PASSIVE SAMPLING TECHNOLOGY UPDATE TEAM

Instructions for ITRC Passive Sampling Technology Update Guidance Document External Review

(Comments Due on or Before: Tuesday, April 2, 2024)

The ITRC Passive Sampling Technology Update team has prepared an update to existing ITRC Passive Sampling Guidance Documents and added to with current and relevant information on Passive Sampling Technologies. Within this work product, are 24 Passive Sampling technologies as well as media, data, and regulatory considerations. The team has also developed several case studies for each technology, included in the external review zip file.

Review/Comment Request: Please focus your comments on the content, thoroughness, and usefulness of the documents. While it is helpful to identify and comment on sections of text that are redundant, confusing, unclear, or unnecessary, it is not necessary to identify and provide comments on typographical errors and general grammar unless those errors have an impact on content understanding; ITRC will use a professional technical editor to review and revise this document for spelling, grammar, and consistency in format

Logistics:

- **Download the Comment Spreadsheet from ITRC Connect here.**
- Contact the Program Advisor (Devin Seckar; Dseckar@ecos.org) with questions, comments, or concerns on accessing or commenting on this document.
- Submit comments using the following link (or the similar link embedded in the Comment Spreadsheet): Distribution List for Comments on the ITRC Passive Sampling Technology Update Work Products

Thank you again for your time and participation in External Review!

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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 sunsetted in 2007. In the ensuing years, emerging concerns about high-profile contaminants, interest in reducing purge water volume, sampling cost reduction (and re-allocation to remediation), 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 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, porewater, sediment, soil gas, indoor air, outdoor air, soil, and non-aqueous 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 have been included to demonstrate the use and effectiveness in real-world conditions, and guidance is included to help transition sites to passive sampling, appropriately, bring confidence to the science and enable more sustainable management and monitoring of 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.

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 the sampling device being exposed to media in ambient equilibrium during the sampler deployment period. The passive samplers in this document are classified into three technology types based on the sampler mechanism and nature of the collected sample. The three technology types discussed are 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.
- **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. 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. 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). 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). 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 also discusses the following three Non-Passive Sampling Technologies that are summarized below and further discussed in Section 6. These non-passive 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 within this document, active sampling methods rely on the mechanical action of 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; utilizing a pump, vacuum, or physical removal method introduces variables (i.e., 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 a number of 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 benefit of increased site accessibility.

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 QA/QC procedures should be followed for all sampling methods.

2. PASSIVE SAMPLING USE 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 within this document are groundwater, surface water, porewater, sediment, soil gas, indoor/outdoor air, soil, and NAPL.

2.1 Terminology

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

- **Groundwater** is described as water that can be found in the subsurface in the annular spaces between soil, sand, and rock and is accessed by monitoring wells. While groundwater does exhibit a flow direction, its velocities are typically much slower than surface water.
- **Surface water** is described as permanent or reoccurring water open to the atmosphere under either high-flow (rivers or streams) or low-flow (ponds, oceans, 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. While the majority of surface water flows towards oceans, it may also undergo infiltration into groundwater aquifers where the ground surface is higher than the prevailing water table.
- **Porewater** in this document refers to sediment porewater rather than soil porewater. In the context of this document, porewater 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 described as 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 described as a medium consisting of primarily solid minerals and/or organic particles that are deposited as a result of 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 described as gaseous elements and chemicals that are located 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 described as 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 exterior of the buildings and structures or from within structures that cannot be sealed from external sources.
- **NAPL** is the acronym for Non-Aqueous Phase Liquid and refers to typically organic liquids that are immiscible or not soluble in water. There are two types of NAPL: Light Non-aqueous Phase Liquids (LNAPL), which are less dense than water, and Dense Non-aqueous 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 have to 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 (i.e., 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 it may be subject to leakage from surface runoff ***(USEPA Ground Water Issue, EPA/540/S-96/5045, Puls, Robert W., and Barcelona, Michael J., April 1996)***. 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, 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 always represents a flow-weighted average across the length of the saturated open interval (Imbrigiotta and Harte 2020, 202). While 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 if 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, the ITRC suggests 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 what depth to deploy passive samplers during sampling events. Passive and active samples from wells with shorter screen intervals (e.g., 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 acquire a representative sample, maintain personnel safety, and minimize the generation of waste for disposal. While 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, such as snow, ice, swampy, and tidal conditions, 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 since 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, like pumping, add another variable to where the sample originates since they induce flow toward the well.

Well Construction: Will the type of sampling equipment fit within the constraints of the well casing diameter, the depth from which the sample must be recovered, and required sample volume? There are not many options for pumps that will fit wells smaller than 2-inches in diameter, while there are a number of 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 while most passive sampling methods simply require a longer suspension tether and reel to hold the tether. Since passive samplers are limited to the volume of water in the well and should only 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. Laboratories should be contacted as part of sampling design to determine the minimum sample volume that meets data quality objectives (DQOs) so that passive samplers may be used, and the benefits may be realized.

Investigative Derived Waste (IDW) Disposal: Local regulations and site capabilities dictate how purge water from active sampling methods is disposed. If the wastewater is regulated, as in the case of per- and polyfluorinated substances (PFAS), then the local conditions favor using passive methods, which produce little or no contaminated purge water.

2.2.2 Surface Water Considerations

Careful judgement 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 (i.e., 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, sink hole- 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 which has to be safeguarded to maintain liner integrity, and the surface of the wastewater is over 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.

Other limitations of sampling approaches may be appropriate when sampling slow moving water, fast moving water, or stagnant water. The sampling strategy must be carefully orchestrated to collect samples that are representative of conditions that address the sampling 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 utilizing 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 data quality objectives. 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.

The three non-passive syringes and discrete/interval devices identified in Section 6.1 of this document may be utilized if discrete depth interval sample collection is a priority for a particular project to satisfy certain data objectives. While not considered truly passive, these devices collect water samples without allowing the sample to contact air and without any sort of purging process. Workplan development should consider limitations on volume requirements. HydraSleeve and Snap Samplers can be utilized to obtain representative samples from specific depth intervals in either very low velocity flowing or in standing water conditions. Additionally, 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

On-site collection of sediment porewater 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 surface water section 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 additional concerns for logistics as well as health and safety that are not discussed herein. 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 retrieval of samplers, additional concerns may need to be addressed. Samplers may be affected by boat traffic or human disturbance in the time between access events. It is recommended that if there is a need to revisit a sampling location, careful consideration 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 of the sampler with contact information.

Porewater 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. A primary consideration during porewater 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 over time, 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 as much as possible. Quality assurance/quality control samples and background samples are another component of an investigation that should be considered. Identifying locations for background and duplicate samples is a critical part of determining the performance and validity of samplers during investigation or remedial monitoring.

Porewater 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.

Ex-Situ vs In-Situ Porewater Sampling

Freely dissolved concentrations (C_{free}) of hydrophobic organic compounds (HOCs) in porewater 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) (USEPA, 2012). 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 porewater. Most of the passive samplers discussed in this document are deployed in environmental media in the field, which is called *in-situ* deployment. For porewater sampling, in-situ deployment is preferred when it is critical to understand 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). However, achieving equilibrium by the in-situ approach is often difficult for HOCs since the uptake kinetics of strongly hydrophobic organic compounds to polymeric sampling devices are particularly slow.

Polymeric sampling devices can also be deployed under controlled laboratory settings to determine C_{free} of HOCs, which is called *ex-situ* deployment. In the ex-situ deployment approach, 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 porewater. Ex-situ sampling with well-mixed sediment slurry samples can achieve equilibrium more quickly as compared to in-situ sampling, and it has been accepted for partitioning investigations, treatability testing, and sediment toxicity assessment (Ghosh et al., 2014). Porewater concentrations of HOCs based on in-situ and ex-situ sampling generally agreed within a factor of two to three (Apell and Gschwend, 2016; Reininghaus et al., 2020). 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; Burgess et al., 2017; Michalsen et al., 2020; Jonker et al., 2022).

Passive samplers described in this document for sediment porewater 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 porewater 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 logistical 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 as well as a field sampling plan should be prepared to address these considerations.

Sediment is often heterogenous, 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 porewater. 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, within Section 5.3.10.

2.2.5 Soil Gas Considerations

In assessing vapor intrusion at a site, it is common to complete subsurface soil gas investigations. Whether using passive sampling devices or collecting subsurface vapor in cannisters, 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 these investigations are also important considerations for soil gas. Active methods can require well construction to be at least five feet below ground surface (bgs) to ensure enough packing material can be installed and that ambient air is not sampled through short circuiting. The active methods 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. Passive soil vapor sampling has the potential to complete the lateral delineation of a contaminant plume at a reduced cost and in less time. However, one 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 cannister samples. Analytical results obtained from passive samplers require known sampling rates to back calculate soil vapor concentrations. Careful consideration is needed to determine if the passive sampler has known uptake rates for given COCs at a site. Additionally, environmental factors such as temperature, humidity, wind speed, and barometric pressure, can influence sampling rates. These environmental factors can positively or negatively affect sampling rates and thus impact accuracy. It may be necessary to measure these environmental factors in the field to determine if observed site conditions are comparable to laboratory conditions used to develop sampling rates.

Compared to cannisters, 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

The same passive samplers can be used for soil gas and indoor air investigations, sampler-specific considerations (e.g., chemical selection, cost savings, etc.,) identified in *Soil Gas Considerations* also apply to indoor air. Indoor air sampling does, however, pose some unique challenges, including variability of contaminant concentrations, flow and ventilation within a structure, background sources, and the added complication of human tampering.

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*, 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 (i.e., 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. This can help identify indoor sources prior to sampling.

Passive sampling devices are discrete and inconspicuous compared to cannisters, 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. The added benefit of the passive sampling devices going unnoticed is that occupants are less likely to tamper with the devices; however, the samplers are cheaper than cannisters 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 for entering a structure (i.e., residential, commercial, and/or industrial building), drilling into the subsurface, nor installing a conduit-like structure, like a soil vapor probe or a groundwater monitoring well. In many cases, whether utilizing active or passive sampling methods, all that is required is a sample collection device (i.e., a passivated canister and flow controller for active or a sorbent tube for passive). 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 settings for where and when to collect. The three most common are wind direction, season, and weather. One must 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 in order 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 (i.e., rain or snow), while conditions like barometric pressure may also have an effect on analytical results.

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, so as 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, one 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 they have the appropriate PPE. Many outdoor air samples are also collected on the roofs of buildings, for which, the field personnel should consider any additional PPE that may be needed. Additionally, whether using an active or passive sampler, field personnel must make sure to consider public perception and ease any safety concerns. These sampling devices are not common in the everyday lives of most people and may more easily lead to fear and/or curiosity.

Another set of considerations one 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 (i.e., a photoionization detector or multi-gas meter). When monitoring outdoor air for dust, field meters are typically the primary sampling method. One must ensure that they have the proper monitoring device(s) for the task at hand and that said devices are properly calibrated and charged. Additionally, one may have to consider security equipment to prevent tampering. These may include a chain and lock, a protective container, and simply caution tape. And 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 samples 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.

Passive sampling devices are discrete and inconspicuous compared to cannisters, which can reduce risk perception and tampering from the public. Small devices may go unnoticed by the public and therefore not cause distractions or elevated risk concerns. The added benefit of the passive sampling devices going unnoticed is tampering is less likely to occur; however, the samplers are cheaper than cannisters 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 samples collected at depth (> 2 feet below grade). Surface soil samples are generally quick to prepare for the sample collection, not as destructive to the site, and less costly. The process of collecting the at-depth soil sample can be very expensive (equipment) and time consuming to prepare for the collection. When planning a soil sampling event considerations such as soil lithology, weather, site constraints, and equipment needed must also be accounted for.

Soil can be grouped into four main categories: coarse-grained soils (sands and gravels), fine grained soils (silts and clays), organic soils, and peat. 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 hard to maneuver. Traditional soil sampling at depth would require large equipment like a drill rig. This can make the sampling of certain locations difficult because of the space needed to operate the equipment.

2.2.9 NAPL Considerations

Although passive samplers can be used for NAPL collection, they do not provide a general advantage over non-passive 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, an undisturbed section of the soil column would be important to retrieve to complete characterization of the NAPL mobility or transmissivity within the unconsolidated material. While standard soil-collection methods can produce NAPL samples, the collection of soil that has not been disturbed by mechanical forces is important 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 is present in association with groundwater or surface water, caution should be taken in the use of passive samplers, as is the case with non-passive samplers, due to potential interference/contamination of the sampler or media being tested. Non-passive methods used in the collection of a NAPL sample from a monitoring well or surface water are discussed in **Section 6**.

The table below includes a comprehensive list of passive sampling devices, the type of sampling technology and the applicable media.

695 *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
HydraSleeve	Grab	●	●							
Snap Sampler	Grab	●	◗							
Thin-Walled Soil Samplers	Grab								●	◗
Passive Diffusion Bag (PDB)	Equilibration	●	●	●						
Dual Membrane Passive Diffusion Bag Sampler (DMPDB)	Equilibration	●	●	●						
Nylon Screen Passive Diffusion Sampler (NSPDS)	Equilibration	●	●	●						
Peeper Sampler	Equilibration	●	●	●						
Regenerated Cellulose Dialysis Membrane Sampler (RCDM)	Equilibration	●	●	●						
Rigid Porous Polyethylene Sampler (RPPS)	Equilibration	●	◗	◗						
Ceramic Filter	Equilibration	●	●	●						
Polymeric Sampling Devices	Equilibration	●	●	●		●	●	●		
PISCES Sampler	Accumulation		●							
AGI Universal Sampler	Accumulation	●	●	●		●	●	●		
Polar Organic Chemical Integrated Sampler (POCIS)	Accumulation	●	●	●						
Sentinel	Accumulation	●	●	●						
Semipermeable Membrane Devices (SPMD)	Accumulation	●	●	●		●	●	●		
DGT Sampler	Accumulation	●	●	●						
Min Traps	Accumulation	●								
Radiello Sampler	Accumulation	●	◗			◗	●	●		
Waterloo Membrane Sampler	Accumulation					●	●	●		
Beacon Sampler	Accumulation					●	●	●		
Dart Sampler	Accumulation				●				●	●
Fossil Fuel Traps	Accumulation					●				●
Bio-Trap Sampler	Accumulation	●	◗							

Table Key:

● = Primary application of technology

◖ =Secondary application of technology

*Note These sampling devices are not passive sampling devices because they cause flow toward the sampling device when activated. They are included for discussion because they recover a fixed-volume sample, which, depending on the medium and the sample volume, may meet certain project sampling objectives.

