can be sampled include more than 70 VOCs, including BTEX (benzene), aldehydes, 1,3-butadiene and isoprene, phenols, ozone, ammonia, nitrogen and sulfur dioxides, hydrogen sulfide, hydrochloric acid, and hydrofluoric acid.

# Radiello<sup>®</sup>

Adsorbing Cartridges  
Contained in a Cylindrical  
Diffusive Body

Plastic Supporting  
Plate  
with Clip

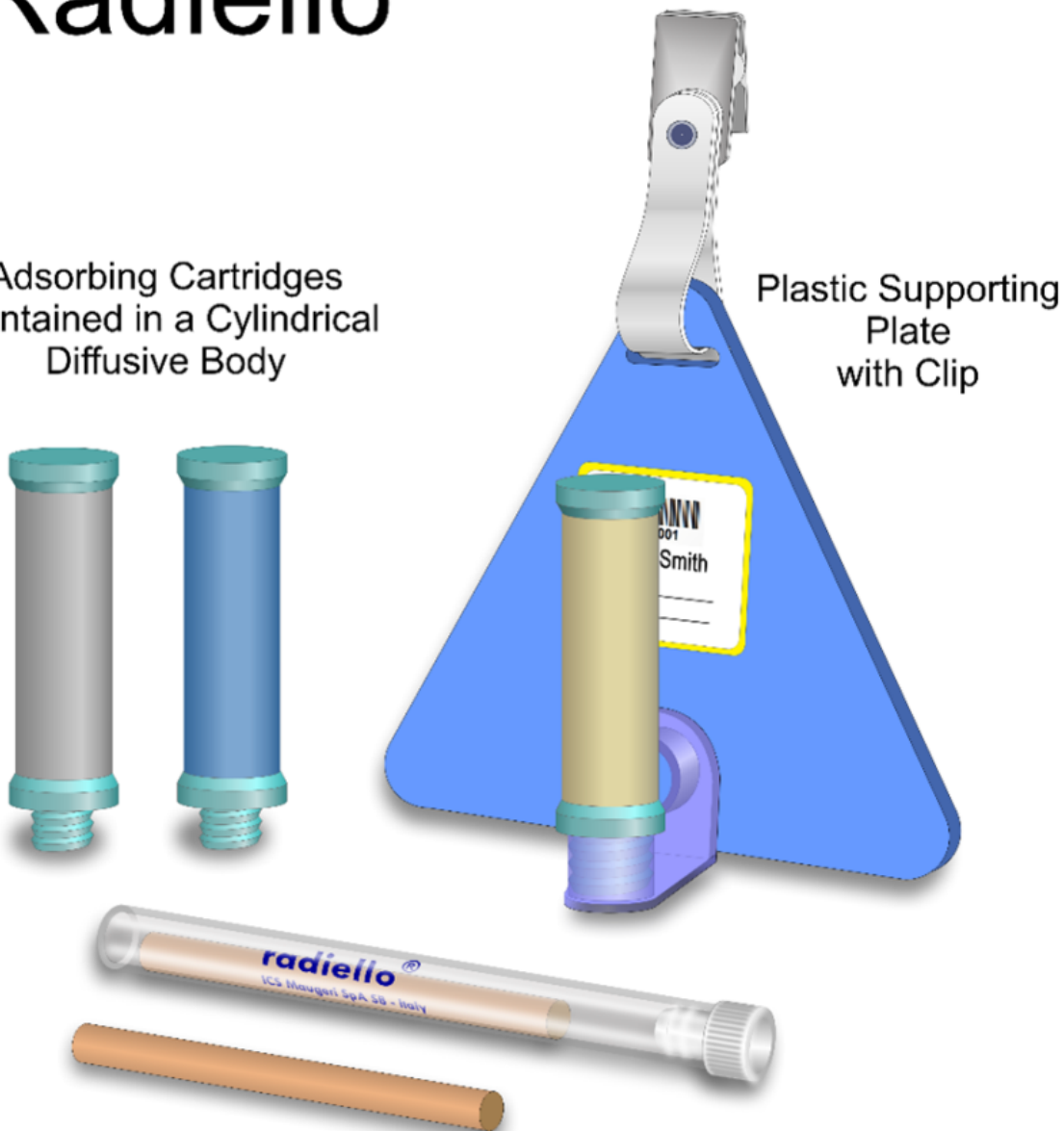


Figure 5-40. Radiello sampler.

Source: NJDEP, used with permission.

### 5.3.7.2 Installation and Use

The minimum requirements of the system include adsorbent cartridge, diffusive body, adhesive labels for sample tracking, and support plate for attaching diffusive body-cartridge assembly. The components may be purchased separately, or starter kits may be purchased that contain all the components of one complete sampler plus an additional adsorbent cartridge. Also available for purchase, Radiello ready-to-use diffusive samplers come preassembled with the adsorbent cartridge preloaded into the diffusive body that can be readily snapped into the preassembled adapter and support plate. Available optional accessories include outdoor shelter and in-field thermometer and reader.

The sampler is received from the supplier sealed in a glass tube. Prior to sampling, the adsorbent cartridge is transferred from the glass tube into an appropriate diffusive body, which is screwed onto a triangular support plate (either horizontally or vertically). Start date/time can be documented on sample identification label (with barcode) and inserted into sampler

pocket.

The adsorbent cartridge is selected based on the compound class of interest (refer to the product manual for the technology) and can consist of a pure adsorbent material or a chemically coated adsorbent. Each adsorbent cartridge is sealed in a glass or plastic tube, which is placed in a transparent, thermally sealed polyethylene bag. The adsorbent cartridge is loaded into the diffusive body and attached to the support plate. A tethered clip is used to attach the support plate to a desired location, for example, to hang from a stand (ambient air monitoring) or clipped to a garment (for breathing zone monitoring).

The diffusive bodies are cylindrical diffusive barriers threaded at one end so they can be attached to the support plate. Vertical adapters (to orient the diffusive body to be parallel to the triangular support plate) can also be used (shown in Figure 5-40). When needed, the diffusive bodies can be reused and cleaned with a mild detergent as they will collect dust, especially during outdoor sampling. It is generally recommended to replace the diffusive body after four to five washings.

Four different diffusive bodies (white, RAD120; blue, RAD1201; yellow, RAD1202; and gray, RAD1203) are available, each used for specific adsorbent cartridges and applications (for example, the yellow diffusive body is indicated for use with thermal desorption cartridges for sampling of BTEX while the white diffusive body is indicated for use with solvent desorption cartridges for sampling of BTEX), as specified in the Radiello Manual.

Once the sampling period is complete, the adsorbent cartridge is transferred from the diffusive body back into the original sealed glass tube without touching the adsorbent itself. The end date/time and temperature can be documented on the label. The cartridge can be stored in a polyethylene bag after sampling before desorption/analysis. The cartridges are desorbed for analysis by chemical (solvent) or thermal extraction, depending on the specific cartridge. Although thermal desorption (TD) cartridge adsorbents may be used multiple times, the solvent-extracted adsorbent cartridge is designed for one-time use.

### 5.3.7.3 Advantages

- This hydrophobic sampler is well suited for humid environments by use of a diffusive body that is water repellent and applicable for outdoor air sampling when deployed beneath a shelter.
- The radial design of the Radiello allows airborne analytes 360° access to the diffusive surface and adsorbent material, resulting in a significantly higher uptake rate and faster sampling compared to traditional axial-type passive samplers.
- The diffusive body is said to be “touch- and chemically inert,” making them easy to handle. The diffusive body is water repellent and applicable in wet weather. Available accessories such as the “outdoor shelter” box protect the sampler from unfavorable weather conditions.
- Different adsorbents may be used based on the target compounds of concern. Higher sampling volumes, greater adsorbent capacity, and higher uptake rate reportedly contribute to minimal reverse diffusion and greater uptake rate consistency, which will result in more reproducible results.
- Uptake rates are the amount of a chemical adsorbed to a sorbent material per time. Instead of being calculated, uptake rates are measured under a range of conditions (chemical concentration, temperature, relative humidity, air speed, with and without interfering compounds, etc.), resulting in more precise quantification.
- The raw materials and each lot of finished products are quality compliance-checked to ensure low background contamination noise levels and ensure that performance standards are met.
- The high uptake rates and high capacity allow sampling time from 15 minutes to weeks, while achieving low reporting limits and a broad concentration range (1ppb-1,000 ppm).
- The Radiello system predominantly uses solvent/chemical desorption, and therefore does not require thermal desorption equipment. Thermal desorption and gas chromatography/mass spectrometry (TD-GC/MS) systems are also available for precise and very sensitive measurements using the RAD145 adsorbent cartridge.

### 5.3.7.4 Limitations

- Uptake rates can be obtained by comparison to experimental measurements by other sampling methods (for example, active sampling or real-time monitoring instruments) or to theoretical models. In a review study, Lutes et al. ( Lutes et al. 2010<sup>[MYFHCP TL]</sup> Lutes, Christopher, Carl Singer, Robert Uppencamp, Ronald Mosley, and Dale Greenwell. 2010. “Radon Tracer as a Multipurpose Tool to Enhance Vapor Intrusion Assessment and Mitigation.”

[https://events.awma.org/education/Posters/Final/Lutes\\_RadonPoster.pdf](https://events.awma.org/education/Posters/Final/Lutes_RadonPoster.pdf).) compared both thermally and solvent-extracted Radiello samplers with TO-15 samples and reported TO-15 results to be overall slightly higher than those from the Radiello samplers ( Lutes et al. 2010<sup>[MYFHCP TL]</sup> Lutes, Christopher, Carl Singer, Robert Uppencamp, Ronald Mosley, and Dale Greenwell. 2010. "Radon Tracer as a Multipurpose Tool to Enhance Vapor Intrusion Assessment and Mitigation." [https://events.awma.org/education/Posters/Final/Lutes\\_RadonPoster.pdf](https://events.awma.org/education/Posters/Final/Lutes_RadonPoster.pdf).) They also reported poor agreement between Radiello samplers and TO-15 samples for polar compounds—vinyl chloride, for example.