2.2.10 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, PTFE containing materials should not be used when sampling for PFAS. In situations where certain chemicals may adsorb to the sampler material 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 is accepted in decision-making in the U.S. EPA's Superfund Program at contaminated sediment sites. Specifically, passive sampling has been used in several phases of the remediation process at over 20 sediment sites around the United States. In contrast, passive sampling of ground water 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 or misconceptions about the technologies, their use, or the state of the science can lead to a reluctance by regulators and other stakeholders 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 for use 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. As part of preparing this updated guidance, ITRC surveyed state regulators with respect to current regulatory language surrounding passive sampling technology use and deployment.

Using passive sampling methods can benefit both the regulated community and regulators as well. Passive sampling technology is often 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, since 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 and whether passive sampling technologies are employed in their states. The results of that survey are summarized below.

Figure 3- 1: Passive Sampling Regulatory Acceptance State Map

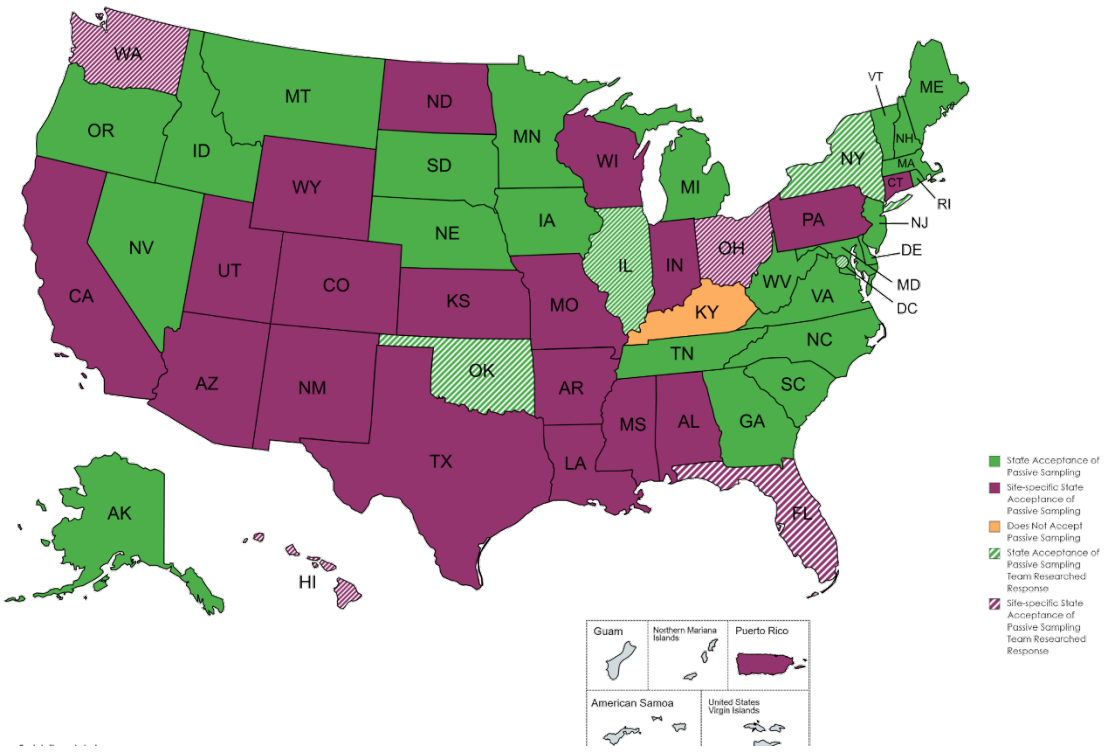


Figure 3-1 Key:


= State Acceptance of Passive Sampling


= Site-Specific State Acceptance of Passive Sampling

= Does Not Accept Passive Sampling


= No Response from State


= Site-specific State Acceptance of Passive Sampling Team Researched Response

Some of the common concerns among regulators are discussed in the subsections below. To support state regulators in the decision-making process surrounding passive sampling technology, Appendix TBD provides answers to a list of frequently asked questions and indicates where additional detail can be found in this document.

3.1 Site Specific Regulatory Program Concerns

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 and/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.

Some of the common concerns within the regulatory community are discussed below.

- 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, for example, whether natural groundwater flow through a well carries chemicals.
- through the well at the same concentrations found in the larger aquifer.
- Whether the mechanism of the sampler, for example diffusion through a membrane or grabbing from a column, acquires a representative sample of the specific chemicals.
- Less frequently, questions arise about whether external factors, such as biofouling, scaling, or sediment load, will affect sample validity.
- When a transition from active methods to passive sampling is proposed for a site, there can be questions about 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, or 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 use of passive sampling methods when used appropriately.

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. Rigorous testing of these technologies has taken place before they become commercially available and, in many cases, examples of their use and data available from the application of passive technologies is readily available.

While 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 (e.g., 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 multi-media 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 vary 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 varies by state. 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 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 needs be able to demonstrate that the use of passive sampling technologies meets the states' performance standards during remedial activities. See Section 4 for comparison methods that can be helpful when 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 the level of precision and accuracy commensurate with the intended use and meets 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, your state should be consulted if preapproval is required.

3.6 Prior Regulatory Approval

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 non-use) 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 your project is located in, 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 is 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 4.0**) 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 whether the results acquired using the new method will be substantially the same as those acquired by the previously used and accepted method and whether the regulators will accept results acquired by the passive sampling method. Different 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 the 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 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 low 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 your sample results. A project-specific plan should consider site-specific field data and 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. Factors that should be considered include:

- 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/anerobic 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.

1. 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 is long-term, consistent, and stable data available.
2. 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. While 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.
3. Side-by-side Comparison: The proposed (passive) and the current (active) methods are performed 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 for groundwater monitoring are usually employed at a representative set of wells, rather than all the wells.

   When conducting side-by-side 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 site objectives are required, the differences in results can usually be explained by further study of the local hydrogeologic and geochemical conditions.

4.3 Statistical Comparisons

What statistical methods will be employed to compare each data pair?

The USGS provides guidance 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, T.E., and Harte, P.T., 2020):

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

RPD is a common statistical tool used to compare two data points in side-by-side sampling evaluations. 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 ug/L to 5 ug/L is only a difference of 3 ug/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, other statistical methods or techniques may be appropriate.

The 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, T.E., and Harte, P.T., 2020). Additionally, "if the two sampling methods collect the same concentrations, the points will plot on or close to the 1:1 correspondence line" (Imbrigiotta, T.E., and Harte, P.T., 2020). Outliers may represent well-specific anomalies such as turbidity.

4.4 Other Comparison Considerations

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

1. Do the data appear to follow the trend from the past several active sampling events?
2. Are there any field notes, such as "high turbidity" or "well pumped dry" that might point to localized well influences?
3. Do the passive sampling results lead to the same site decisions as the historical data?
4. 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 are additional considerations or analysis needed.
5. For example, 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?
6. Were equivalent QA/QC methods employed for all methods being compared?
7. If comparison of results is favorable, what other practical considerations for the different methods might be relevant to evaluate for your site (i.e., safety, cost/efficiency, equipment and staffing needs, sustainability, IDW management)?

5. PASSIVE SAMPLING TECHNOLOGIES

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

- Grab sampler: Devices that recover a grab well water sample.
- Equilibrium sampler: Devices that rely on diffusion of the analytes for the sampler to reach and maintain equilibrium with the sampled medium.
- Accumulation sampler: Devices that rely 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.

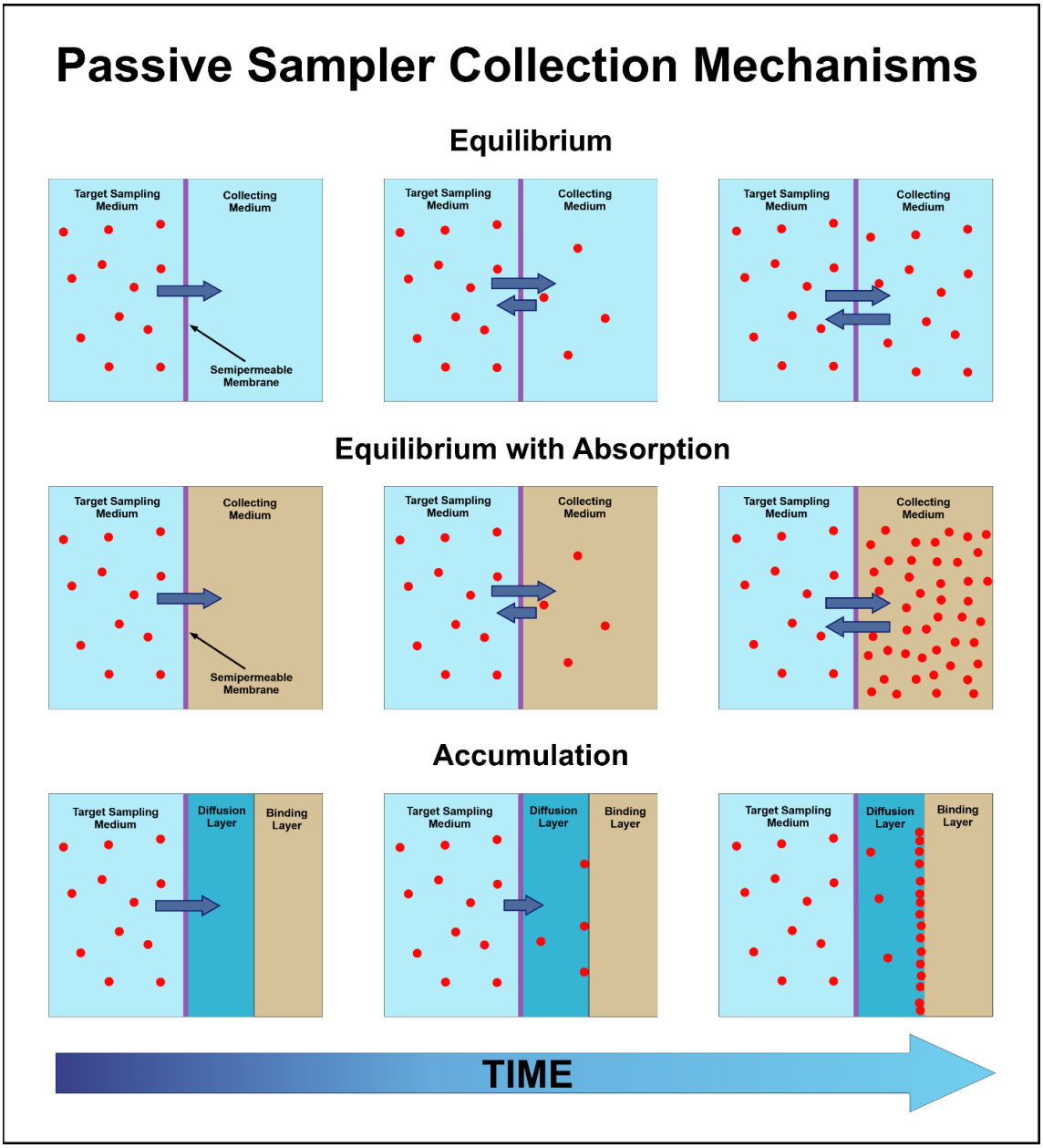
In this new guidance document, the three different classification names adopted in the previous ITRC documents are maintained for consistency and simplicity, but their definitions have been slightly modified to be accurate in terms of sampler mechanisms and consistent with other references.

EQUILIBRIUM SAMPLERS

Equilibrium samplers such as the Passive Diffusion Bag (PDBs), Nylon Screen Passive Diffusion Sampler (NSPDS), Rigid Porous Polyethylene Sampler (RPPS), Regenerated Cellulose Dialysis Membrane Sampler (RCDM), Dual Membrane PDBs (DMPDBs), Regenerated Cellulose Dual Membrane PDBs (RC-DMPDBs), and Peepers rely on diffusion of chemicals from the surrounding water, through a semipermeable membrane(s), into a collecting medium inside the samplers. In these samplers the collecting medium is deionized water. When a concentration gradient exists between the water inside the membrane and the water outside the membrane, diffusion of chemicals through the membrane eventually results in concentration 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 selection of membrane type and pore size determines which chemicals can be successfully sampled. The standard PDB, for example uses a single LDPE membrane and can only sample for non-polar VOCs.

The equilibrium samplers used to measure inorganic chemicals, metals, and polar organic compounds in water (e.g., NSPDs, RPPs, RCDMs, DMPDBs, RC-DMPDBs, Peepers) utilize semipermeable membranes with larger pores or different membrane characteristics than the LDPE-based PDB. These membranes allow inorganic chemicals, metals, and polar organic compounds to pass through and diffuse into the water inside the samplers, shown in the top row, *Equilibrium*, (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.

Figure 5- 1: figure used with permission



The deployment periods (residence time) necessary for equilibrium samplers to reach concentration equilibrium varies by chemical and by sampled medium. In groundwater monitoring wells, allowance is made for the time it takes for the groundwater flow to return to its natural flow and refresh the well and for the time it takes for concentration equilibrium to be reached. A conservative minimum residence time of 14 days is often recommended for these samplers to reach concentration equilibrium in groundwater. Once one of these equilibrium samplers reaches concentration equilibrium, it will reflect the chemical concentrations of the sampled medium during the previous 1 to 5 days of residence time.

Because equilibrium samplers maintain dynamic equilibration, i.e., 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). 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). For example, when the concentration of a PRC in a NSPD sampler is decreased from 100 mg/L to 50 mg/L during deployment, one 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.