- A singular adsorbent is used, which cannot target very volatile organic compounds, such as vinyl chloride and 1,1-dichloroethene.
- To accurately determine chemical concentrations derived from passive samples, uptake rates are needed. These uptake rates are specific for the compound of interest, the sorbent material, and the sampling duration.
- The uptake rate of passive samplers is affected by environmental parameters such as wind velocity, relative humidity, and temperature. The effective uptake rate under field conditions can differ from the predicted uptake rate obtained under experimental conditions. Therefore, measurements of these sampling conditions must be recorded during the sampling period and accounted for when evaluating the measured concentration of analytes. A study published by Delgado Saborit and Esteve Cano ( Delgado Saborit and Esteve Cano 2007<sup>[P2R22]BN]</sup> Delgado Saborit, J.M., and V.J. Esteve Cano. 2007. "Field Comparison of Passive Samplers versus UV-Photometric Analyser to Measure Surface Ozone in Mediterranean Area." *J Environ Monit*, no. 9, 610-15.) noted that while the Radiello passive samplers performed comparably to the UV-photometric ozone analyzer in measurements of ground-level ozone, one disadvantage was the requirement to determine the effective collection rate of the sampler itself ( Delgado Saborit and Esteve Cano 2007<sup>[P2R22]BN]</sup> Delgado Saborit, J.M., and V.J. Esteve Cano. 2007. "Field Comparison of Passive Samplers versus UV-Photometric Analyser to Measure Surface Ozone in Mediterranean Area." *J Environ Monit*, no. 9, 610-15.). However, they noted the passive samplers could be calibrated against an automatic sampler as a reference of the collection rate efficiency for each sampling period.
- Highly variable ambient chemical concentrations may not be predicted by the controlled conditions used to obtain experimental uptake rate. For example, the presence of other chemicals, and at high ambient concentrations, may interfere with the adsorption of another.
- Passive uptake of a chemical from media is only linear (constant uptake rate) when the concentration of the chemical on the sampler is low. The uptake rate slows as the chemical concentration on the sampler increases and approaches equilibrium. There is no net uptake onto the passive sampler when the sampler reaches equilibrium. However, the Radiello sampler contains a large mass of sorbent to minimize the potential for sorbent saturation.
- Another review ( Wania and Shunthirasingham 2020<sup>[ZY48N]SC]</sup> Wania, F., and C. Shunthirasingham. 2020. "Passive Air Sampling for Semi-Volatile Organic Chemicals." *Environmental Science: Processes & Impacts* 22 (10): 1925. <https://pubs.rsc.org/en/content/articlelanding/2020/em/d0em00194e#!>) of passive air sampling of SVOCs suggested that the Radiello diffusive bodies made of polyethylene are themselves capable of adsorbing SVOCs and interfering with diffusion into the sorbent. Overall, the review concluded that there was much quantitative uncertainty in passive air sampling of SVOCs.
- Compared to thermal desorption, the solvent desorption method requires additional sample preparation steps with potential for analytical interference from formation of artifacts. The solvent extraction method also has lower desorption efficiency compared to the thermal desorption method. Lack of automation is one drawback for the solvent desorption method.
- Compared to the solvent desorption method, thermal desorption requires high temperatures for effective release of sorbed compounds, which could lead to degradation of certain compounds and even some sorbent materials. However, the thermal desorption method may be automated, unlike the solvent desorption method.

## 5.3.8 Waterloo Membrane Sampler (Solvent-extracted)

### 5.3.8.1 Description and Application

The Waterloo Membrane Sampler (WMS) (Figure 5-41) is a "tube-style permeation passive sampler" used for sampling indoor/outdoor air and soil gas and is designed with a thin hydrophobic polydimethylsiloxane (PDMS) membrane placed across the face of a sorbent-filled vial ( Grosse et al. 2014<sup>[W8ZYUK8]</sup> Grosse, Doug, Robert Truesdale, Heidi Hayes, Dr. Helen Dawson, Dr. Todd McAlary, and Chris Lutes. 2014. "Passive Samplers for Investigations of Air Quality: Method Description,

Implementation, and Comparison to Alternative Sampling Methods.” EPA/600/R-14/434. National Risk Management Research Laboratory.

<https://nepis.epa.gov/Exe/ZyNET.exe/P100MK4Z.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2011+Thru+2015&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C11thru15%5CTxt%5C0000015%5CP100MK4Z.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C->

&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL#.). The type of sorbent used can be either a very strong sorbent requiring solvent extraction (charcoal type) or a weak absorbent amenable to thermal desorption (graphite carbon black type); however, currently a thermal desorption option is not available. Solvent extraction laboratory preparation methods result in lower analytical sensitivity and therefore a requirement for longer sample duration than thermal desorption methods with higher analytical sensitivity that require shorter sample duration. VOC vapors permeate through the PDMS membrane, which is itself a sorptive material, and are trapped by the sorbent medium inside the vial. The mass of each chemical is determined by gas chromatography-mass spectrometry (GC-MS) and a time-weighted average concentration can be calculated using experimentally measured validated uptake rates for many common VOCs. As stated by SiREM, concentrations in the sampled air can be calculated as show in Equation 6 ( SiREM, n.d.<sup>[NX77826D]</sup> SiREM. n.d. “Instructions for Soil Gas Sampling with WMS-LU TM Samplers.” <https://www.siremlab.com/waterloo-membrane-sampler-wms/>):

### Equation 6

$$C = M / (t \times UR)$$

where:

C = concentration in sampled air ( $\mu\text{g}/\text{m}^3$ )

M = mass on sampler (picograms)

t = sampling time (min)

UR = known analyte-specific uptake rate (mL/min)

# Waterloo Membrane Sampler™



Figure 5-41. Waterloo Membrane Sampler.

Source: NJDEP, used with permission.

## 5.3.8.2 Installation and Use

The following summary of the instructions on installation and use of the WMS were taken from SiREM for collecting indoor and outdoor air samples. Detailed instructions and additional instructions for soil gas sampling are on the SiREM website.

The sampler is shipped in a thermally sealed polycoated aluminum pouch and should not be opened until the sampler is ready for use (Figure 5-42) to prevent cross contamination. Within the pouch is a glass vial that has the WMS sampler and a carbon pack "MiniPax" (a), a wire hanger (to deploy the sampler) (b), a nylon line (approximately 10 feet) to help with deployment (c), and Teflon tape for re-sealing the glass vial once the sample has been collected (c) (Figure 5-41) ( SiREM, n.d.<sup>[1]</sup> SiREM. n.d. "Directions for Collecting Indoor and Outdoor Air Samples with the Waterloo Membrane Sampler TM." <https://siremlab.com/wp-content/uploads/2021/02/WMS-SOP-passive-air-sampling.pdf>).



WMS™ sampler shipping pouch



Close up of sampler membrane

Do not store/use WMS™ samplers near, volatile chemical sources including perfume, felt markers, etc. and avoid touching the sampler membrane.



Contents of sampler shipping pouch

Figure 5-42. The Waterloo Membrane Sampler.

Source: SiREM, adapted with permission.



WMS™ sampler inside 20 ml glass vial



Aligning WMS™ sampler in wire hanger



Bending wire to insert WMS™ sampler

Figure 5-43. The WMS being prepped for deployment.

Source: SiREM, adapted with permission.

After removing the sampler from the glass vial, position the sampler upside down and insert into the wire hanger (Figure 5-43). Hang the sampler at the desired location using the nylon line and wire loops at the top of the wire hanger, with the membrane facing downward (Figure 5-43) ( SiREM, n.d.<sup>[1]</sup> SiREM. n.d. "Directions for Collecting Indoor and Outdoor Air Samples with the Waterloo Membrane Sampler TM."

<https://siremlab.com/wp-content/uploads/2021/02/WMS-SOP-passive-air-sampling.pdf>). Once sampling is complete, remove the sampler from the wire hanger (Figure 5-44). Next, take out the MiniPax from the 20 mL glass vial and place it in the aluminum pouch. Place the sampler back in the glass vial and seal with the cap and tape and put the vial in the bubble pack and place in the aluminum pouch and seal (Figure 5-44) ( SiREM, n.d.<sup>[1]</sup> SiREM. n.d. "Directions for Collecting Indoor and

Outdoor Air Samples with the Waterloo Membrane Sampler TM.”

<https://siremlab.com/wp-content/uploads/2021/02/WMS-SOP-passive-air-sampling.pdf>).



**Deployed sampler with line**



**Removing WMS™ sampler from wire hanger**



**Sampler re-packaged**

Figure 5-44. The WMS in deployment, retrieved, and repackaged.

Source: SiREM, adapted with permission.

### 5.3.8.3 Advantages

- Hydrophobic sampler is well suited for humid environments ( Seethapathy and Górecki 2010<sup>[CQ9GTRX]</sup> Seethapathy, Suresh, and Tadeusz Górecki. 2010. "Polydimethylsiloxane-Based Permeation Passive Air Sampler. Part II: Effect of Temperature and Humidity on the Calibration Constants." *Journal of Chromatography A* 1217 (50): 7907–13. <https://doi.org/10.1016/j.chroma.2010.10.057>.)
- For soil gas sampling, leaks in sampling trains are not a concern compared to active sampling methods and no leak check procedures are required ( Dawson, McAlary, and Groenevelt 2015<sup>[CC38ULK2]</sup> Dawson, Helen, Todd McAlary, and Hester Groenevelt. 2015. "Passive Sampling for Vapor Intrusion Assessment." Technical Memorandum TM-NAVFAC EXWC-EV-1503. <https://www.siremlab.com/wp-content/uploads/2021/02/NAVFAC-2015-Passive-Sampling-for-Vapor-Intrusion-Assessment.pdf>.)
- The Waterloo Membrane Sampler is insensitive to wind velocity (beneficial for outdoor and mitigation vent-pipe monitoring or soil vapor extraction system sampling) ( Seethapathy 2009<sup>[XCTW4YI2]</sup> Seethapathy, Suresh. 2009. "Development, Validation, Uptake Rate Modeling and Field Applications of a New Permeation Passive Sampler." UWSpace: University of Waterloo. <http://hdl.handle.net/10012/4870>.)
- Thickness and porosity of PDMS membrane can be modified to vary the sampler uptake rates so they are less than the lowest expected soil gas replenishment rate when sampling soil in low soil permeability conditions. However, new uptake rates will need to be determined for the modified sampler through an uptake rate validation study or estimation by theoretical determination. Known or expected geologic or other environmental conditions that will reduce the diffusion rate of gases should be noted by the field team ( Seethapathy and Górecki 2010<sup>[CQ9GTRX]</sup> Seethapathy, Suresh, and Tadeusz Górecki. 2010. "Polydimethylsiloxane-Based Permeation Passive Air Sampler. Part II: Effect of Temperature and Humidity on the Calibration Constants." *Journal of Chromatography A* 1217 (50): 7907–13. <https://doi.org/10.1016/j.chroma.2010.10.057>.; McAlary et al. 2014<sup>[2XRDAAS]</sup> McAlary, Todd, Xiaomin Wang, Andre Unger, Hester Groenevelt, and Tadeusz Górecki. 2014. "Quantitative Passive Soil Vapor Sampling for VOCs--Part 1: Theory." *Environmental Science. Processes & Impacts* 16 (3): 482–90. <https://doi.org/10.1039/c3em00652b>.; McAlary et al. 2014<sup>[X2WJXVHU]</sup> McAlary, Todd, Hester Groenevelt, Suresh Seethapathy, Paolo Sacco, Derrick Crump, Michael Tuday, Brian Schumacher, Heidi Hayes, Paul Johnson, and Tadeusz Górecki. 2014. "Quantitative Passive Soil Vapor Sampling for VOCs--Part 2: Laboratory Experiments." *Environmental Science. Processes & Impacts* 16 (3): 491–500. <https://doi.org/10.1039/c3em00128h>.; McAlary et al. 2014<sup>[AGSA9AEW]</sup> McAlary, Todd, Hester Groenevelt, Paul Nicholson, Suresh Seethapathy, Paolo Sacco, Derrick Crump, Michael Tuday, et al. 2014. "Quantitative Passive Soil Vapor Sampling for VOCs--Part 3: Field Experiments." *Environmental Science. Processes & Impacts* 16 (3): 501–10. <https://doi.org/10.1039/c3em00653k>.)
- The Waterloo Membrane Sampler can fit within a subslab vapor point for leakproof subslab monitoring ( Vachon 2023<sup>[36H87MW5]</sup> Vachon, Melody. 2023. "Waterloo Membrane Sampler." SiREM LAB (blog). November 27, 2023. <https://www.siremlab.com/waterloo-membrane-sampler/>.)