Equation 1

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

where:
f_e = fraction of equilibrium (-)
C_t = concentration of PRC in passive sampler at time t
C_0 = initial concentration of PRC in passive sampler

The mechanisms of the equilibrium samplers discussed above are relatively simple and intuitively understandable. 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 than the sampled medium. These may be non-aqueous organic solvents, or solid-phase, polymer materials that come to equilibrium with the sampled medium over time. A chemical diffuses 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 than 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

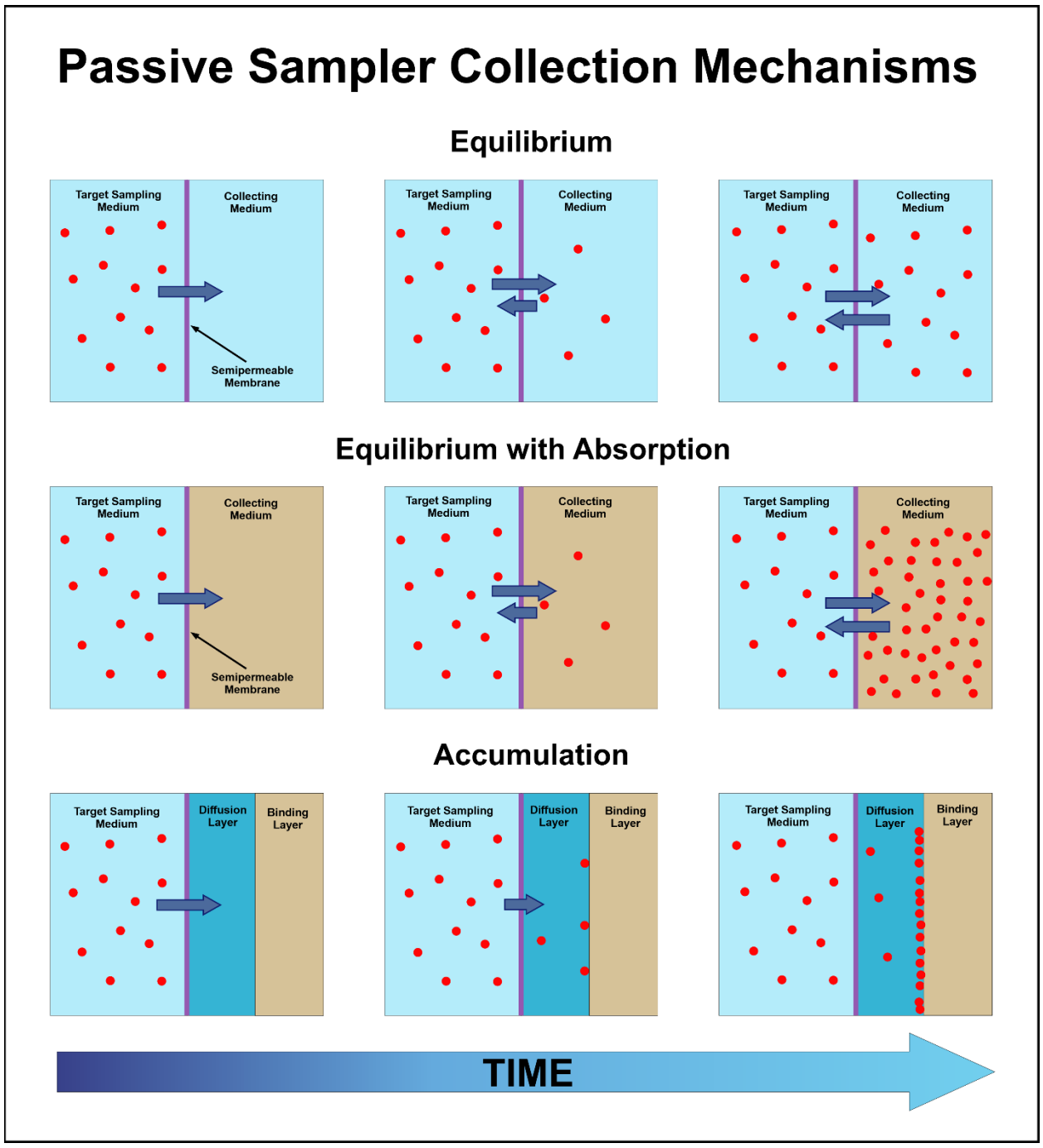
not be 1:1 when the collecting medium is not the same as the sampled medium, though the ratio will remain constant once equilibrium has been reached.

The equilibrium samplers discussed below (i.e., polymeric sampling devices (the LDPE sampler, POM, and PDMS-coated SPME fiber), SPMD, and PISCES) utilize the partitioning and equilibration of chemicals, specifically hydrophobic organic compounds (HOCs) such as PAHs, PCBs, DDX, 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, hydrophobic organic chemicals 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 below (i.e., polymeric sampling devices, SPMD, and PISCES) have also historically been referred to as equilibrium samplers (Mayer et al., 2003; Cornelissen et al., 2008; Grundy et al., 2023). While 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 than the sampled medium have a partitioning ratio that is not 1:1 and the concentration in the sampler has to be calculated by measuring the collected mass and using the uptake rate to calculate the concentration.

The second row, *Equilibrium with Absorption*, in the figure below illustrates the chemical uptake by a passive sampler (Figure 5-1). Generally, equilibrium samplers are deployed into environmental media for a certain period aiming to nearly or fully achieve chemical equilibrium.

Figure 5- 2: used with permission from NJDEP.



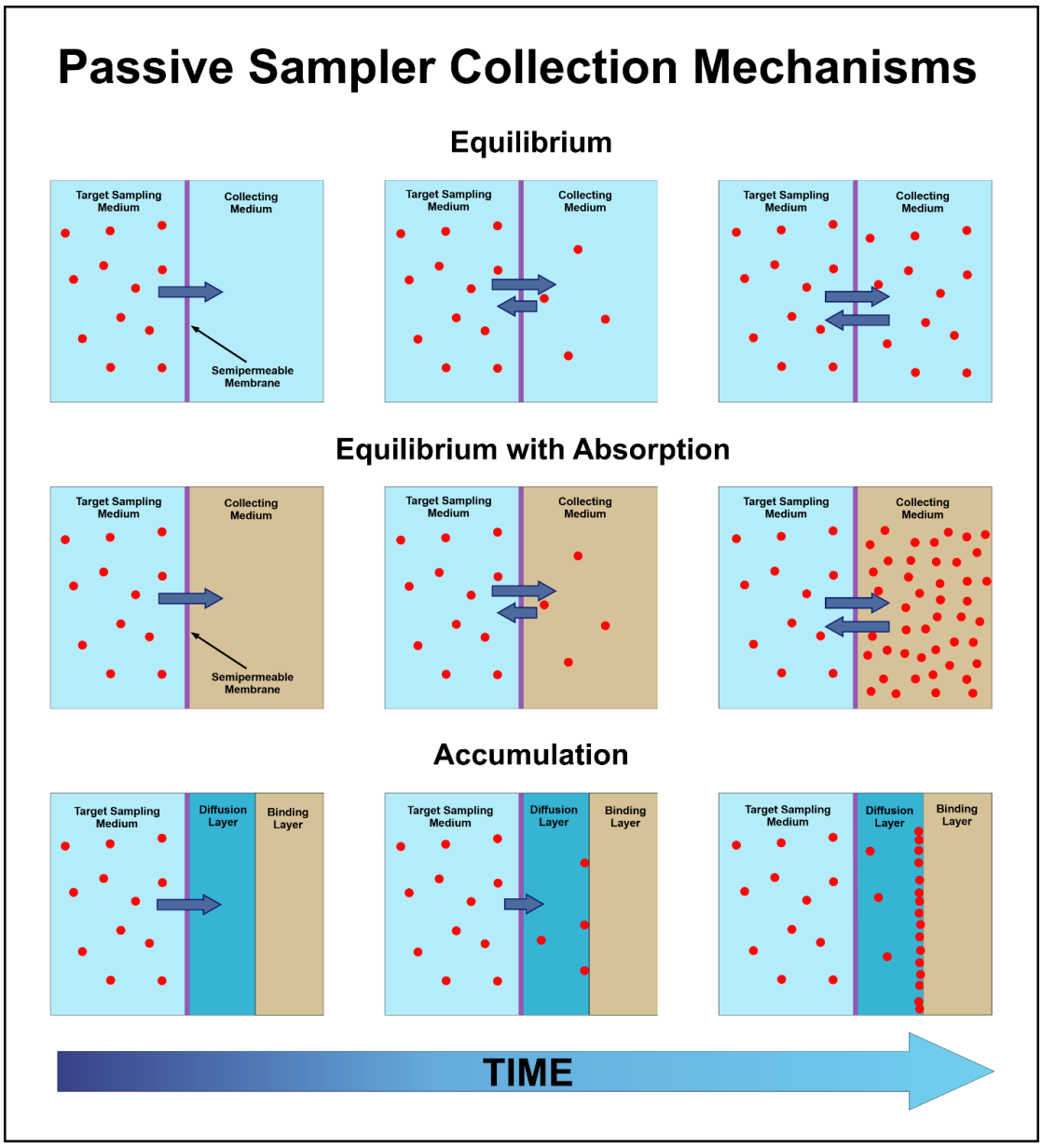
Equilibrium samplers collect samples optimally in the equilibrium sampling media (Figure 5-1). However, some also work in kinetic and transient sampling as long as the fraction of equilibrium is estimated using PRCs. This is often the case for passive sampling of strongly hydrophobic organic compounds (e.g., 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. Polymeric sampling devices are often spiked with isotope-labeled compounds

(e.g., deuterated PAHs and ^{13}C-labeled PCBs) to determine the fraction of equilibrium for hydrophobic organic compounds.

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 and adsorption, precipitation, or other interfacial accumulation of chemicals on collecting media to concentrate chemicals in the samplers over time. Reactions occurring in the collecting media are practically irreversible, in contrast to chemical partitioning in equilibrium samplers in which chemicals reversibly partition between different phases. In accumulation samplers, reactants in the collecting media will be eventually used up by reacting with target chemicals. Target chemicals do not significantly desorb, degrade, or diffuse out from accumulation samplers. Therefore, accumulation samplers are valid only in the kinetic or transient sampling regimes, as shown in the bottom row, *Accumulation*, of Figure 5-1. 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: used with permission from NJDEP.



5.1 Grab Sample Technologies

A passive grab sampler is defined as one that 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. In order 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 non-passive samplers.

Some of the advantages common to all passive grab samplers in groundwater 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.

Table 5 – 1 lists chemical families that can be analyzed using the noted passive sample (USGS, 2020).

1141 *Table 5 - 1 (see separate excel to for a user-friendly view)*

Passive Grab Sampling Technologies	Hydrasleeve	Snap Sampler	Thin-Walled Soil Samplers
Chemical Constituents and Characteristics			
Field physiochemical characteristics (Temp, pH, SC, DO, ORP)	ALL	ALL	N/A
Major cation and anions (Ca, Mg, Na, K, HCO_3, Cl, SO_4, F, Br)	ALL	ALL	ALL
Nutrients (NO_3, NO_2, NH_4, PO_4)	ALL	ALL	ALL
Trace Elements (Metals) (Fe, Mn, Al, Ag, Zn and others)	ALL	ALL	ALL
Perchlorate (ClO_4)	ALL	ALL	ALL
Organic Carbon (dissolved or total)	ALL	ALL	TOC Only
Dissolved Hydrocarbon Gases (Methane, ethane, ethene)	ALL	ALL	N/A
Volatile Organic Compounds (Chlorinated solvents, BTEX)	ALL	ALL	ALL
Semi-volatile Oranics (1,4-Dioxane, BN, Phenols, PAH, PCB, dioxins, furans)	ALL	ALL	ALL
Pesticides, Herbicides, and Fungicides (organoCl, organoPO_4)	ALL	ALL	ALL
Explosive Compounds (RDX, HMX, TNT)	ALL	ALL	ALL
Poly- and perfluoroalkyl substances (PFASs)	ALL	ALL	ALL
Pharmaceuticals (Drugs, fragrances, hormones)	ALL	ALL	NT
Minerals (pyrite, mackinawite)	ALL	ALL	ALL
Microbial Population sampling (e.g. Dehalococcoides)	All	Some*	NT

1142

Table Key	
ALL	All 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

Acronym Key:
[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO3, bicarbonate; Cl, chloride; SO4, sulfate; F, fluoride; Br, bromide; NO3, nitrate, NO2, nitrite; NH4, ammonium; PO4, phosphate; Fe, iron; Mn, manganese; Al, aluminum; Ag, silver; Zn, zinc; BTEX, benzene, toluene, ethylbenzene and xylene; RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane; TNT, trinitrotoluene; organoCl, organo-chlorine; organoP04, organo-phosphate; PAH, polycyclic aromatic hydrocarbons; BN, base-neutral organics; PCB, polychlorinated biphenyls; ClO4, perchlorate; PFOS, perfluorooctane sulfonic acid; PFOA, perfluorooctanoic acid; PFNA, perfluorononanoic acid, NT, not tested]

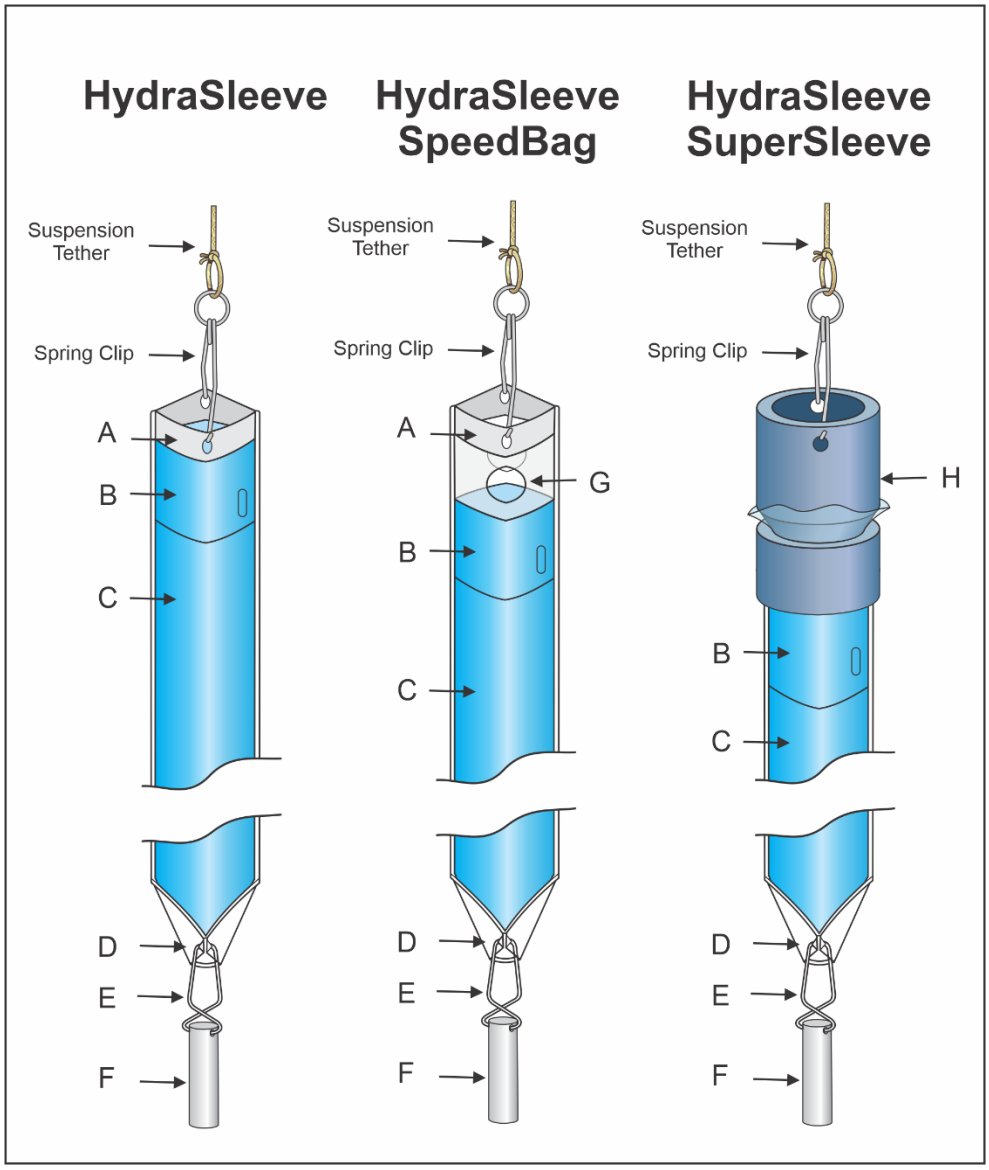
5.1.1 Hydrasleeve™

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 (e.g., VOCs, SVOCs, metals, pesticides, anions, cations, explosive compounds, perchlorate, 1,4- dioxane, PFAS) and physical parameters (e.g., 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 5-2) 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 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.

Figure 5- 4: used with permission from NJDEP.



All HydraSleeve samplers are made from a collapsible, flexible tube of low- or high-density polyethylene (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 into 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 re-usable 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 for 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 therefore a standard 2-inch diameter HydraSleeve with an 8-ounce weight displaces only about 75ml 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.

Standard HydraSleeve and HydraSleeve SuperSleeves have a small cup-shaped space that forms above the check valve, outside the empty sample chamber, when the spring clip is attached. In a 2-inch diameter HydraSleeve this space fills with about 50ml of well water as the sampler is lowered into the water. It is recommended to allow a minimum of 12 hours residence time, before sampling, to allow the water in this space to equilibrate with the well water at the sample interval, under typical well conditions. 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 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. As long as 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 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 to 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 exactly 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 as long as there is a stable surface at the bottom of the water for the bottom weight to rest so the sleeve can be compressed from the top down. Because HydraSleeves are lightweight and only require 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." 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.

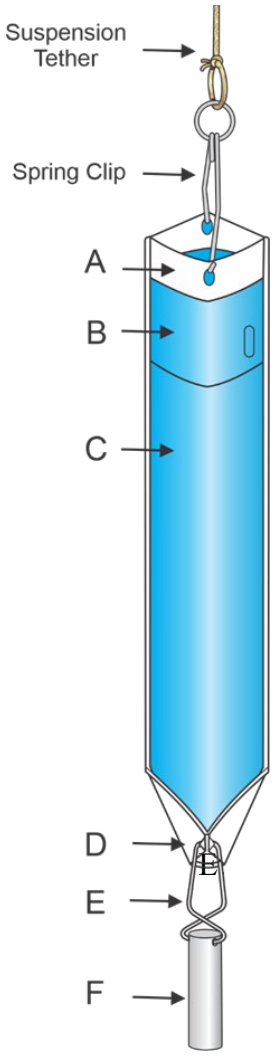
Individual HydraSleeve volume varies by the diameter and length selected to fit the available saturated screen. A single HydraSleeve can acquire greater than 2 liters from a typical 2-inch monitoring well with 10 feet of saturated screen. A single HydraSleeve sized for a 2-inch well with 5 feet of saturated screen can recover over 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

The basic HydraSleeve (Figure 5-3) 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 and then the sample are decanted into sample bottles (not shown).
- An optional Top Collar Weight (not shown in Figure 1) may be connected to the top of the HydraSleeve to compress the sleeve closer to the bottom of the well.

Figure 5- 5: used with permission from NJDEP.



* *SuperSleeves require two-piece Top Collars, instead of the white reinforcing strips, to attach the sleeve to the spring clip.*

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 doesn't 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.

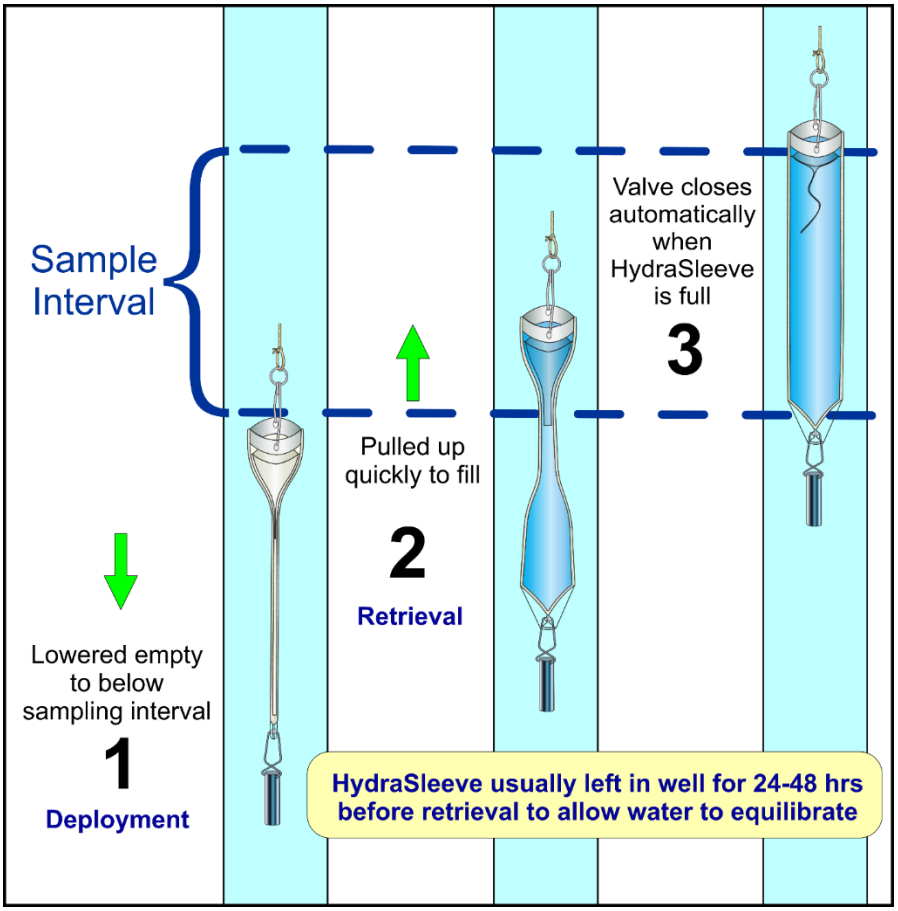
The captured sample represents the interval above the starting position of the top of the HydraSleeve, upward for a distance approximately equal to (or slightly greater than, depending on the specific sampler and retrieval method) the length of the sampler, when properly sized to the well diameter. Upon retrieval, the HydraSleeve is punctured near the bottom with the provided straw and the sample is carefully transferred to the appropriate containers for laboratory for 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 5-4). Residence time is usually 24 – 48 hours but is dependent on groundwater well flow conditions.
2. Left in-place (still empty) until the well restabilizes / equilibrates.
3. Return to the site to sample, 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. Figure used with permission from NJDEP.



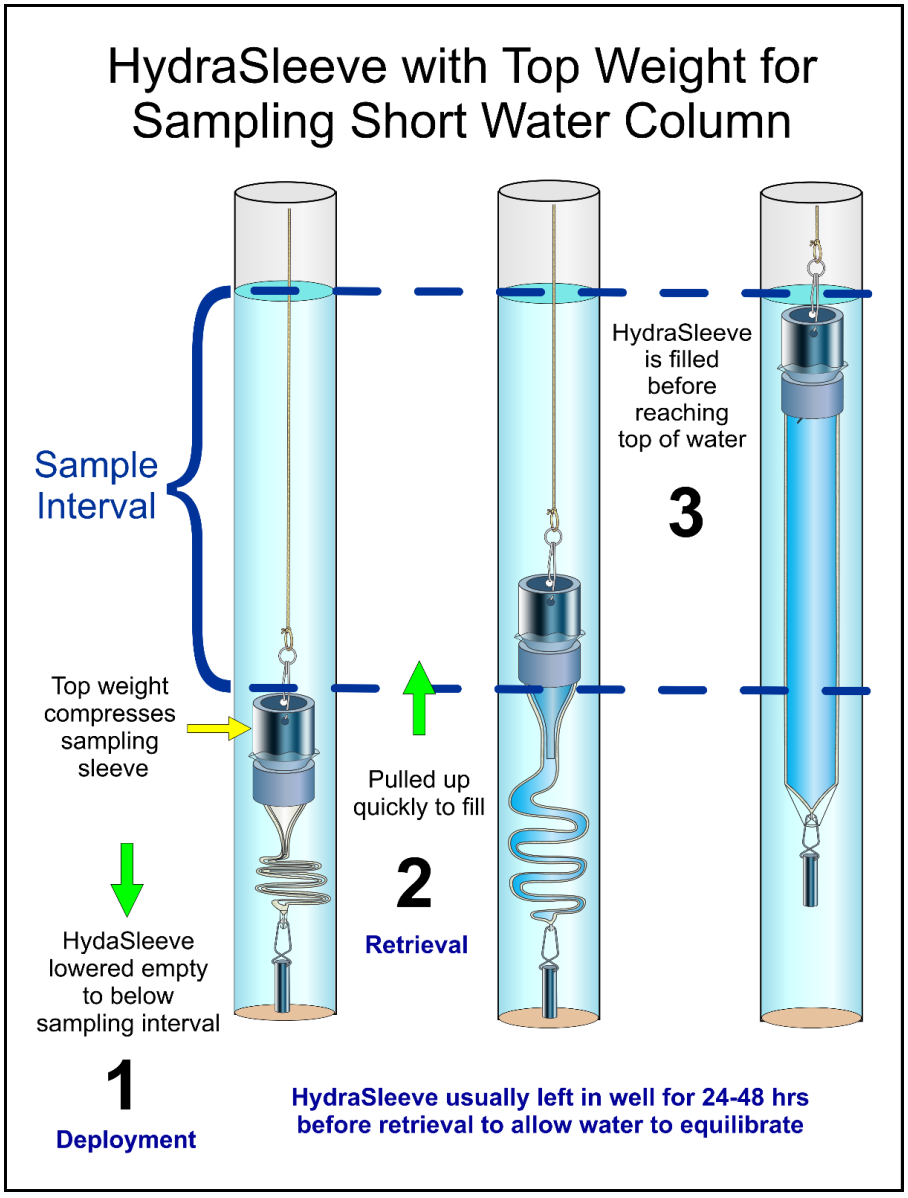
Use

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 1-3).

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 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. This allows for sufficient saturated screen to fill the sleeve before it reaches the top of the saturated interval of the screen (Figure 5-5). 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.*

Figure 5- 7: used with permission from NJDEP.



5.1.1.3 Advantages

These are advantages that apply to the Hydrasleeve:

- Shown to be the lowest cost passive sampling method for groundwater (McClellan AFB 2005).
- Provides the largest sample volume capability of passive samplers for the same saturated screen length.
- Collects a "Whole-Water" sample containing everything in the water within the sample interval, so no limit to CoCs.
- Collects an unfiltered sample (this may be an advantage or limitation depending

on site DQOs. HydraSleeve samples can be filtered after sample recovery if needed).

- Is suitable for sampling wells for assessment, short-term, and long-term groundwater monitoring.
- 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.
- Can be used in narrow, constricted, or damaged wells as small as 1-inch diameter ("OW-63 PFAS Investigation Work Plan" 2022).
- Can be manufactured to custom lengths to fit project-specific screen lengths or sample volumes.
    - HydraSleeve-SuperSleeves have available options for sampling PFAS.
    - 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

The following limitations apply to the Hydrasleeve samplers:

- Collects an unfiltered sample (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 is dependent 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 logistical 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 non-rigid nature of device and spillage.