### 5.3.8.4 Limitations

- For soil gas sampling, low soil permeability conditions can result in the uptake of VOCs in the vapor phase at a greater rate than the replenishment rate of VOCs. This condition would also result in a sorbent pumped tube or an evacuated canister's inability to collect a sample due to a vacuum being created.
- Sampler must be suspended vertically so adsorbent within vial covers the entire surface of the PDMS membrane.
- Saturation of the sampler could occur due to exposure to high chemical concentrations over an extended period of time ( Salim et al. 2019<sup>[ZTWWSZJ]</sup> Salim, Faten, Marios Ioannidis, Alexander Penlidis, and Tadeusz Górecki. 2019. "Modelling Permeation Passive Sampling: Intra-Particle Resistance to Mass Transfer and Comprehensive Sensitivity Analysis." *Environmental Science. Processes & Impacts* 21 (3): 469–84. <https://doi.org/10.1039/c8em00565f>.)

- Competition could develop between strongly adsorbing VOCs displacing less strong ( Dawson, McAlary, and Groenevelt 2015<sup>[CC38ULK2]</sup> Dawson, Helen, Todd McAlary, and Hester Groenevelt. 2015. "Passive Sampling for Vapor Intrusion Assessment." Technical Memorandum TM-NAVFAC EXWC-EV-1503. <https://www.siremlab.com/wp-content/uploads/2021/02/NAVFAC-2015-Passive-Sampling-for-Vapor-Intrusion-Assessment.pdf>.; Salim et al. 2019<sup>[ZTWIWSZJ]</sup> Salim, Faten, Marios Ioannidis, Alexander Penlidis, and Tadeusz Górecki. 2019. "Modelling Permeation Passive Sampling: Intra-Particle Resistance to Mass Transfer and Comprehensive Sensitivity Analysis." Environmental Science. Processes & Impacts 21 (3): 469-84. <https://doi.org/10.1039/c8em00565f>.)
- Poor recovery can occur from use of strong sorbent with strongly sorbed compounds that are not completely released from the sorbent during analysis ( Dawson, McAlary, and Groenevelt 2015<sup>[CC38ULK2]</sup> Dawson, Helen, Todd McAlary, and Hester Groenevelt. 2015. "Passive Sampling for Vapor Intrusion Assessment." Technical Memorandum TM-NAVFAC EXWC-EV-1503. <https://www.siremlab.com/wp-content/uploads/2021/02/NAVFAC-2015-Passive-Sampling-for-Vapor-Intrusion-Assessment.pdf>.; McAlary 2015<sup>[MSK5T38A]</sup> McAlary, Todd. 2015. "Development of More Cost-Effective Methods for Long-Term Monitoring of Soil Vapor Intrusion to Indoor Air Using Quantitative Passive Diffusive-Adsorptive Sampling Techniques." Cost and Performance Report ER-200830. SERDP and ESTCP. <https://apps.dtic.mil/sti/pdfs/ADA621730.pdf>.)
- Compared to thermal desorption, the solvent desorption method requires additional sample preparation steps with potential for analytical interference from formation of artifacts. The solvent extraction method also has lower desorption efficiency compared to the thermal desorption method. Lack of automation is one drawback for the solvent desorption method.
- Some components of this sampler may contain PFAS, which should be considered based on project DQOs.

## 5.3.9 Beacon Sampler

### 5.3.9.1 Description and Application

Beacon samplers (Figure 5-45) are a trade name of the passive adsorbent samplers developed and provided by Beacon Environmental (Bel Air, MD). They can be used for both air and soil gas sampling, as well as in conduits (for example, sewer lines) and vapor extraction piping. The samplers contain two pairs of hydrophobic carbonaceous adsorbents in an inert container with an opening of known dimension that all VOC vapors pass through at a constant (and known) rate ( Grosse et al. 2014<sup>[W8ZYUK8]</sup> Grosse, Doug, Robert Truesdale, Heidi Hayes, Dr. Helen Dawson, Dr. Todd McAlary, and Chris Lutes. 2014. "Passive Samplers for Investigations of Air Quality: Method Description, Implementation, and Comparison to Alternative Sampling Methods." EPA/600/R-14/434. National Risk Management Research Laboratory. <https://nepis.epa.gov/Exe/ZyNET.exe/P100MK4Z.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2011+Thru+2015&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C11thru15%5CTxt%5C00000015%5CP100MK4Z.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL#>.) The concentration gradient from the surroundings to the sorbent provides the driving force for diffusion of VOC vapors into the sampler.

Beacon passive samplers are deployed for a designated sampling period, typically ranging from days to weeks, and then collected and analyzed by thermal desorption extraction of the VOCs from the sorbent to measure the sorbed mass of each chemical during the sampling period. Beacon's passive sampling procedures are in accordance with ASTM standards D5314 & D7758. As stated in USEPA 2014, the average concentration over the sampling period can be calculated as follows (Equation 7):

### Equation 7

$$C = M / (UR \times t)$$

Where:

C = time-weighted average air concentration ( $\mu\text{g}/\text{m}^3$ )

M = mass of VOC retained by passive sampler ( $\mu\text{g}$ )

UR = uptake rate ( $\text{mL}/\text{min}$ , compound-specific); also called “sampling rate”

t = sampling duration (min)

Sampling duration can be measured with high levels of accuracy, and the mass of VOC retained is analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) following accredited USEPA Method 8260D, TO-17, 325B, or TO-15 ( Clark et al. 2008<sup>[LACT2FJJ]</sup> Clark, James N., Deborah Goodwin, Harry O'Neill, and Joseph E. Odencrantz. 2008. “Application of Passive Soil Gas Technology to Determine the Source and Extent of a PCE Groundwater Plume in an Urban Environment.” Journal of Remediation-In Press, July, 8. <https://beacon-usa.com/wp-content/uploads/2021/05/Regional-Groundwater-Investigation.pdf>). Accordingly, the uptake rate (sampling rate) is the most critical variable for accurately determining air concentrations when using any passive samplers ( Grosse et al. 2014<sup>[W6ZYUK8]</sup> Grosse, Doug, Robert Truesdale, Heidi Hayes, Dr. Helen Dawson, Dr. Todd McAlary, and Chris Lutes. 2014. “Passive Samplers for Investigations of Air Quality: Method Description, Implementation, and Comparison to Alternative Sampling Methods.” EPA/600/R-14/434. National Risk Management Research Laboratory. <https://nepis.epa.gov/Exe/ZyNET.exe/P100MK4Z.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2011+Thru+2015&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C11thru15%5CTxt%5C0000015%5CP100MK4Z.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyURL#>).

# Beacon Sampler

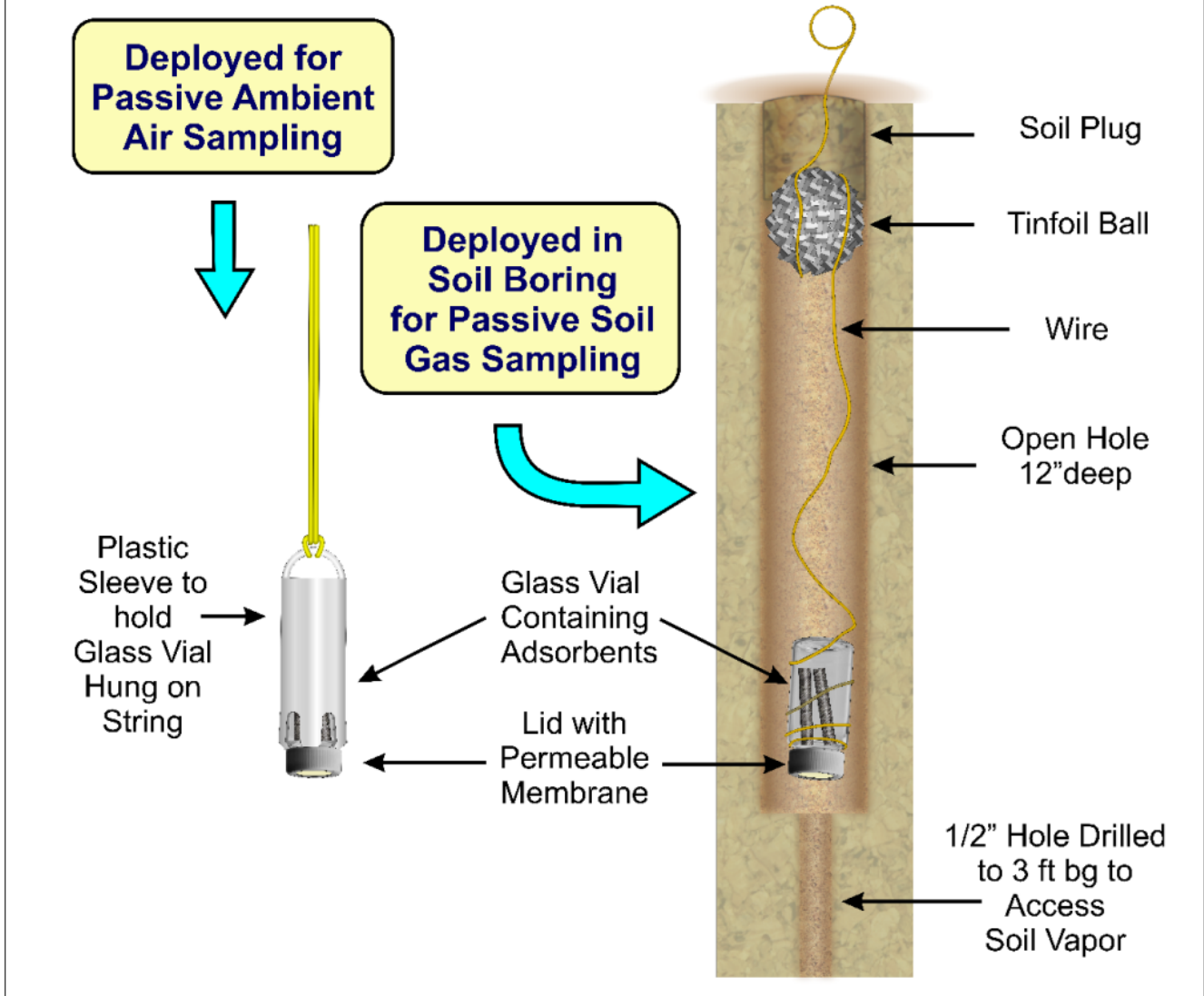


Figure 5-45. Beacon sampler.

Source: NJDEP, used with permission.