5.1.2 Snap Sampler

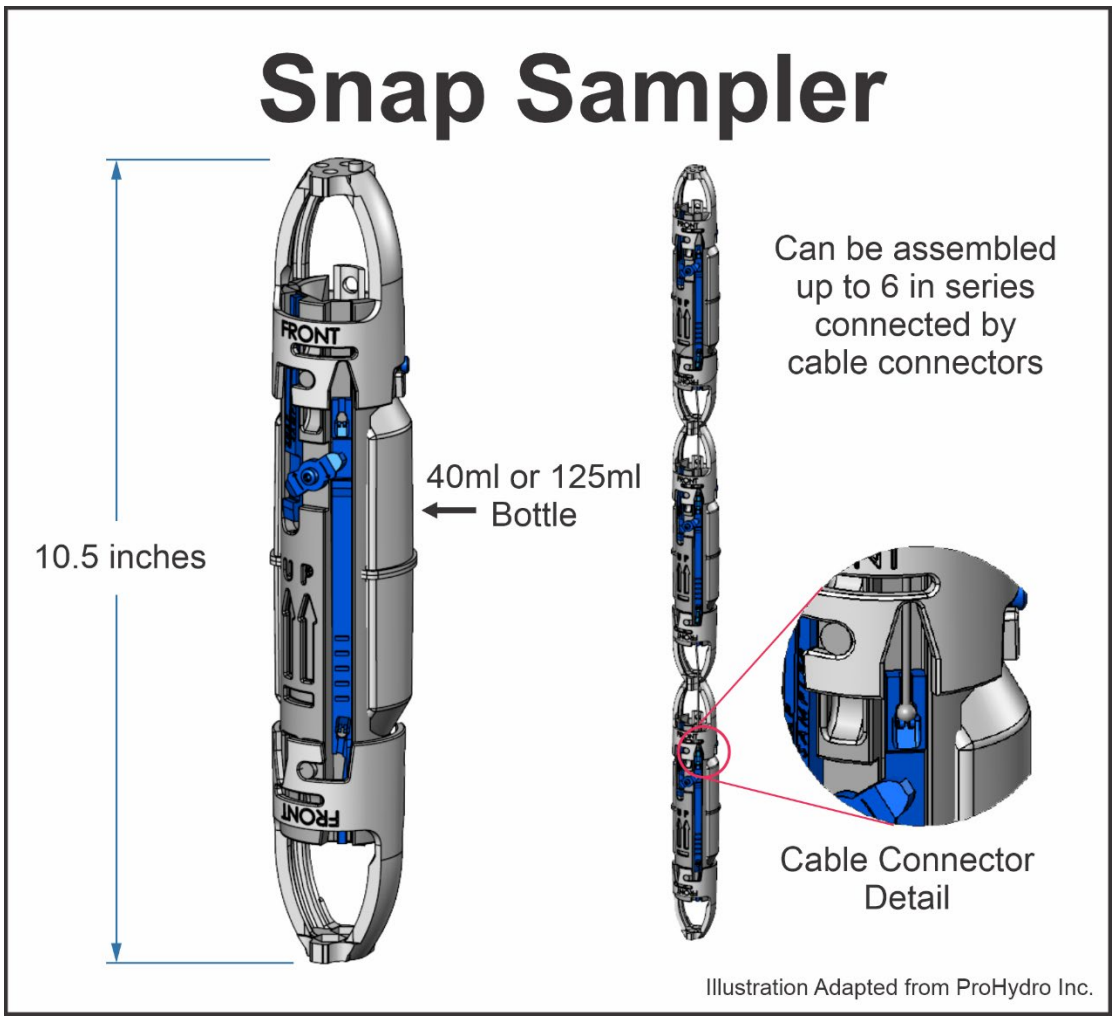
5.1.2.1 Description and Application

The Snap Sampler is a grab-sampling device that collects a whole water sample at a fixed sampling depth up to 2,500 feet below ground surface. The Snap Sampler 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 collect the sample, the bottles are triggered to close 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 like turbidity from motion in the water column.

Figure 5- 8: used with permission from NJDEP.



5.1.2.2 Installation and Use

The Snap Sampler is a dedicated sampling device/method where 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: a 40ml size that holds the double-ended 40ml glass VOA vial; a 125/250/350ml size that holds 125ml, 250ml, or 350ml double-ended HDPE bottles; and a narrow 250ml size that a single 250ml double-ended HDPE bottle. Two-inch diameter wells are limited to 40ml to 250ml bottles. Four inch or larger wells are not limited to bottle size.

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 only collect 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 in order to have the dedicated equipment assembled and deployed in advance of the first sampling event. Well construction details—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 assure 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 re-stabilization period is recommended for the Snap Sampler for passive deployments. It may take as little as 24 hours to re-stabilize for passive sampling varying 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. For example, different compounds volatilize differently, 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 handing. 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). 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 reattached, Snap Caps set into the open position, and the string 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

- Collects a whole water sample, allowing analysis for any dissolved or suspended chemical, including field parameters.
- Collects 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 non-target sample position.
- Collects from a consistent depth position without sampler motion.
- Allows 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.
- Requires one mobilization for long-term sampling event to both collect and replace bottles.
- Eliminates or reduces IDW.

5.1.2.4 Limitations

- Must be deployed in wells 2 inches in diameter or larger.
- Collects a maximum volume of 1.5L of water with a single string of samplers in a 2-inch well and 2.1L in a 4-inch well.

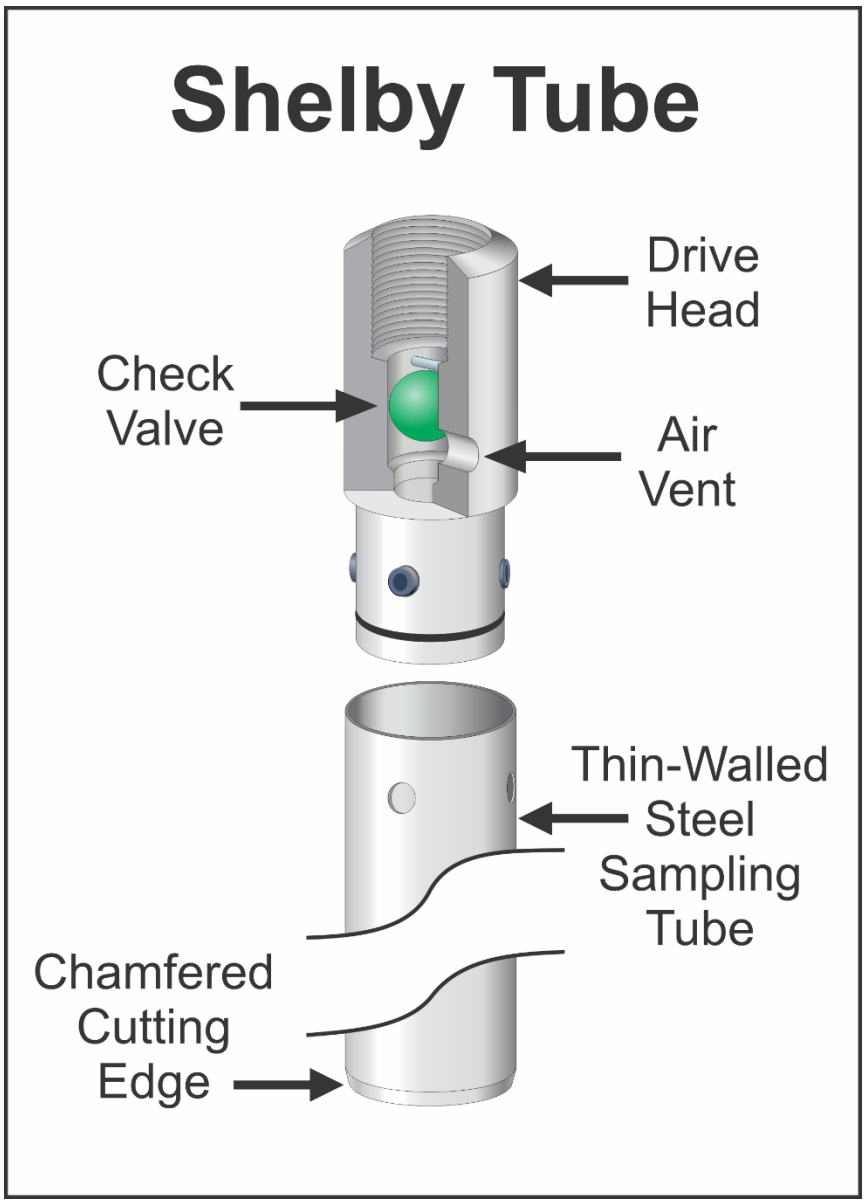
5.1.3 Thin-Walled Soil Samplers

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 or Acker thin-walled samplers and are made from steel, stainless steel, galvanized steel, or brass. The thin-walled samplers minimize soil disturbances (e.g., friction, compaction, and other soil displacements) compared to other types of samplers (e.g., 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.

Figure 5- 9: used with permission



5.1.3.2 Installation and Use

The Shelby tube is the most common type of thin-walled sampler and is 30 inches in length and comes in variety of outside diameter (OD) dimensions. Tubes with at least a 3-inch OD and 2.875-inch inside diameter (ID)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 string of drill rod and is lowered into the borehole to the pre-determined 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, i.e., the sample is partially or completely unretrievable, then leave the tube in place for approximately 10 to 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 process of 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

- Can sample at discrete depths.
- Provides an undisturbed soil and/or NAPL sample.
- Provides location and depth specific NAPL verification and characterization.

5.1.3.4 Limitations

- Limited to soils that can be penetrated by the thin wall of the sampler.
- 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 porewater) 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.

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 aqueous sample inside an 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 re-stabilize 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 (i.e., loss, 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 lists chemical families that can be analyzed using the noted passive sample (USGS, 2020).

Table 5 - 2(see separate excel to for a user-friendly view)

Passive Equilibration Sampling Technologies	PDB	Nylon Screen	RCDM	Dual Membrane	RPPS	Ceramic Diffusion Sampler	Peeper	Polymeric	PISCES
Chemical Constituents and Characteristics									
Field physiochemical characteristics (Temp, pH, SC, DO, ORP)	Some	Some	Some	All	Some	Some	Some	N/A	N/A
Major cation and anions (Ca, Mg, Na, K, HCO_3, Cl, SO_4, F, Br)	N/A	All	All	All	All	N/A	All	N/A	N/A
Nutrients (NO_3, NO_2, NH_4, PO_4)	N/A	All	All	All	All	N/A	All	N/A	N/A
Trace Elements (Metals) (Fe, Mn, Al, Ag, Zn and others)	N/A	Some	Some	All	Some	N/A	All	N/A	N/A
Perchlorate (ClO_4)	N/A	All	All	All	All	N/A	All	N/A	N/A
Organic Carbon (dissolved or total)	N/A	All	All	All	All	NT	Some (dissolved)	N/A	N/A
Dissolved Hydrocarbon Gases (Methane, ethane, ethene)	All	All	All	All	All	NT	All	N/A	N/A
Volatile Organic Compounds (Chlorinated solvents, BTEX)	Some	Some	Some	All	Some	Some	All	N/A	N/A
Semi-volatile Oranics (1,4-Dioxane, BN, Phenols, PAH, PCB, dioxins, furans)	Some	Some	Some	Some	Some	Some	NT	Some	Some
Pesticides, Herbicides, and Fungicides (organoCl, organoPO_4)	N/A	NT	NT	Some	NT	NT	NT	NT	Some
Explosive Compounds (RDX, HMX, TNT)	N/A	Some	Some	Some	Some	NT	NT	N/A	N/A
Poly- and perfluoroalkyl substances (PFASs)	N/A	NT	Some	Some	NT	NT	Some	N/A	N/A
Pharmaceuticals (Drugs, fragrances, hormones)	NT	NT	NT	Some	NT	NT	NT	N/A	N/A
Minerals (pyrite, mackinawite)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Microbial Population sampling (e.g. Dehalococcoides)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table Key	
ALL	All 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

Acronym Key:
[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO3, bicarbonate; Cl, chloride; SO4, sulfate; F, fluoride; Br, bromide; NO3, nitrate, NO2, nitrite; NH4, ammonium; PO4, phosphate; Fe, iron; Mn, manganese; Al, aluminum; Ag, silver; Zn, zinc; BTEX, benzene, toluene, ethylbenzene and xylene; RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane; TNT, trinitrotoluene; organoCl, organo-chlorine; organoP04, organo-phosphate; PAH, polycyclic aromatic hydrocarbons; BN, base-neutral organics; PCB, polychlorinated biphenyls; ClO4, perchlorate; PFOS, perfluorooctane sulfonic acid; PFOA, perfluorooctanoic acid; PFNA, perfluorononanoic acid, NT, not tested]

5.2.1 Passive Diffusion Bag Sampler (PDB)

5.2.1.1 Description and Application

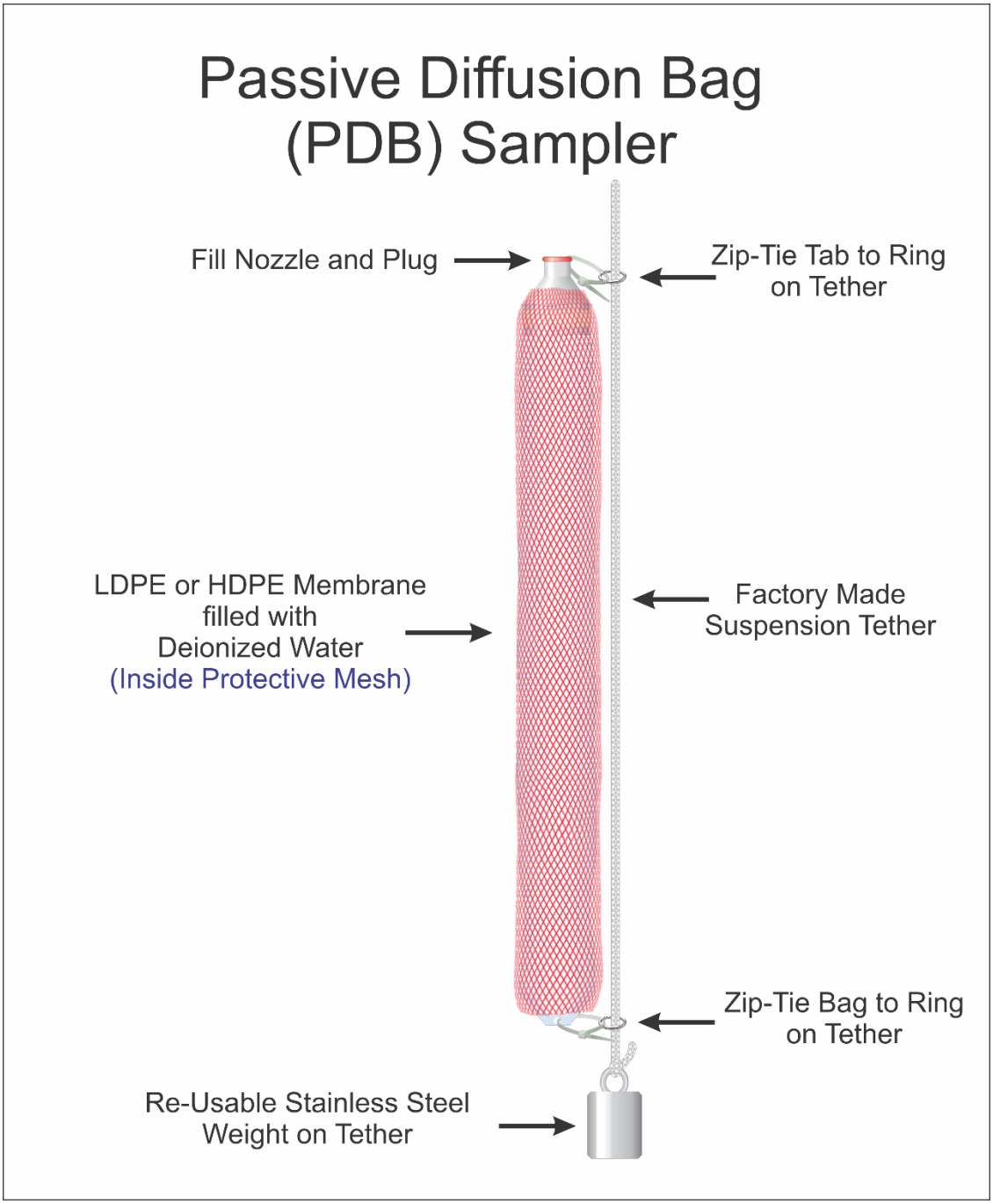
Passive diffusion bag (PDB) samplers are a relatively mature passive diffusion technology, having been developed in the late 1990s. The technology has been evaluated against traditional purge sampling techniques in groundwater and has become a widely accepted technique for determining concentrations of VOCs in groundwater, surface water, and sediment porewater. PDB samplers can be used to collect samples for analysis of most non-polar VOCs, in addition to select SVOCs (including naphthalene) and dissolved hydrocarbon gases (methane, ethane, ethene) (USGS 2020).

PDBs operate using the principles of molecular diffusion across the semipermeable polyethylene membrane. The deionized 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 porewater) 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). 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).

A PDB sampler consists of a low-density polyethylene (LDPE) sleeve filled with deionized water. The LDPE sleeve (typically 2 to 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 (i.e., groundwater, surface water, or sediment porewater) .

PDB samplers are commercially available, either pre-filled 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 5-8). PDB samplers are typically 12 to 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 Small Diameter PDB Samplers (1" & Larger Wells)," 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 Small Diameter PDB Samplers (1" & Larger Wells)," 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 Small Diameter PDB Samplers (1" & Larger Wells)," n.d.). Other tether materials can be used if they meet project DQOs.

Figure 5- 10: used with permission from NJDEP.



5.2.1.2 Installation and Use

Operating a PDB is straightforward. To deploy the dive 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 porewater), PDB samplers are typically placed within protective canisters, which are tethered to a polypropylene or

equivalent line and secured to a stationary object (e.g., 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 porewater, PDBs are deployed by manually pushing the protective cannister 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.

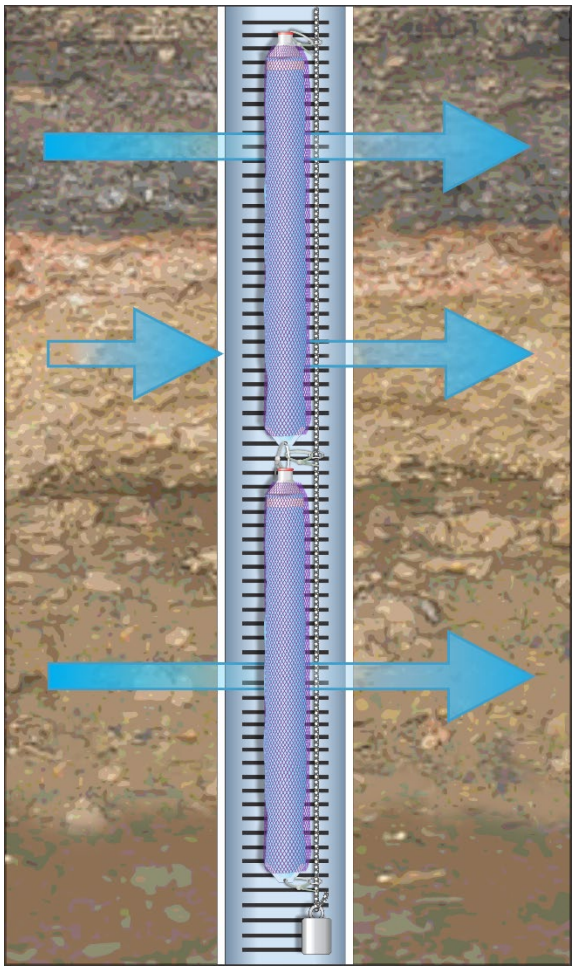
Equilibration times are well and compound dependent. The recommended minimum equilibration period for PDBs is 10 to 14 days, although equilibration of many VOCs may actually occur within 1 to 4 days. Additional time may be required for low-yield groundwater aquifers. The installation of the sampler can cause the water in 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). 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). Target chemicals in the aquifer are transported into the well through the screen by natural flow. This technique results in significant cost savings as opposed to purge and pumping techniques as a result of pumping and purging field times being eliminated and wastewater disposal reduced.

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 5-9. Hanging the samplers as such can result in the collection of information about the well’s hydrogeological attributes and determining the correct positioning of future single PDB samplers.

Figure 5- 11: Deployment of PDB samplers to vertically profile well, used with permission from NJDEP.



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 porewater. Since polyethylene-based PDBs are semi-permeable, certain compounds are restricted from diffusing through the membrane. Because the semi-permeable PDB membrane only allows diffusion of non-polar 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 PCE, to be collected to measure remediation progress or effectiveness.

Metals and other non-organics are not generally sampled using a PDB sampler because they cannot diffuse through the membrane. Compounds with a molecule size less than 10 angstroms, like non-polar 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 porewater.

- 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 LPDE 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 indefinitely without degrading.
- 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 over 700 feet below ground surface.
- The PDB is a disposable sampler, reducing decontamination time.

5.2.1.4 Limitations

- Because the range of chemicals that are able to 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. These samples are representative of concentrations over an extended length of time. 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 (i.e., karst aquifer).
- 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™) is an equilibrium-based passive diffusion sampler that has been commercially available since 2014 for monitoring aqueous media, particularly groundwater (“DMPDB,” n.d.). 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.

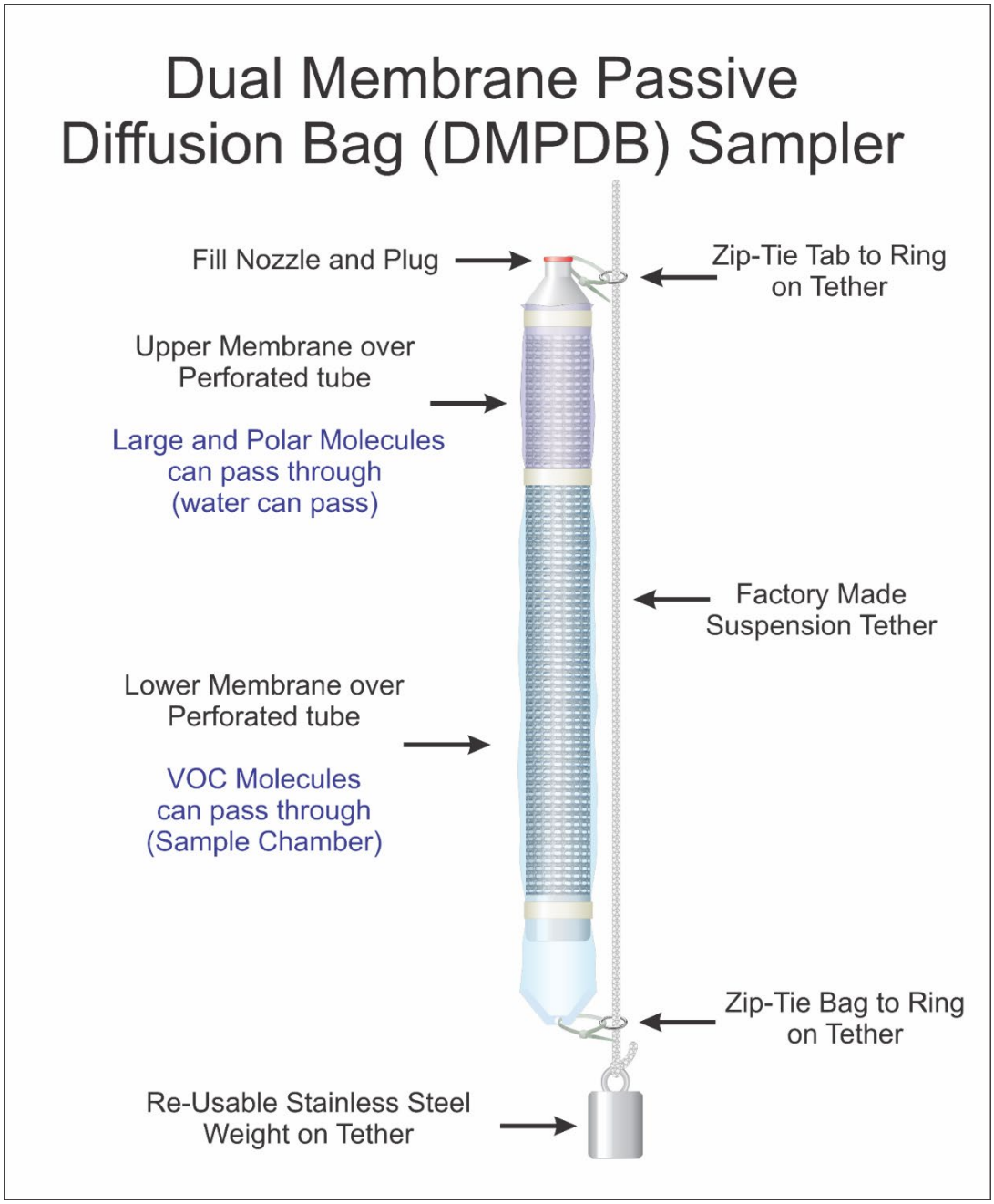
The DMPDB consists of two semipermeable membranes wrapped in series around a frame made of a rigid, perforated polypropylene tube (1.75" diameter), forming a single sample reservoir. The membrane on the lower section of this tube is made of low- or high-density polyethylene (LDPE or HDPE), which allows 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 µm pores). The upper membrane porosity allows for 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 porewater. 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 porewater through installation of a screened cannister. Cannisters should be installed to assure 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.

Figure 5- 12: used with permission from NJDEP.



5.2.2.2 Installation and Use

The DMPDB is filled with deionized 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. While VOCs are able to 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 re-stabilize 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 re-stabilization) 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, like PFAS and 1,4-Dioxane, equilibrate within about a week after well stabilization. Others, like 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. Since 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 (ITRC doc) and PFAS

Data from DMPDB use for a variety of compounds and water quality parameters is 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, the manufacturer should be contacted.

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 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 a 2-inch schedule 80 wells.

5.2.2.3 Advantages

- Lab and/or field studies have shown that the DMPDB is 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.
- Allows consistency in collection depth over repeated sampling events due to predetermined sample location (tether for groundwater or sampler housing for other media).
- Allows for easier vertical profiling to investigate stratified contaminant zones, multiple well screens, and bedrock fracture zones using discrete pre-determined sample depths.
- Allows the collection of field parameters including dissolved oxygen, pH, and temperature due to upper membrane design.
- Constructed of non-biodegradable 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.
- Reduces cross-contamination risk since samplers are single use and are deployed using systems dedicated to sample locations. (e.g., tethers or sediment canisters)
- Eliminates or substantially decreases 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, the DMPDB 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

- Provides limited sample volume, requiring consideration of laboratory sample volume requirements.
- The standard version requires field personnel to fill sampler with deionized water in the field. Due to the hydrophilic polyamide upper membrane, the sampler cannot be transported pre-filled and must be handled and deployed upright once filled to prevent spilling.
- Restricted by monitoring well or sampler housing construction, requiring an inner diameter of at least 2 inches or larger to avoid abrasions if obstructions or rough edges are encountered.

- Requires extended deployment time of 2 to 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.

5.2.3 Nylon Screen Passive Diffusion Sampler (NSPDS)

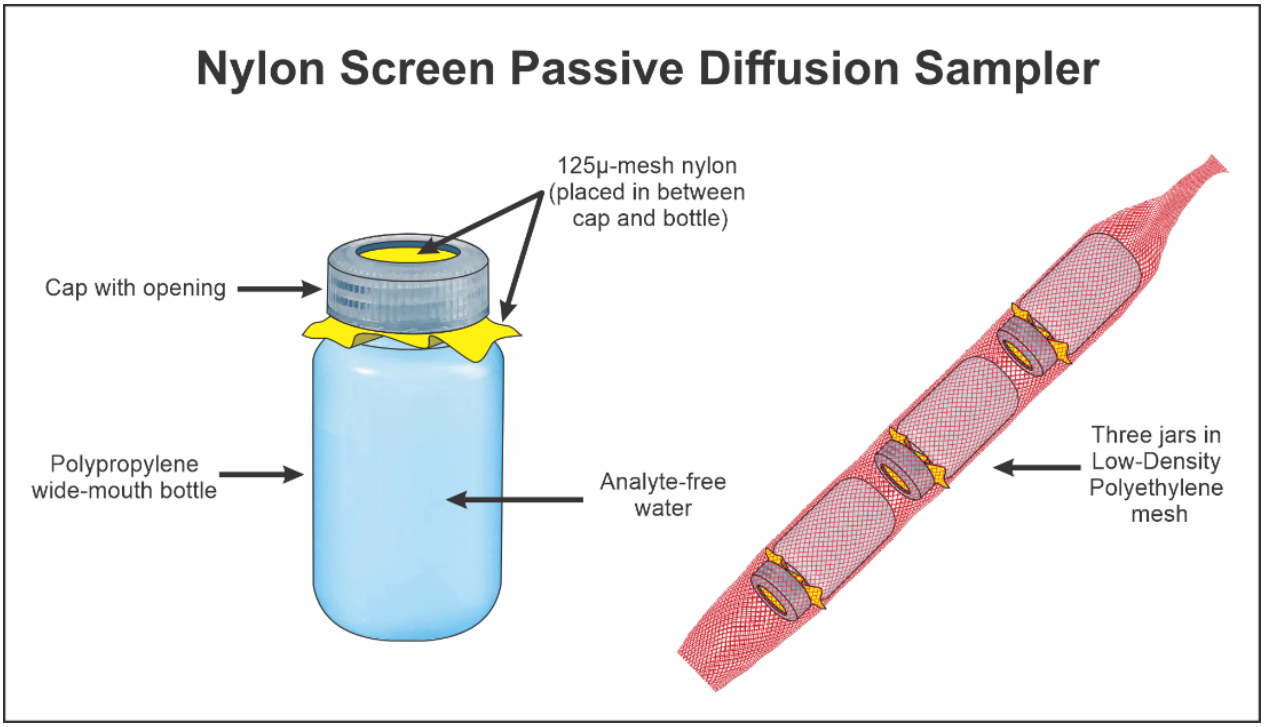
5.2.3.1 Description and Application

NSPDS, also known as Nylon Screen Diffusion Sampler (NSDS), is a passive equilibrium sampler for surface and groundwater. NSPDS were developed to sample for a broader array of analytes than the PDB sampler (Belluomini, et al., 2008). The NSPDS device is constructed using polypropylene wide-mouth bottles, a ring style cap, and a square of nylon mesh screen which are typically 125 to 250 micrometers (µm).