## 5.3.9.2 Installation and Use

### Passive soil gas (PSG) sampler

Beacon PSG samplers can be installed (Figure 5-46) to various depths depending on the project objectives. A standard approach involves drilling a 1½-inch diameter hole to a depth of 12-14 inches and a ½-inch hole to a depth of 36 inches. A 12-inch length of pipe is then installed into the larger hole so that it rests ½ inch below grade. A Beacon PSG sampler is next installed open-end down, into the pipe so that it rests at the bottom of the pipe. The hole above the pipe is plugged with an aluminum foil ball and covered to grade with soil or a thin ½-inch concrete patch when sampling through impervious surfacing. As an option, a mechanical plug can be used to seal the hole through impervious surfacing during the sampling period and between sampling events. The dates and times of deployment and retrieval of each sampler are recorded on the chain of custody that is returned with the samples to Beacon for analysis following analytical procedures described in USEPA Method TO-17 and TO-15 to target a range of compounds from vinyl chloride to lighter PAHs. The holding time from sample collection until analysis is 30 days, and no ice or preservatives are required during shipment.

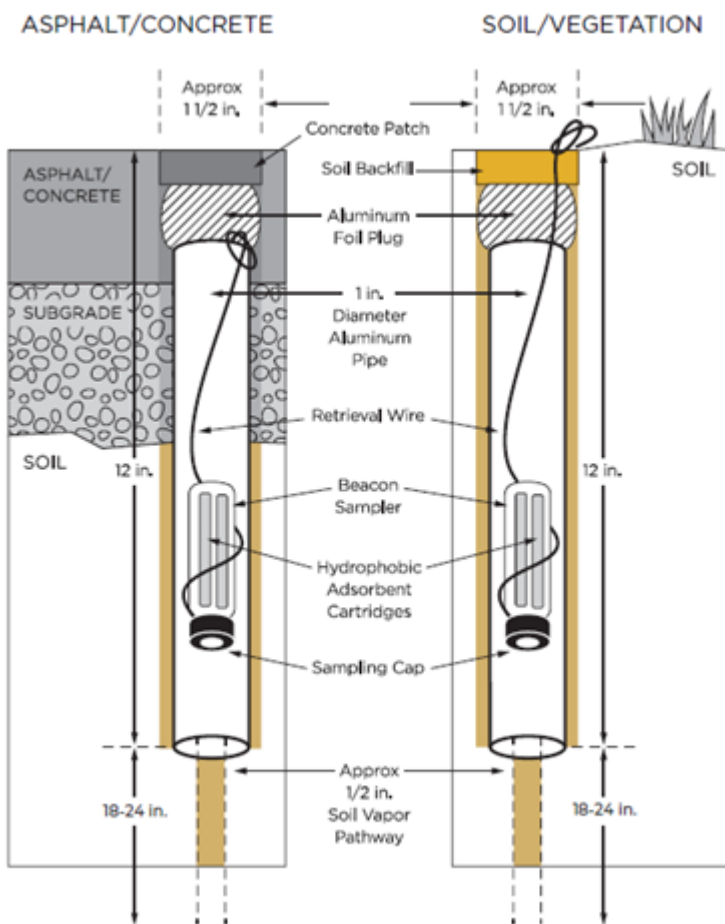


Figure 5-46. Beacon sampler installation.

Source: Beacon Environmental, used with permission.

### **Beacon passive air sampler**

To prepare a Beacon passive air sampler, cut a piece of string long enough to hang the sampler at the desired height and place the string within easy reach. Replace the white solid cap on the sampler with a black sampling cap (a one-hole cap with a screen meshing insert). Remove one of the Beacon samplers (a glass vial containing two sets of hydrophobic adsorbent cartridges) from the sampler bag. Slide the sampler into the Beacon sampler holder all the way or until it clicks into place, with the sampling cap facing out from the holder. Secure the string to the holder to suspend the sampler. For indoor air, the sampler is suspended in the air typically within the breathing zone. The sampler can also be used to sample gas in conduits (for example, sewer lines) and vapor extraction piping, as well as outdoor air. Following the sampling period, the sampling cap is removed and replaced with the solid shipping cap, which is tightened to be gas-tight. The dates and times of deployment and retrieval of each sampler are recorded on the chain of custody that is returned with the samples to Beacon for analysis following analytical procedures described in USEPA Method TO-17 and TO-15 to target a range of compounds from vinyl chloride to lighter PAHs. The holding time from sample collection until analysis is 30 days and no ice or preservatives are required during shipment.



Figure 5-47. Beacon passive air sampler.

Source: Beacon Environmental, used with permission.

### **ChloroSorber passive sampler**

The ChloroSorber sampler (Figure 5-48) targets a range of chlorinated compounds from vinyl chloride to tetrachloroethene with low-level detection limits in air or sewer gas. Sample collection instructions to be followed can be found on the Beacon website ( "Instructions - Beacon Environmental" 2024<sup>[MCKU7F6]</sup> "Instructions - Beacon Environmental." 2024. 2024. [https://beacon-usa.com/resources/instructions/.](https://beacon-usa.com/resources/instructions/)). To sample air, the storage cap is removed from the sampling end of the tube and replaced with a diffusion cap that allows air to enter the tube and the VOCs present to be adsorbed onto the sorbent bed following the principles of diffusion. The sampler is suspended in the air by wire or string typically within the breathing zone for indoor air samples. The ChloroSorber can also be used to sample gas in conduits (for example, sewer lines) and vapor extraction piping, as well as outdoor air. Following the sampling period, the diffusion cap is removed and replaced with the storage cap, which is tightened to be gas-tight for storage and transport. The dates and times of deployment and retrieval of each sampler are recorded on the chain of custody that is returned to Beacon with the samples for analysis following analytical procedures described in USEPA Method TO-17 and TO-15 to target a range of chlorinated compounds from vinyl chloride to tetrachloroethene at low trace reporting limits. The holding time from sample collection until analysis is 30 days and no ice or preservatives are required during shipment.



Figure 5-48. ChloroSorber sampler.

Source: Beacon Environmental, used with permission.

### 5.3.9.3 Advantages

- Data are reported in units of concentration ( $\mu\text{g}/\text{m}^3$ ). Quantitative uptake rates were experimentally determined and validated for the Beacon sampler and ChloroSorber in a third-party study that included other passive samplers with known uptake rates as a reference and was completed over 7-, 14-, and 26-day exposure periods. The experiments were carried out by the Health and Safety Executive (HSE), United Kingdom, in a standard atmosphere generator based upon procedures described in ISO 6145-4:20042. HSE's methods for the determination of hazardous substances are the source of most of the published uptake rates in the relevant international standard methods (for example, ISO 16017-2)<sup>3</sup>. Quantitative uptake rates for 13 key chlorinated and aromatic VOCs were determined and verified for the passive samplers. In this six-replicate third-party study, the devices showed excellent performance with great linearity and reproducibility.
- The Beacon sampler contains two different hydrophobic adsorbents enabling the sampler to be used to target a broad range of organic compounds with one analysis from vinyl chloride to the lighter polycyclic aromatic hydrocarbons PAHs, such as naphthalene, acenaphthene, and fluorene. The use of two adsorbents extends the range of target analytes beyond other passive samplers that use only one adsorbent.
- The hydrophobic sampler is well suited for humid environments by use of hydrophobic adsorbents. As noted in ISO 16017-2, passive samplers are suitable for use in atmospheres of up to 95% relative humidity for all

hydrophobic sorbents ( "Indoor, Ambient and Workplace Air - Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography - Part 2: Diffusive Sampling"

2003<sup>[G9KAUVKL]</sup> "Indoor, Ambient and Workplace Air - Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography - Part 2: Diffusive Sampling." 2003. The International Organization for Standardization (ISO). <https://webstore.ansi.org/standards/iso/iso160172003>).

- Beacon samplers have simple application and installation. All materials for sampling procedures are provided in a well-organized sampling kit with detailed instructions.
- Analyses of all samples are completed by Beacon Environmental following accredited USEPA methods, and USDOD Environmental Laboratory Accreditation Program (ELAP) and/or National Environmental Laboratory Accreditation Program (NELAP) procedures.
- The ChloroSorber can target chlorinated compounds at low detection limits (for example < 0.04 µg/m<sup>3</sup> for vinyl chloride with a 14-day sampling duration).
- For soil gas sampling, no sampling train is used, so no leak check procedures are required, as they are for active soil gas sampling.
- The sampler can be oriented vertically in either direction or horizontally for sample collection.
- Sampler shelters custom designed for the Beacon sampler and ChloroSorber are available for protection from weather when sampling outdoor air, in accordance with USEPA Method 325A requirements ( USEPA 2019<sup>[7GAQZ5DE]</sup> USEPA. 2019. "Method 325A - Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection." USEPA. [https://www.epa.gov/sites/default/files/2019-08/documents/method\\_325a.pdf](https://www.epa.gov/sites/default/files/2019-08/documents/method_325a.pdf)).
- As an option, a mechanical plug used to suspend the soil gas sampler can seal the hole through impervious surfacing during the sampling period and between sampling events.

#### 5.3.9.4 Limitations

- The detection limits are based on the sampling duration, and extended sampling periods may be required to meet target screening levels.
- Thirteen chlorinated VOCs were tested in the HSE laboratory for validated uptake rates, and Graham's Law of gas diffusion is used to calculate the uptake rates for other VOCs. However, all chlorinated compounds targeted by the ChloroSorber were included in the HSE uptake rate study.
- For soil gas sampling, low soil permeability conditions can result in the uptake of VOCs in the vapor phase at a greater rate than the replenishment rate of VOCs. This condition would also result in a sorbent pumped tube or an evacuated canister's inability to collect a sample due to a vacuum being created.
- Sample analysis is performed exclusively by Beacon Environmental. Third-party analysis is not available.

### 5.3.10 Dart Sampler

#### 5.3.10.1 Description and Application

The Dart sampler (Figure 5-49) is a type of polymeric sampler used to delineate an area of interest for PAHs in sediments and similar soft soils. The technology is deployed when traditional mechanized sampling (such as laser-induced fluorescence (LIF), traditional soil borings, etc.) is limited by site constraints - potentially unsafe for mechanized sampling or where the site would be adversely affected by access for mechanized sampling. This technique often applies to PAHs that exist as a component of NAPL in sediments but has been shown to apply to dissolved-phase PAHs as well ( Hawthorne, St. Germain, and Azzolina 2008<sup>[PR83Y68P]</sup> Hawthorne, Steven B., Randy W. St. Germain, and Nicholas A. Azzolina. 2008. "Laser-Induced Fluorescence Coupled with Solid-Phase Microextraction for In Situ Determination of PAHs in Sediment Pore Water." *Environmental Science & Technology* 42 (21): 8021-26. <https://doi.org/10.1021/es8011673>). Accordingly, the Dart sampler is especially useful for high-resolution NAPL characterization at sites where it can generally be difficult and expensive to profile NAPLs, such as shorelines, marshes, shallow bodies of water adjacent to refineries, or former manufactured gas plants or creosote sites ( Hawthorne, St. Germain, and Azzolina 2008<sup>[PR83Y68P]</sup> Hawthorne, Steven B., Randy W. St. Germain, and Nicholas A. Azzolina. 2008. "Laser-Induced Fluorescence Coupled with Solid-Phase Microextraction for In Situ Determination of PAHs in Sediment Pore Water." *Environmental Science & Technology* 42 (21): 8021-26. <https://doi.org/10.1021/es8011673>). The Dart sampler contains a rod coated with a nonfluorescing solid-phase extraction (SPE) media, which is also used in labs for USEPA-approved cleanup and preconcentration of PAHs in traditional grab

samples ( "Darts," n.d.<sup>[RR9P8B7W]</sup> "Darts." n.d. Dakota Technologies. Accessed February 10, 2024. <https://www.dakotatechnologies.com/products/darts.>). The technique relies on the fluorescing property of PAHs that have sorbed into the SPE material under excitation by ultraviolet laser light.

# Dart System

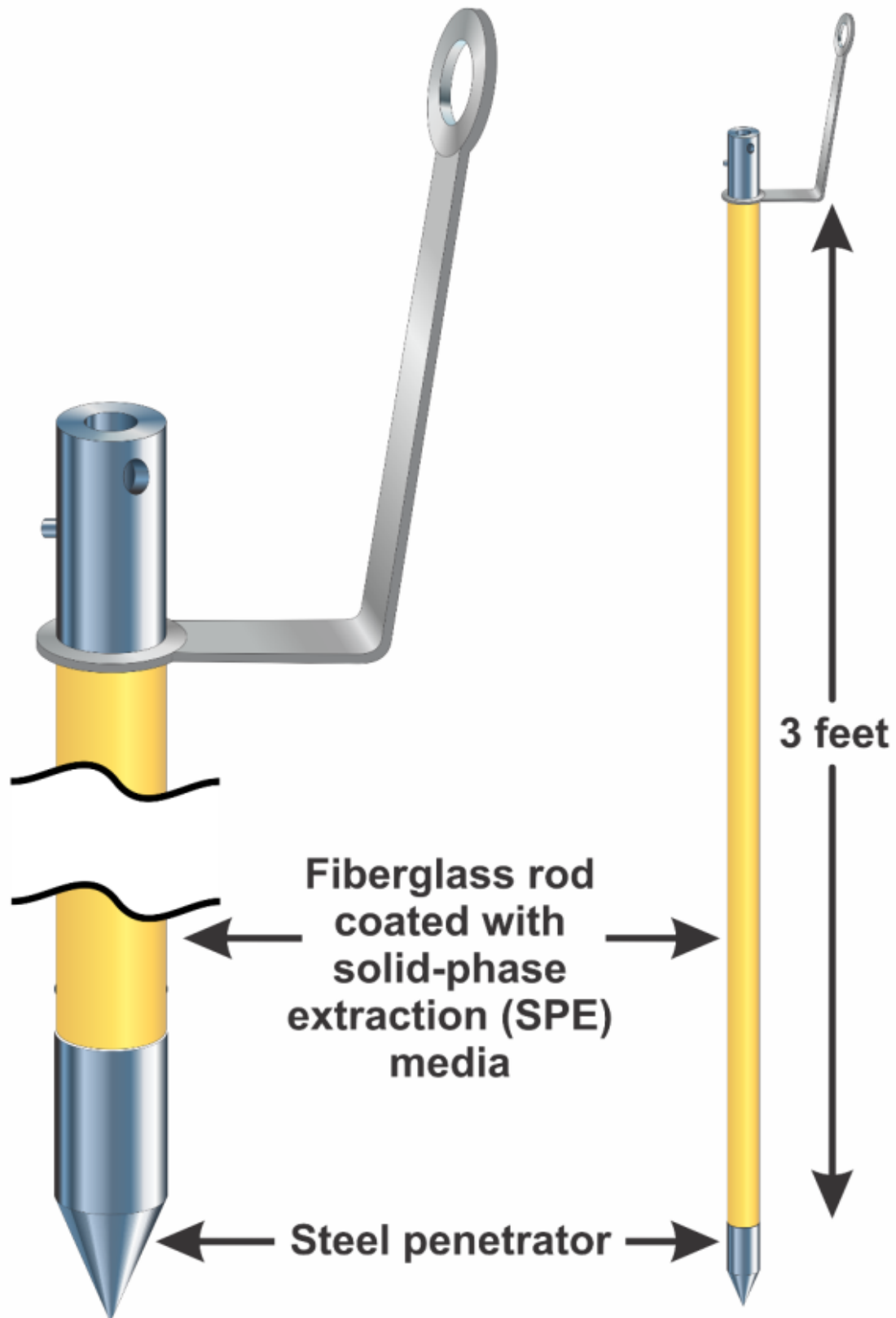


Figure 5-49. Dart sampler.

Source: NJDEP, used with permission.

### 5.3.10.2 Installation and Use

The Darts are driven 1–20 feet down into the sediments. The target depth depends on soil conditions or survey need. Three- and six-foot Darts are standard. Once the Darts are planted, PAHs are attracted to and absorbed into the SPE media because of the PAHs' high affinity for the SPE material. Typically, 24–48 hours of equilibration time is adequate, after which the Darts are retrieved, wrapped in foil to isolate darts from each other, packaged, and sent to the manufacturer (Dakota Technologies (Dakota)) for reading. Once the PAHs have migrated into the Dart's SPE coating, they are stored in solid solution and remain contained there. Refrigeration may not be needed.

The Darts are processed through an LIF reader by technicians from Dakota. The LIF and Dakota's ultraviolet optical screening tool (UVOST) are very similar ( "Darts," n.d.<sup>[RR9P8B7W]</sup> "Darts." n.d. Dakota Technologies. Accessed February 10, 2024. <https://www.dakotatechnologies.com/products/darts>.) A lathe-like device is used to rotate the Dart while the UVOST system logs a detailed reading of the PAH fluorescence (in units of %RE (reference emitter)) vs. depth, typically at very high resolution (>100 readings/ft) to "read" the sorbed PAHs' fluorescence along the Dart's entire length and circumference ( "Darts," n.d.<sup>[RR9P8B7W]</sup> "Darts." n.d. Dakota Technologies. Accessed February 10, 2024. <https://www.dakotatechnologies.com/products/darts>.) The result is a LIF log that looks approximately identical to a UVOST log. Similar to UVOST, the LIF response correlates monotonically to the total-available-PAH content of the NAPL in sediment vs. depth and distinguishes between different petroleum product types. After processing, the clients are sent a JPG file of the graphical log and high-resolution data files.

### 5.3.10.3 Advantages

- Samples do not require ice or low temperature storage after collection.
- There is no waste disposal of soil or groundwater.
- Data are digitized.
- The Dart sampler provides location- and depth-specific NAPL verification and characterization.

### 5.3.10.4 Limitations

- Lighter end light nonaqueous phase liquids (LNAPLs) such as kerosene and gasoline do not contain high enough PAHs to transfer in a convenient (24-48 hour) time span.
- Soil matrix effects influence fluorescence results (finer grain soils slow the transfer rate).
- Limits of detection decrease with porosity (grain size).
- Units of fluorescence intensity (%RE) cannot be directly converted to concentration levels unless a calibration study is conducted of site-specific NAPL on site-specific sediment.

## 5.3.11 Fossil Fuel (CO<sub>2</sub>) Traps

### 5.3.11.1 Description and Application

Fossil fuel traps (also known as CO<sub>2</sub> traps) (Figure 5-50) are at-grade passive samplers that measure time-integrated CO<sub>2</sub> fluxes through the surface at petroleum-contaminated sites. CO<sub>2</sub> traps are patented canisters that contain a strongly basic solid-state sorbent material, which converts the CO<sub>2</sub> that passes through to stable carbonates that are retained in the trap. In addition, the traps are designed to allow for a "built-in" location-specific background correction. The CO<sub>2</sub> flux rates are then used to determine the rate of naturally occurring biodegradation of LNAPL, or natural source zone depletion (NSZD) rates. The traps provide a method for the comparison of natural LNAPL losses (NSZD) to losses from active remedies.

The CO<sub>2</sub> traps have two layers of sorbent. The first layer, at the top, captures ambient CO<sub>2</sub>, which eliminates ambient interference in the bottom sorbent. The second sorbent layer is at the bottom and absorbs CO<sub>2</sub> released from the soil. Because the fossil fuel trap is open to the atmosphere and the CO<sub>2</sub> is captured by the sorbent and does not build up within the head space, the gas flow is not disturbed, and the diffusion gradient is not altered ( "Fossil Fuel Traps CO<sub>2</sub> Traps – a Passive Soil Gas Sampling Method.," n.d.<sup>[ZDQJLJ]</sup> "Fossil Fuel Traps (CO<sub>2</sub> Traps) – a Passive Soil Gas Sampling Method." n.d. E-Flux – Passive Gas Sampling-Based Measurement of Natural Soil Contaminant Degradation (NSZD). Accessed February 12,

2024. <https://www.soilgasflux.com/co2-traps/the-science/>). Consequently, gas flow and the diffusion gradient are unaffected. In some contexts, modern CO<sub>2</sub> contributions (that is, from natural soil respiration processes) can be significant, requiring consideration for estimating an accurate biodegradation rate. Under these conditions, the modern CO<sub>2</sub> contributions would be subtracted from the net CO<sub>2</sub> flux measurement ( "Fossil Fuel Traps CO<sub>2</sub> Traps - a Passive Soil Gas Sampling Method.," n.d.<sup>[ZDQJLJ]</sup> "Fossil Fuel Traps (CO<sub>2</sub> Traps) - a Passive Soil Gas Sampling Method." n.d. E-Flux - Passive Gas Sampling-Based Measurement of Natural Soil Contaminant Degradation (NSZD). Accessed February 12, 2024. <https://www.soilgasflux.com/co2-traps/the-science/>). However, to eliminate this modern carbon interference, every bottom layer of the sorbent is precisely analyzed for its radiocarbon (<sup>14</sup>C) content (ASTM D6866-18) ( "Fossil Fuel Traps CO<sub>2</sub> Traps - a Passive Soil Gas Sampling Method.," n.d.<sup>[ZDQJLJ]</sup> "Fossil Fuel Traps (CO<sub>2</sub> Traps) - a Passive Soil Gas Sampling Method." n.d. E-Flux - Passive Gas Sampling-Based Measurement of Natural Soil Contaminant Degradation (NSZD). Accessed February 12, 2024. <https://www.soilgasflux.com/co2-traps/the-science/>).