The bottles are filled with the appropriate type of deionized 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 deionized water prior to installation. Therefore, a concentration gradient exists between the compounds in the target aqueous media (groundwater, surface water, or porewater) 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- 13: used with permission from NJDEP.



5.2.3.2 Installation and Use

For deployment in wells, the NSPDS samplers are placed inside a mesh liner, which is attached to the hanging line with zip ties. The samplers can be arranged in stacks depending on the volume of water needed for analyses. The micron nylon mesh of the bottle(s) is faced downward to minimize mixing of water in the samplers with shallower well water during recovery (Vroblesky, Petkewich, and Campbell 2002). 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). Over time, chemicals diffuse across the nylon screen and equilibrate with the water inside the sampler. After retrieval, the sampled media needs to be prepared to be sent to the laboratory for analysis by either The content of the sampler is either transferring the sampled media to laboratory sample containers, and sent to the for analysis, or the cutout 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). As seen by the work from Webster et al. (1998), samplers facing down in water with a high ionic strength are unsuccessful equilibrating as a result of density differences between the sampler and ambient water

(Vroblesky, Petkewich, and Campbell 2002). It is ideal to orient the sampler so that the sampler membrane faces the well screen. According to Vroblesky et al. (2002), 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 et al., 2002). 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. 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 of 2003 (Vroblesky, Scheible, and Teall, 2003) on a suite of metals, and again, with the exception of silver, the NSPDS showed good transfer from test jars into sampler water. Subsequent studies by Columbia in August 2003 with samplers more suitable for 2-inch diameter wells (30- and 60-mL bottles with heights of about 60 mm and volume/area of up to 175) showed poor comparisons with water in test jars. Literature searches have been unsuccessful in finding citations that reference a nylon screen sampler being used for SVOC collection ("Passive (No Purge) Samplers" 2020).

Webster et al. (1998) examined the influence of orientation on bottles having similar design factors (however, he used a polysulfone membrane) and found that when deployed in saline pore water, bottles oriented with the opening toward the side equilibrated significantly quicker than bottles oriented with the opening up or down.

5.2.3.3 Advantages

- Good for most analytes.
- Eliminates or reduces IDW.
- Does not require specialized equipment (e.g., generator, compressed gases).
- Can sample at discrete intervals to prevent groundwater mixing.
- Can stack devices to profile screen length.
- Has a small sampling interval, which provides good profile location for identifying contaminant stratification.
- Decontamination of the sampler is minimal. 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, NSPDS samplers 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 a number of 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.

5.2.4 Peeper Sampler

5.2.4.1 Description and Application

Peeper samplers (i.e., dialysis cells or Hesslein In-Situ Porewater Sampler) 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 porewater 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). 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 O2 (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., RBCA) or Federal/State Cleanup Criteria.

Peeper samplers can be stacked in a specially designed corer to sample discrete depths, direct driven for near surface (1 to 3 meters) evaluation or placed in a shallow rectangular array for near surface area distribution determinations. Prior to deployment, peepers are filled with an appropriate grade of water (e.g., distilled, deionized, 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 don't 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 porewater 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 porewater. Peeper equilibration time can range from hours to a month, depending on peeper construction, target chemicals, and site-specific soil/sediment properties. Peeper samplers 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- 14: used with permission from NJDEP.

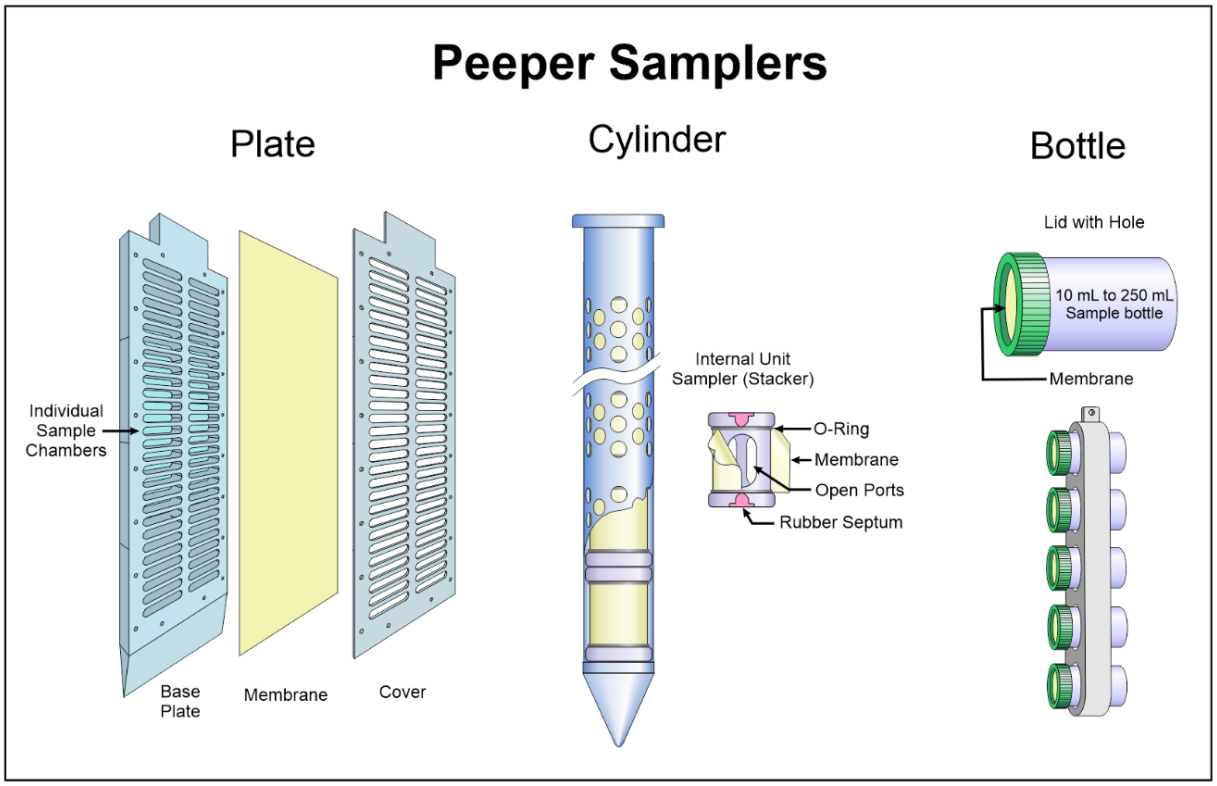


Table 5- 1

Style	Type	Application	Installation
Plate	Hesslein	shallow sediments	hand-push, slide hammer
	sHRPP	shallow sediments	hand-push, slide hammer
Cylinder	Standard	shallow sediments	hand-push, slide hammer
	HRPP	deep sediments, shallow groundwater	slide hammer, diverless push-pole, dive team, direct-push rig tooling
Bottle	PsMS	monitoring wells	lower using rope/cable
	Speeper	shallow sediments, monitoring wells	hand-push, diverless push-pole, lower using rope/cable

	PFASsive	shallow sediments, monitoring wells	hand-push, diverless push-pole, lower using rope/cable

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). Peeper samplers can be constructed of LEXAN®, acrylic, Teflon™, stainless steel or other millable material. Material selection is a function of site-specific characteristics (i.e., 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 over 100 mL. Common peeper sampler structures can be divided into three categories: plate, cylinder, and bottle (Figure 5-1 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 meters 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 LDPE 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 porewater. 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 (i.e., 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 AFB, near Sacramento, California (Parsons 2004). The PsMS samplers constructed for use in the McClellan AFB study were comprised of a rigid 2-inch long, 2-inch outer diameter section of PVC pipe covered on both ends with flexible 0.2-micron polysulfone membrane (Parsons 2005). The volume of each PsMS canister is approximately 108 mL (Parsons 2005). 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 (Webster et al., 1998) led to the deployment of the PsMSs in an orientation where the membrane is positioned horizontally.

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) (Garza-Rubalcava et al. 2022). 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 (Figure 7-4) (Jackson and Hatzinger 2020). The three different cell types and corresponding functionalities of the HRPP are:

- Equilibrium cells used to quantify contaminant concentrations and geochemical indicators (e.g., NO3−, NO2−, Cl−, Mn, Fe, SO42−). Equilibrium cells function similarly to traditional peeper sampling methods.
- Velocity cells used to measure multi-directional interstitial velocity (cm/d) based on mass transfer of a conservative tracer (e.g., 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 porewater 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.

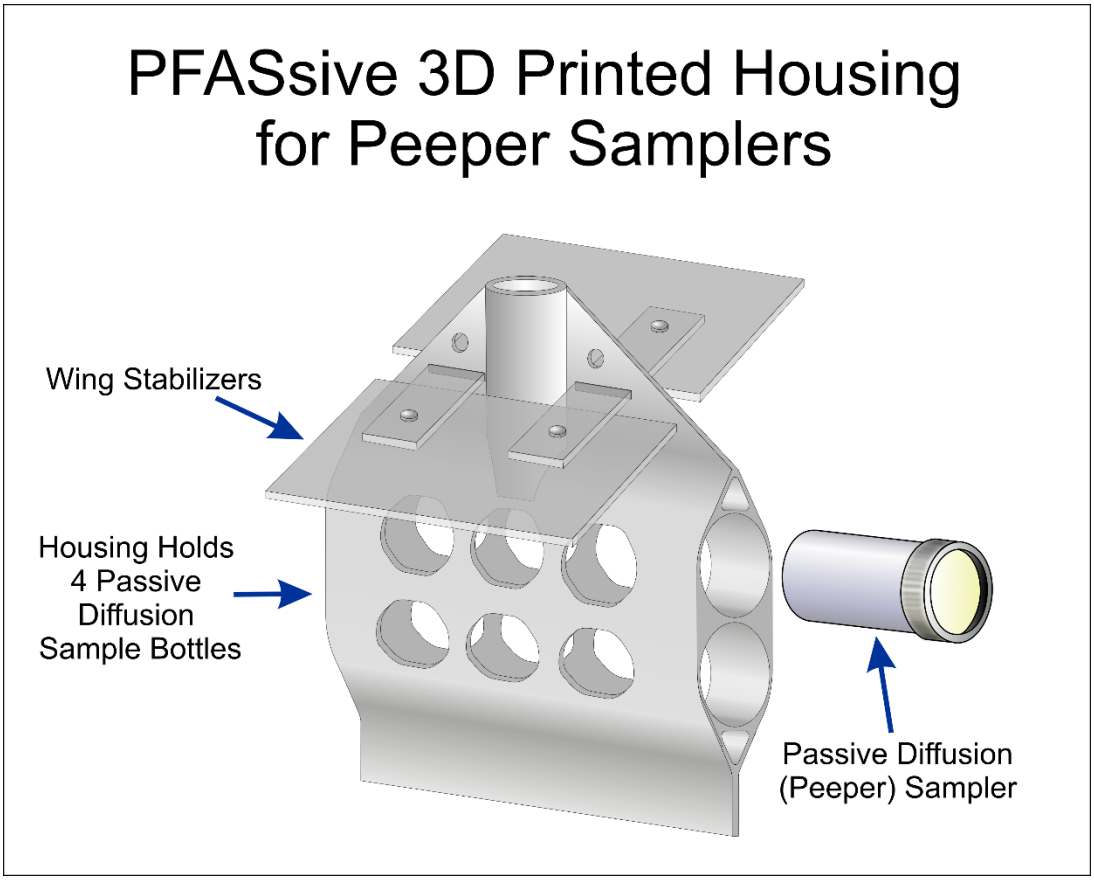
The sediment HRPP (sHRPP) is a modified HRPP design that is optimized for characterization of surface water sediments (vs. shallow aquifers). The sHRPP is a 3-ft-long, 5-inch-wide stainless-steel modified plate peeper design that includes the same functionalities as the HRPP but has higher resolution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

SPeeper™ and PFASsive™ are modified bottle peeper designs comprised of one or more 60-mL LDPE bottles capped with either polyethersulfone (SPeeper™) or polycarbonate (PFASsive™) membrane (Figure 5-13 and 5-14). 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 porewater.

Figure 5- 15: SPeeper™ modified bottle peepers are designed for diverless deployment in sediments.

Photo source: SiREM Labs, used with permission.

Figure 5- 16: used with permission from NJDEP.



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 porewater 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 is beneficial in refining conceptual site models and optimizing targeted monitoring/remediation, leading to long-term cost savings.

5.2.4.4 Limitations

- 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 PsMSs can range from hours to a month depending upon the contaminant of interest, sediment type, peeper sampler volume, and membrane pore size. A week to 14 days is the most common time period to allow for 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 the publication *Environ. Science & Technology* 32: 1727-1733.
- PsMS samplers are typically designed to fit into wells with a minimum inside diameter of 4 inches. The membrane orientation was only demonstrated in one direction (perpendicular to horizontal flow). The samplers should be constructed under water to ensure that the capsule is completely filled with purified water prior to deployment.
- 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 pre-fabricated 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, normal shipping procedures specified by your laboratory should be followed.

5.2.5 Regenerated-Cellulose Dialysis Membrane Sampler (RCDM)

5.2.5.1 Description and Application

Regenerated-cellulose dialysis membrane (RCDM) samplers are equilibrium-based diffusion samplers, developed to sample dissolved inorganic and organic chemicals in groundwater, porewater, 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 is comprised of tube, filled with deionized water, which has two layers. A high-grade regenerated-cellulose dialysis membrane is contained within a protective layer of LDPE mesh. The regenerated cellulose diffusion membrane has a pore size of 0.0018-microns and a molecular weight cut-off (MWCO) of 8000 Daltons. Particulates from groundwater and surface water samples are not able to pass through, and therefore, RCDM samplers only collect dissolved chemicals. RCDM samplers have been constructed using 31.8 mm (1.25 inches) and 63.7 mm (2.5 inches) filled-diameter membranes.