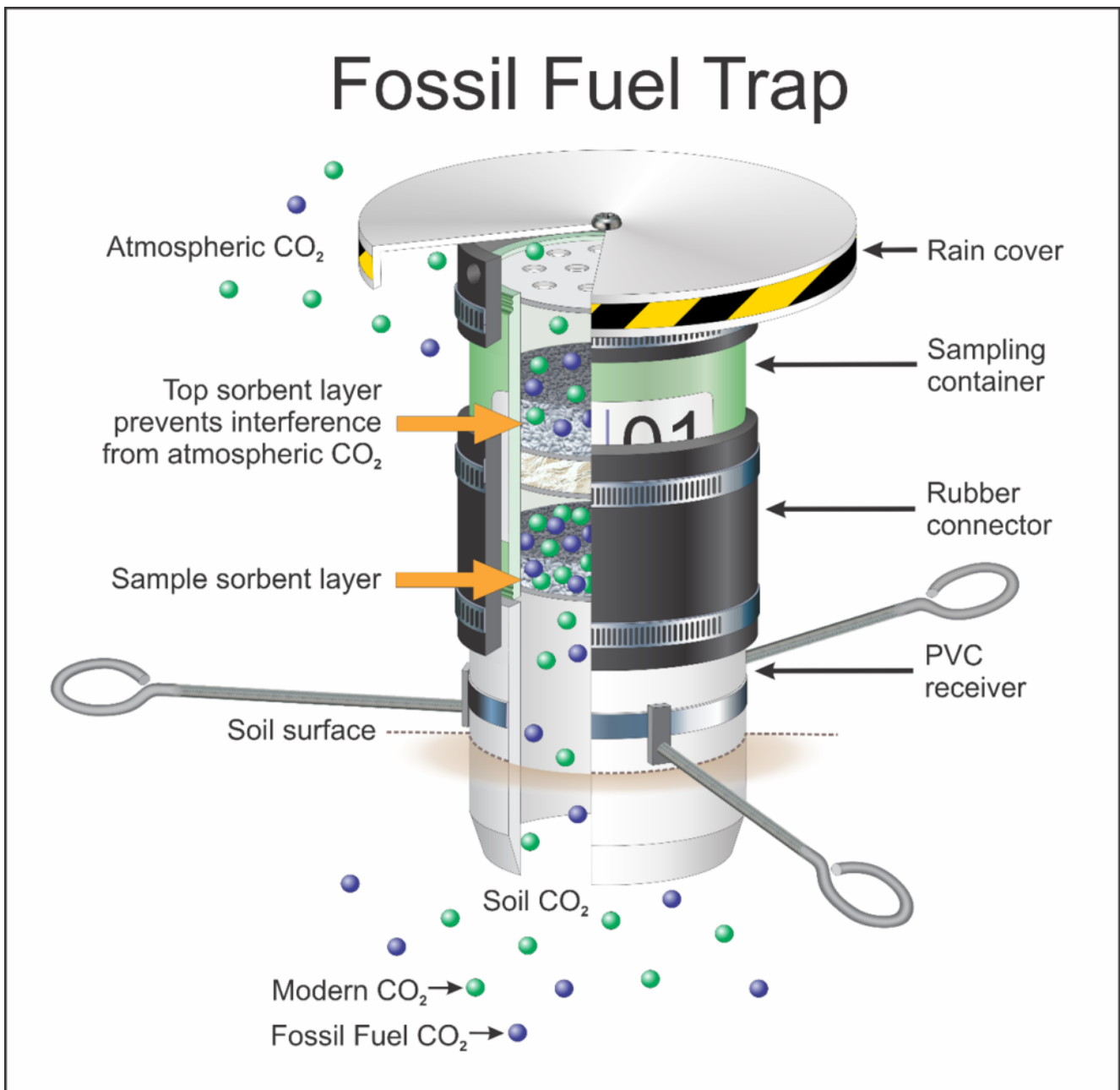


Figure 5-50. Fossil fuel trap sampler.  
Source: NJDEP, used with permission.

### 5.3.11.2 Installation and Use

The use of a CO<sub>2</sub> trap requires installation of a PVC collar provided with the trap inserted several inches into the ground with the trap placed on top. Anchors and a rain hood are then added to secure the trap and protect it from the elements. The

standard deployment time for fossil fuel traps is 14 days (although this time frame can be modified within a range of 5–28 days without further modification of the traps) ( “Fossil Fuel Traps CO<sub>2</sub> Traps – a Passive Soil Gas Sampling Method.” n.d.<sup>[ZDQJLJ]</sup> “Fossil Fuel Traps (CO<sub>2</sub> Traps) – a Passive Soil Gas Sampling Method.” n.d. E-Flux – Passive Gas Sampling-Based Measurement of Natural Soil Contaminant Degradation (NSZD). Accessed February 12, 2024. <https://www.soilgasflux.com/co2-traps/the-science.>).

Following the 2-week sampling period, deployed traps and one undeployed trap (a trip blank) are collected and sent to the manufacturer’s laboratory (E-Flux, LLC, of Fort Collins, CO) for analysis of total CO<sub>2</sub> and petrogenic CO<sub>2</sub> via unstable isotope analysis (<sup>14</sup>C radiocarbon dating). The unstable isotope <sup>14</sup>C is present in modern carbon sources, but due to a half-life of 5,600 years, is not present in fossil fuel carbon sources. This “built-in” location-specific background correction results in much more reliable petrogenic CO<sub>2</sub> flux estimation than can reasonably be accomplished via other CO<sub>2</sub> flux methods. The CO<sub>2</sub> flux is then converted to a depletion rate by multiplying by an appropriate stoichiometric ratio, which describes the mass relationship between CO<sub>2</sub> and the specific LNAPL compound of interest. Measuring the total CO<sub>2</sub> flux over an extended period gives a time-integrated estimate of the soil CO<sub>2</sub> flux. This extended period also accounts for temporal variability including atmospheric pressure fluctuations and weather changes.

### 5.3.11.3 Advantages

- CO<sub>2</sub> traps do not require power, so they can be deployed in remote locations.
- They are easy to use and can be installed by local site personnel without specialized training.
- They can produce time-integrated average flux measurements, accounting for diurnal and daily fluctuations.
- They can be used for <sup>14</sup>C analysis to differentiate fossil fuel-generated CO<sub>2</sub> from modern CO<sub>2</sub> interference, providing location-specific background correction ( “Fossil Fuel Traps CO<sub>2</sub> Traps – a Passive Soil Gas Sampling Method.” n.d.<sup>[ZDQJLJ]</sup> “Fossil Fuel Traps (CO<sub>2</sub> Traps) – a Passive Soil Gas Sampling Method.” n.d. E-Flux – Passive Gas Sampling-Based Measurement of Natural Soil Contaminant Degradation (NSZD). Accessed February 12, 2024. <https://www.soilgasflux.com/co2-traps/the-science.>).

### 5.3.11.4 Limitations

- CO<sub>2</sub> traps cannot be used in areas with impermeable surface cover that limits atmospheric-soil gas exchange (for example, asphalt, concrete, or other liners).
- Saturated soil (due to recent high precipitation events) can hinder CO<sub>2</sub> mobility to the surface, thus biasing the results from this method low.
- Their use may not be valid at sites where <sup>14</sup>C-enriched chemicals have been used or sites in the vicinity of nuclear reactors or waste.
- They have a higher cost than other CO<sub>2</sub> flux methods, which may limit the number of traps used at a site.

## 5.3.12 Bio-Trap Sampler

### 5.3.12.1 Description and Application

Bio-Trap samplers (Figure 5-51) are passive samplers that collect microbes over time to better understand biodegradation potential ( “Bio-Trap Samplers,” n.d.<sup>[YKRJK3FC]</sup> “Bio-Trap Samplers.” n.d. Microbial Insights (blog). Accessed February 13, 2024. <https://microbe.com/bio-trap-samplers/>). BACTRAPs are another activated carbon-based sampler available for use. For the Bio-Trap, Bio-Sep beads, a unique sampling matrix, are key to the approach. The beads are 2–3 mm in diameter and are constructed from a composite of Nomex and powdered activated carbon ( “Bio-Trap Samplers,” n.d.<sup>[YKRJK3FC]</sup> “Bio-Trap Samplers.” n.d. Microbial Insights (blog). Accessed February 13, 2024. <https://microbe.com/bio-trap-samplers/>).

# Bio-Trap<sup>®</sup>

2-3 mm diameter Bio-Sep<sup>®</sup> beads provide substrate for microbial growth



Figure 5-51. Bio-Trap sampler.

Source: NJDEP, used with permission.

### 5.3.12.2 Installation and Use

Once deployed in a monitoring well, the beads adsorb chemicals and nutrients present in the aquifer. This effectively creates an in situ microcosm with an exceptionally large surface area (~600 m<sup>2</sup>/g) that is colonized by subsurface microorganisms (

“Bio-Trap Samplers,” n.d.<sup>[YKRJK3FC]</sup> “Bio-Trap Samplers.” n.d. Microbial Insights (blog). Accessed February 13, 2024.

<https://microbe.com/bio-trap-samplers/>). The Bio-Trap is suspended in the screened interval and left for 30–60 days, depending on study objectives, and then retrieved. Once recovered, DNA, RNA, or phospholipid-derived fatty acids (PLFA) can be extracted from the beads for qPCR, QuantArray or PLFA assays to evaluate the microbial community ( “Bio-Trap

Samplers," n.d.<sup>[YKRJK3FC]</sup> "Bio-Trap Samplers." n.d. Microbial Insights (blog). Accessed February 13, 2024. <https://microbe.com/bio-trap-samplers/>). The Bio-Trap can produce results that can be integrated over time rather than from a single sampling event ( "Bio-Trap Samplers," n.d.<sup>[YKRJK3FC]</sup> "Bio-Trap Samplers." n.d. Microbial Insights (blog). Accessed February 13, 2024. <https://microbe.com/bio-trap-samplers/>). Numerous Bio-Trap samplers can be confined from one another using a double seal cap assembly.

### **5.3.12.3 Advantages**

- Bio-Trap samplers provide an integrated view rather than a snapshot.
- Organisms colonize the traps in situ, selecting for active processes.
- These samplers can be analyzed with any molecular tool.
- The trap has strong adsorptive capability.
- They are versatile.









### **5.3.12.4 Limitations**

- Organisms must actively colonize the trap, so it may miss low-concentration processes or organisms.
- Bio-Trap samplers must be left in the monitoring well for at least 30 days, so teams need two trips to the field for deployment and retrieval.

## 6. Nonpassive Grab Sampling Technologies

The following technologies do not meet the technical definition of a passive sampler in this document (Table 6-1). The following devices introduce “active media transport” through suction or pressure variations or do not allow the sampled media to equilibrate before sample collection. However, these technologies are presented here because they do offer samplers the collection of a “no-purge” and discrete sample from groundwater or surface water. Many of the common advantages covered in Section 3.1 also apply to these technologies. The samplers are discussed here to provide readers with additional devices to collect environmental samples to meet the DQOs for their respective projects, where a truly passive grab sample is not required.

Table 6-1: Nonpassive grab sampling technologies by media type

Sampling Device	Technology Type	Groundwater	Surface Water	Pore-Water	Sediment	Soil Gas	Indoor Air	Outdoor Air	Soil	NAPL
Syringe Sampler	Grab									
Deep Discreet Interval Sampler	Grab									
Horizontal Water Interval Sampler	Grab									

Edit

### 6.1 Syringe Sampler

#### 6.1.1 Description and Application

Syringe samplers (Figure 6-1) are devices designed to capture and preserve a grab water sample by preserving the conditions at the selected depth. The sample is collected without contact with air by precluding sample aeration and pressure changes at the selected depth of monitoring. Although these samplers are not truly passive, the sample can be collected without purging or with a minimal amount of purging. A field filter can be used to filter samples for dissolved metals analysis.

The device is constructed of different materials, including stainless steel and glass components, or HDPE. Devices constructed with those materials can be used multiple times following decontamination. Another sampler is of polycarbonate material and can only be used once ( NJDEP 2022<sup>[3UN3UL5J]</sup> NJDEP. 2022. “Chapter 5 Sampling Equipment.” In Field Sampling Procedures Manual, 2022nd ed., 113. NJDEP.

[https://www.nj.gov/dep/srp/guidance/fspm/manual\\_edition/2022/chapter\\_5\\_sampling\\_equipment.pdf](https://www.nj.gov/dep/srp/guidance/fspm/manual_edition/2022/chapter_5_sampling_equipment.pdf)). The samplers are designed to be compatible with standard off-the-shelf medical syringes of varying volumes ( NJDEP 2022<sup>[3UN3UL5J]</sup> NJDEP. 2022. “Chapter 5 Sampling Equipment.” In Field Sampling Procedures Manual, 2022nd ed., 113. NJDEP.

[https://www.nj.gov/dep/srp/guidance/fspm/manual\\_edition/2022/chapter\\_5\\_sampling\\_equipment.pdf](https://www.nj.gov/dep/srp/guidance/fspm/manual_edition/2022/chapter_5_sampling_equipment.pdf)). The sample volume can be selected to match the project needs.

Generally, syringe samplers are not widely applicable for general well sampling monitoring; however, they are applicable in attempting to collect a discrete, nonpurged sample ( NJDEP 2005<sup>[5W4MLSCA]</sup> NJDEP. 2005. Field Sampling Procedures Manual. 2005th ed. NJDEP. <https://rucore.libraries.rutgers.edu/rutgers-lib/16661/PDF/1/play/>). This is markedly true when gathering an undisturbed aliquot of NAPL from a well or targeting a zone for field analytical measurement ( NJDEP 2005<sup>[5W4MLSCA]</sup> NJDEP. 2005. Field Sampling Procedures Manual. 2005th ed. NJDEP.

<https://rucore.libraries.rutgers.edu/rutgers-lib/16661/PDF/1/play/>). Certain water quality indicator parameters measured in discrete or non-pumped samples are more susceptible to bias from changes in temperature, pressure, turbidity, and

concentrations of dissolved gases based on the location of the sampled well. The DQOs of the project should consider these effects when sampling a discrete interval.

This apparatus can be used to monitor depth profiles in lakes, to sample pools in creeks, and to sample groundwater monitoring wells. For groundwater monitoring wells, the apparatus as specified below is useful for depths/heads of up to 10 feet.

# Syringe Sampler

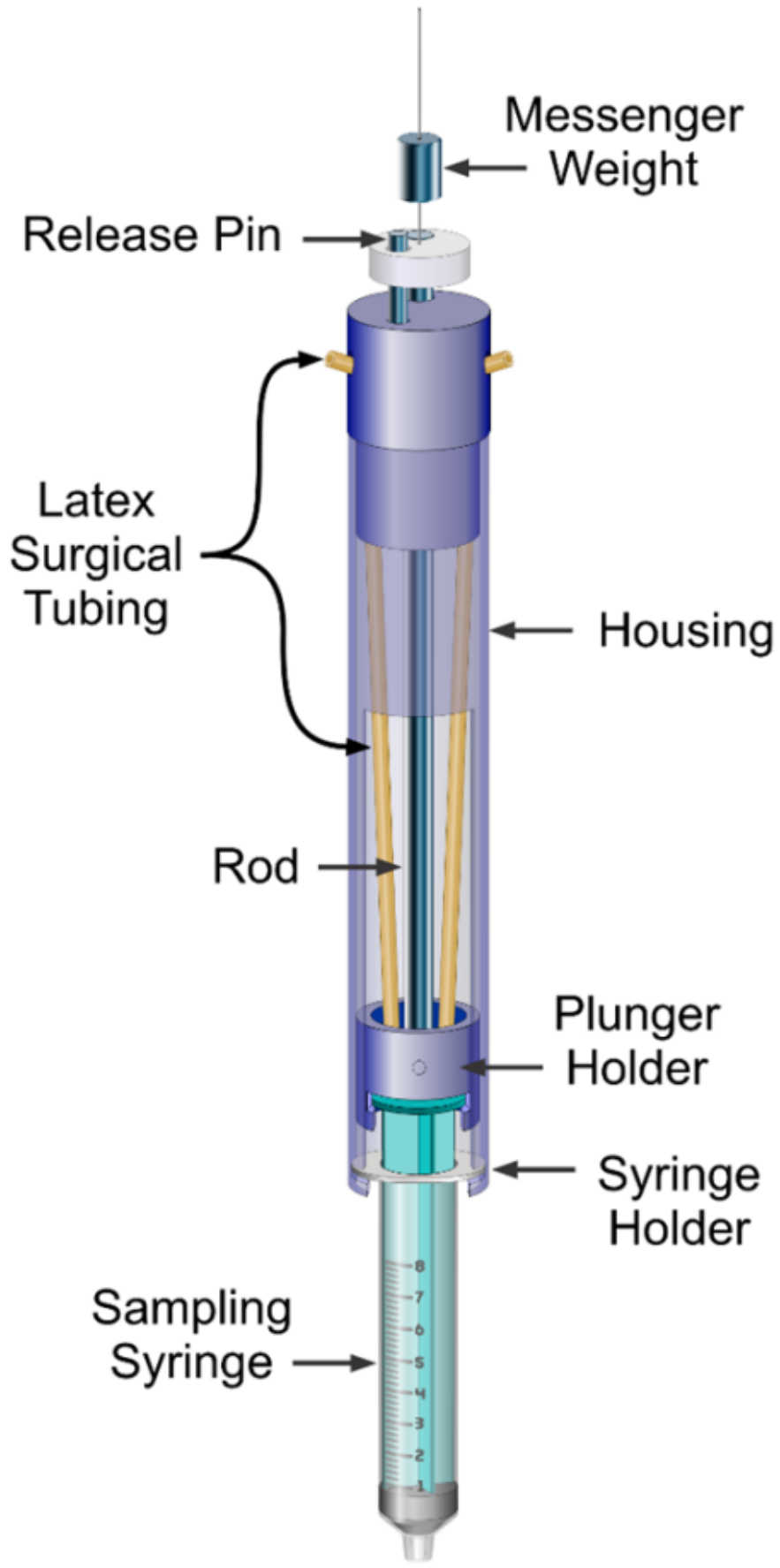


Figure 6-1. Syringe sampler.

Source: NJDEP, used with permission.

### 6.1.2 Installation and Use

The selected syringe is attached to the sampler housing and lowered to the prescribed sampling depth. When the sampler has reached depth, the release pin is tripped, allowing the plunger to be pulled up. This suction allows the sampling medium to be drawn into the syringe. Once the desired volume is achieved, the sampler is removed, and the sample is transferred into the appropriate bottles. The entire apparatus can be decontaminated and reused to sample. Different attachments facilitate the use of syringe samplers, such as Rhizon samplers, which can be used to collect water or undisturbed soil at discrete depths ( "Rhizons," n.d.<sup>[LH9E3MW]</sup> "Rhizons." n.d. Rhizosphere Research Products (blog). Accessed April 29, 2024. <https://www.rhizosphere.com/rhizons/>).

### 6.1.3 Advantages

- Syringe samplers can sample at discrete depths.
- The interior of the sampler is not exposed to the water column.
- Syringe samplers can be used as a collection device for field screening techniques.
- Syringe samplers allow collection of NAPL in monitoring wells for fingerprinting without pumping.

### 6.1.4 Limitations

- Users may have difficulty in collecting quality assurance samples with syringe samplers.
- Use of this device might require regulatory guidance.

## 6.2 Deep Discrete Interval Sampler

### 6.2.1 Description and Application

The Model 425 Discrete Interval Sampler (DIS) (Figure 6-2) was developed by Solinst Canada, Ltd., in 1994. It is designed to acquire representative groundwater samples from a specific sampling zone without the need for purging. A DIS is a no-purge sampler that samples all chemicals including, for example, VOCs and metals, as well as field parameters, and can be used in open bodies of water. The DIS is excellent at gathering samples of product layers in or on top of water (LNAPL or DNAPL). A DIS recovers a discrete sample from a well zone where the sampler is activated, with limited drawdown and negligible agitation of the water column. The DIS is a stainless steel sampler that is pressure sealed. It is activated by a high-pressure hand pump that pressurizes the sample chamber to the pressure of the water column at the intended sample interval, which prevents water from entering the sampler until activated. Ultimately, this prevents loss of VOCs during retrieval of the sampler and avoids contamination from other layers during deployment and retrieval.

The DIS system consists of a stainless steel sampler with PTFE and polypropylene check balls, LDPE (or PTFE or PTFE-lined polyethylene) tubing, a tubing reel, high-pressure hand pump, and a sample release device. The sampler is connected to LDPE airline tubing, which is mounted on a reel, and has an attachment for a high-pressure hand pump and a pressure/vent switch that is used to apply and release pressure on the sampler. Three sampler diameters are available: 1 inch, 1.66 inch and 2 inch, in 2-foot or 4-foot lengths. The sampler can be operated by one person but can be difficult to operate if the well is more than 100 feet.

# Deep Discrete Interval Sampler

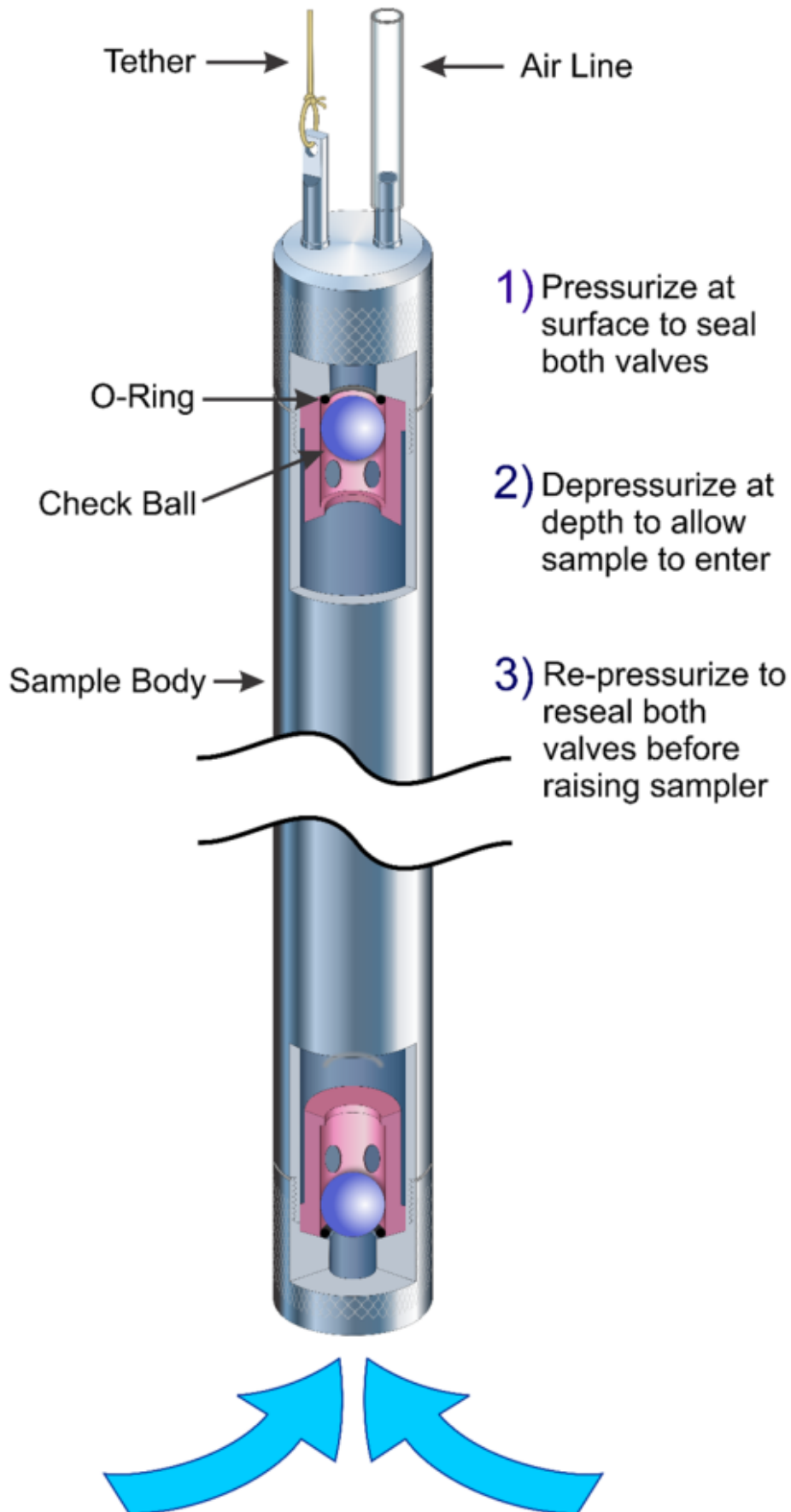


Figure 6-2. Deep discrete interval sampler.

Source: NJDEP, used with permission.

### 6.2.2 Installation and Use

The DIS is pressurized before being lowered to obtain a sample, to prevent water from entering the sampler. At the target depth, the pressure is released. Hydrostatic pressure then fills the sampler with water directly from the sampling zone. Once the sampler is full, it is repressurized and raised to the surface. During this process, check balls prevent water from entering the tubing. The sample is decanted using the sample release device, which regulates flow and minimizes degassing of the sample.

Discrete Interval Samplers are suitable for sampling in groundwater or surface water. The DIS can sample all organic and inorganic chemicals of concern if an adequate volume of sample is recovered for analysis, including but not limited to the following: VOCs, semivolatiles, metals, major cations and anions, dissolved trace metals, dissolved sulfide, dissolved gases (methane/ethene/carbon dioxide), field parameters, Hex Cr, oxygenates, MTBE, explosives, and perchlorate.

### 6.2.3 Advantages

- Discrete Interval Samplers are effective for collecting water samples of any type of chemical.
- They allow discrete sampling in wells, boreholes, and open bodies of water.
- They allow the user to collect samples from a narrow depth range with no movement of the sampler position during collection.
- The sample has not been pumped through tubing.
- Discrete Interval Samplers cause minimal water disturbance.
- They are easy to disassemble for decontamination.
- They avoid purging and disposal of purge water.
- There is reduced cost and time to retrieve samples.
- No gas or electricity is required for operation.
- Discrete Interval Samplers are easy to operate and transport.

### 6.2.4 Limitations

- Discrete Interval Samplers are designed to sample in wells larger than 1 inch in diameter, with no upper limit to well diameter that can be sampled. DIS can also be used to sample from open bodies of water.
- Sampling depth may be a limitation. The Model 425 Discrete Interval Sampler can sample to depths of 300 feet (90 m) below water level, regardless of total depth from surface ( "Discrete Interval Samplers: Model 425 & 425-D Data Sheet" 2021<sup>[TK4WUHUP]</sup> "Discrete Interval Samplers: Model 425 & 425-D Data Sheet." 2021. Solinst. <https://solinst.com/products/data/425.pdf>.)
- They collect a limited sample volume.

## 6.3 Horizontal Surface Water Interval Sampler

### 6.3.1 Description and Application

The horizontal surface water interval sampler (also commonly called a Van Dorn bottle) (Figure 6-3) is a surface water no-purge sampling device that was first developed in the 1950s by Dr. William G. Van Dorn of the Scripps Institute of Oceanography. The sampling devices are cylindrical and generally range between 30 and 45 cm in length and about 10–15 cm in diameter. This range of sizes usually equates to sample volumes between 1.5 and 5.0 liters. The sample collection chamber is usually constructed of rigid polyurethane, polycarbonate, acrylic, or durable impact-resistant PVC. The end caps on these sampling devices are generally lined with soft rubber or other materials such as silicone and/or polyethylene around the outer perimeter to provide a good seal.

The sampling devices have a water collection tube, sometimes referred to as a bottle or chamber by different manufacturers, with varying diameter and length with a sealable end cap(s). Manufacturers provide varying sampler sizes, bottle/tube styles, and materials based on the chemical being sampled. The sampler is attached to a calibrated line to ensure the sampler reaches the prescribed depth. The weight of the sampler ensures a rapid descent and helps to minimize

drift due to currents.

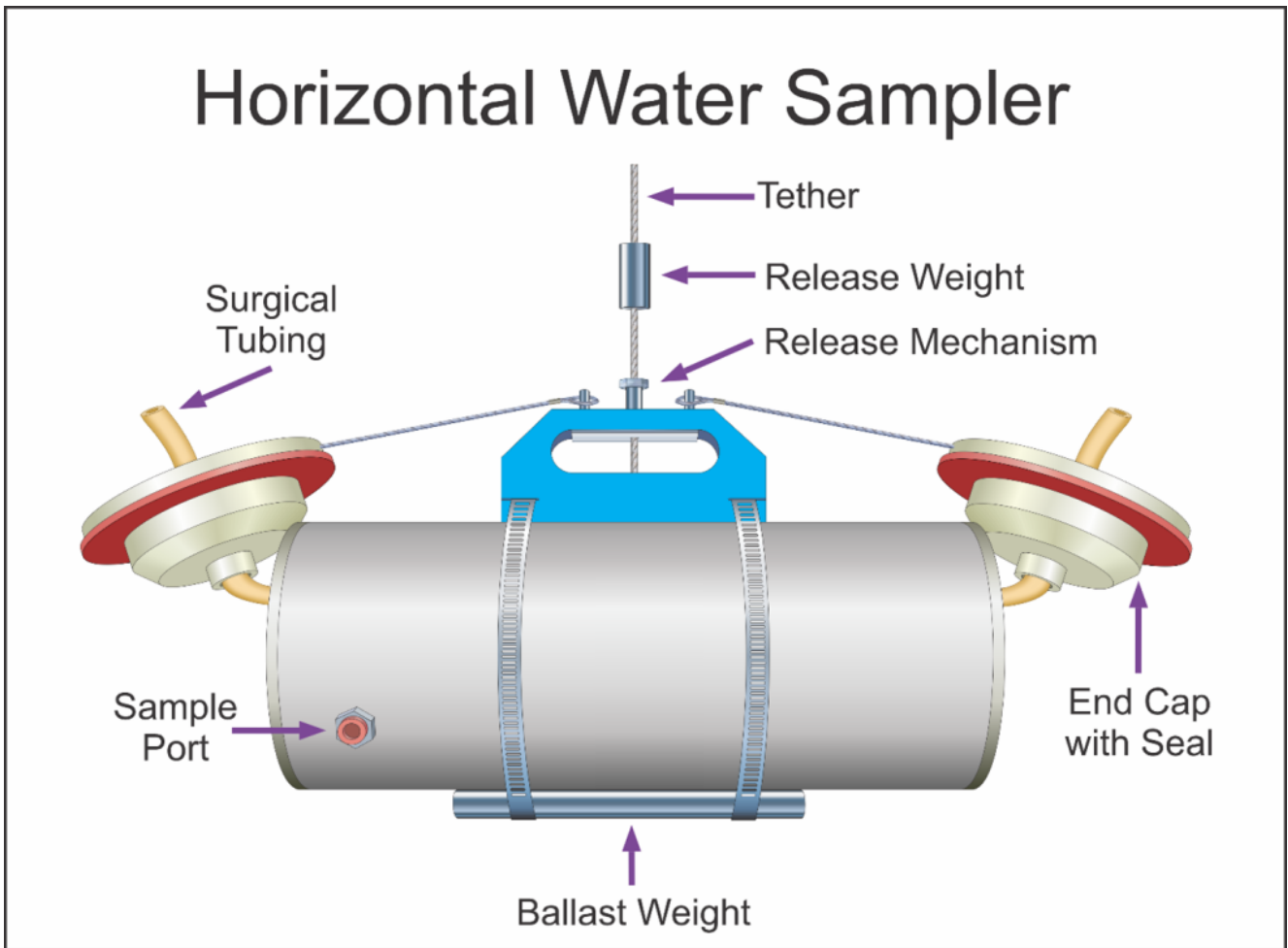


Figure 6-3. Horizontal water sampler.  
Source: NJDEP, used with permission.

### 6.3.2 Installation and Use

Depending on selected sampler materials, horizontal surface water interval samplers may be suitable for sampling metals, other inorganics, organics, other water quality parameters, and biological parameters such as plankton. The water collected by the sampling device will be transferred to laboratory containers. Care should be taken to eliminate bubbles that may form and could get trapped in the VOC vials. Because the sampling devices can be made of varying materials, the materials must be considered based upon the chemicals of interest and the project DQOs. These sampling devices are marketed as either sampling bottles or sampling kits and typically include a tether line that is between 15 and 30 m in length. The tether line provided with these surface water sampling kits often comes with a handle that can be used for retrieving the sample, or otherwise winding up the cord to store it.

To deploy the sampling device, the sampler is attached to the tether line, which may be calibrated with depth markers, to ensure the sampler reaches a specific interval depth. These devices may or may not have a ballast weight to help the sampler sink when deployed. Generally, these sampling devices weigh about two pounds, which is enough weight to ensure a rapid descent and help minimize drift due to currents. When full, the larger styles of devices may be heavy, and use of a winch may be desired for retrieval.

### 6.3.3 Advantages

- After decontamination, horizontal surface water interval samplers can be redeployed multiple times.
- They can collect a grab sample from a relatively thin (10-15 cm) water column, which may be desirable for stratified surface water bodies.

#### **6.3.4 Limitations**

- They can be used only in surface water.
- They can only collect a grab sample.