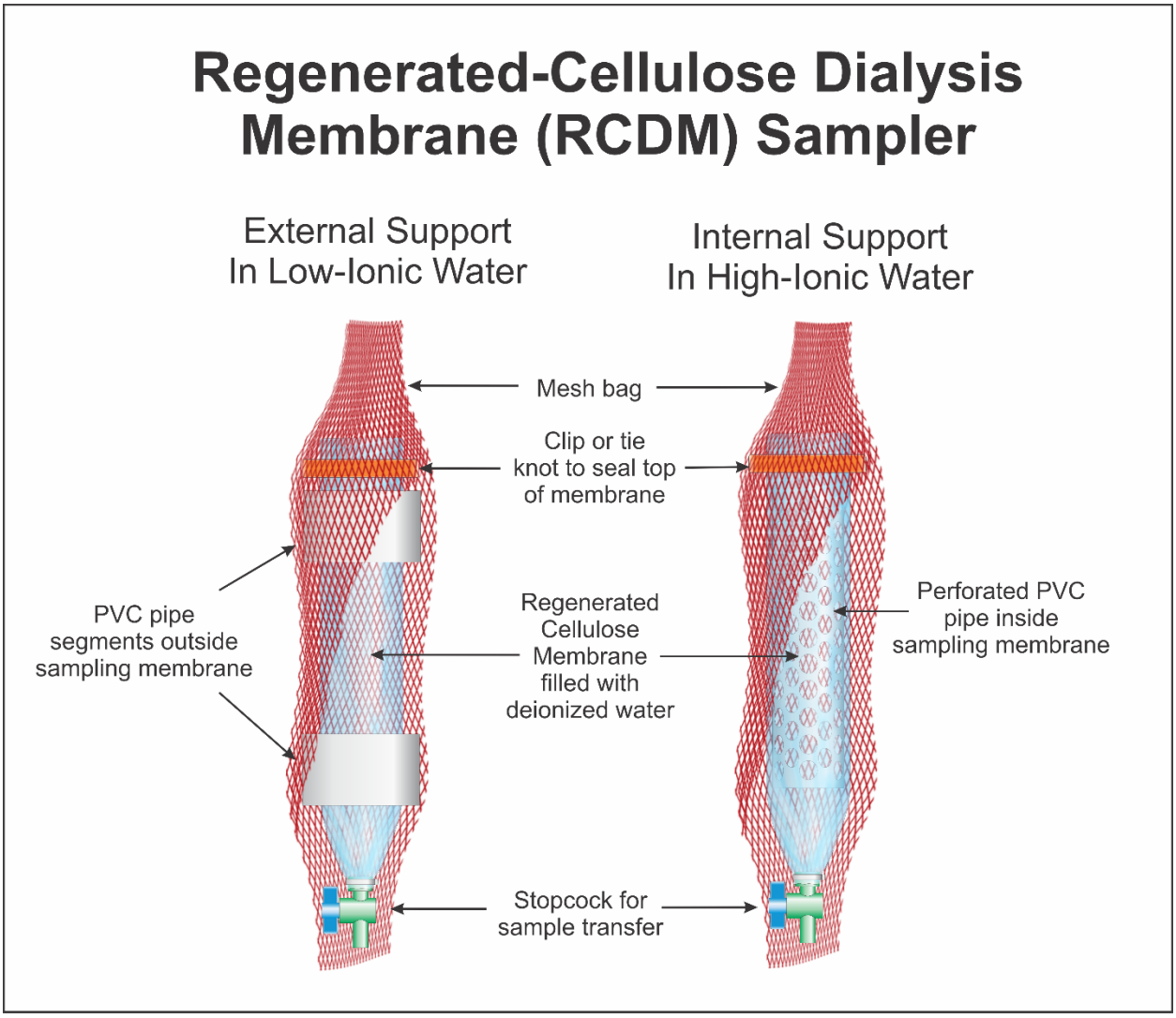
Because the dialysis membrane is hydrophilic, water can diffuse through the membrane. The sampler may be constructed with or without PVC pipes external to the dialysis membrane in low-ionic strength waters. In high ionic strength waters, an internal perforated PVC pipe to support the membrane should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

Fully constructed RCDM samplers are not currently available from any commercial vendors (Imbrigiotta and Harte 2020). However, precleaned dialysis membranes can readily be purchased from several manufacturers. Since dry RCDM membranes 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 deionized 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 et al, 2007). RCDM samplers were unsuccessful in sampling for mercury, tin, and silver in the laboratory over a 4-week equilibration period (Imbrigiotta et al, 2007). These trace metals may form organic complexes that strongly sorb to the membrane.

Figure 5- 17: used with permission.



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 bore hole well at a desired sampling depth consistent with site DQOs. For deployment, the sampler is attached to a weighted suspension-tether, lowered to the intended depth, and the tether secured at the top of the well (Imbrigiotta et al., 2008; Imbrigiotta and Harte, 2020). 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 re-stabilize hydraulically.

- 1–3 days for anions, silica, methane, dissolved organic carbon, all VOCs on the EPA 8260B list (including MTBE) (Ehlke et al., 2004; Harter and Talozi, 2004; Imbrigiotta et al., 2007);
- 3–7 days for most cations and trace elements (Vroblesky et al., 2002; Imbrigiotta et al., 2007);
- 7–14 days for most explosive compounds and perchlorate (LeBlanc, 2003; Parker and Mulherin, 2006; Imbrigiotta and Trotsky, 2011).
- Field equilibration testing has shown that RCDM samplers yield concentrations of VOCs similar to those yield by PDBs and low flow purging and sampling (Vroblesky et al., 2002; Vroblesky and Pravecek, 2002a and b; Imbrigiotta et al., 2002; Vroblesky et al., 2003; Parsons, 2005; Imbrigiotta et al., 2007). It has also been shown 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 (Imbrigiotta et al, 2007; Imbrigiotta and Trotsky, 2011). There is also some preliminary evidence that RCDM samplers are able to recover concentrations of selected PFAS compounds as well as low flow purging also (Imbrigitotta and Fiore, 2021).

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. Regenerated-cellulose dialysis membranes 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 the time of construction and time of deployment to maintain the permeability, flexibility, and strength of the membrane.

- Regenerated-cellulose dialysis membranes 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, et al, 2007). 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)

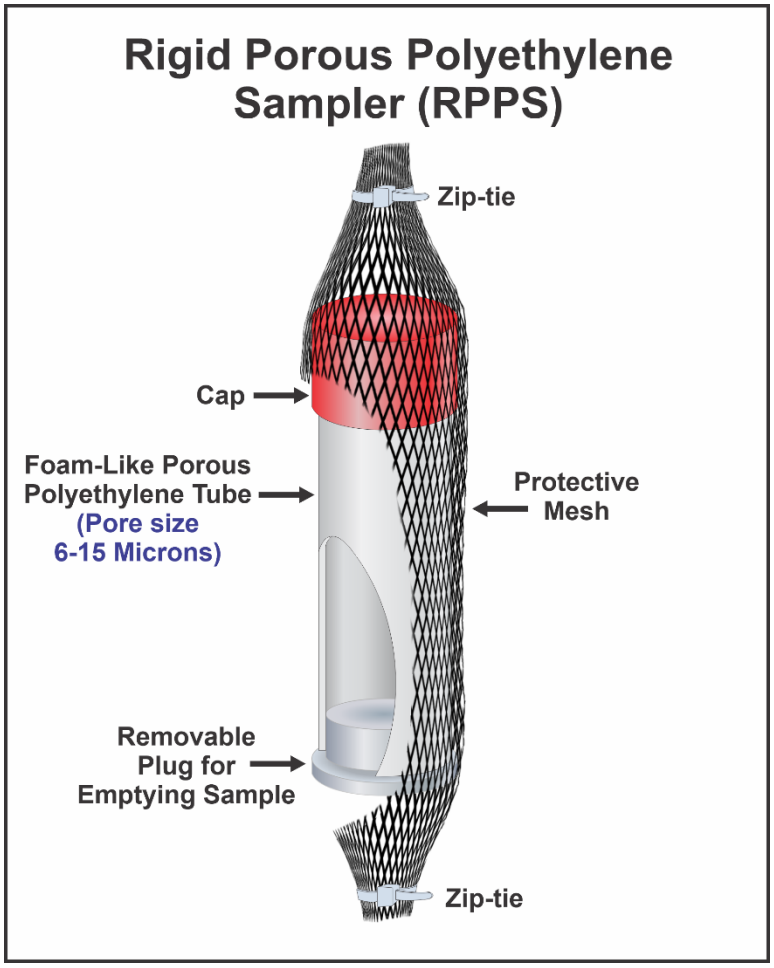
5.2.6.1 Description and Application

Rigid porous polyethylene samplers (RPPSs) 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.

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). The tube is constructed from thin sheets of foam-like porous polyethylene with pore sizes of 6 to 15 microns (Imbrigiotta and Harte 2020). The sampler is filled with DI water, closed at both ends, and additional water 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. While 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). Upon retrieval the original prototype tended to leak sample water through the pores of the porous polyethylene material (D. A. Vroblesky, personal communication, 2004). 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.

Figure 5- 18: used with permission from NJDEP.



5.2.6.2 Installation and Use

The 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 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 were specifically designed to collect groundwater samples from a discrete interval in monitoring or water wells. These samplers are capable of monitoring 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 (Vroblesky, 2004). 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 individual 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 AFB (Sacramento, California) in 2004 (Demonstration of Alternative Groundwater Sampling Technologies at McClellan AFB, Parsons 2005). According to the field demonstration data, the RPPS performs well at monitoring for anions, metals, and hexavalent chromium. While performing 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 hydrophobic organic compounds. 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 (ITRC 2007). 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 pre-filled 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

- Applicable to inorganic and organic analytes
- Is 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 inside 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.

5.2.7 Polymeric Sampling Devices (Low Density Polyethylene Sampler (LDPE), Polydimethylsiloxane (PDMS)-coated glass fiber (SPME fiber), Plyoxymethylene (POM))

5.2.7.1 Description and Application

Polymeric sampling devices have been used for several decades to measure freely dissolved contaminant concentrations of various organic chemicals present in surface water, groundwater, sediment porewater, and air. Polymeric passive samplers rely on absorption of certain hydrophobic organic chemicals into the polymer-based material being utilized for the sampling process. This process relies on the thermodynamic exchange, or equilibrium partitioning, of a contaminant of interest between water or air and the polymeric sampler via diffusion.

Polymeric passive samplers require equilibrium conditions, either achieved (through sufficient exposure time) or partially achieved and corrected (through the use of PRCs), to obtain an accurate measurement of contaminant concentrations. Achieving equilibrium is influenced by multiple factors including the contaminant of interest, the type of sampler used, and other environmental factors. Commonly used PRCs are deuterated or radiolabeled C13 compounds. These PRCs are pre-loaded into a given polymeric passive sampler, and the loss of PRCs after deployment are then quantified and used to correct the concentration when equilibrium is not achieved during the given exposure period (EPA, 2017). Freely dissolved concentration can be determined through the equation below:

Equation 2

$$C_w = C_p/K_p - w$$

Where:
C_w = freely dissolved concentration in water (ng/L)
C_p = concentration in polymer (ng/L)
$K_{p\text{-}w}$ = Polymer-water partitioning coefficient (L/L)
*polymer coefficient will depend on type of polymer used

Analytical methods require extraction of target analytes from the sampler and yield concentrations relative to the polymeric passive sampler. Subsequently, the analytical results can be converted to a concentration relevant to the particular environmental media being sampled through the application of partitioning coefficients. The use of polymeric passive samplers provides a time averaged concentration of freely dissolved organic chemicals at low detection levels without the need for high volume water collection. The use of polymeric passive samplers provides a measurement of the freely dissolved porewater concentration for contaminants, which is considered more

representative of the chemical's bioavailable fraction compared to bulk sediment samples.

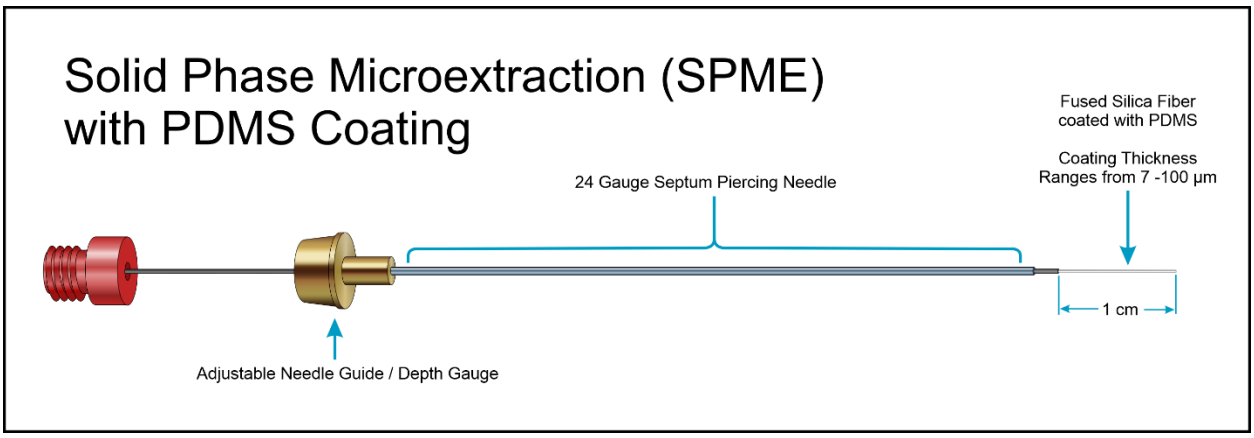
The three polymeric sampling devices have similar, though not identical, sorption properties, but in different geometries or configurations. POM and LDPE are typically configured in thin bulk flat sheets (25 to 100 micrometers [µm]), while PDMS-coated glass fiber is cylindrical shape glass capillaries (100 to 1,000 µm diameter) coated with a thin PDMS polymer (10 to 30 µm).More recently, advances in polymeric sampling have resulted in a shift to reliance on low density polyethylene (LDPE) and polydimethylsiloxane (PDMS)-coated glass fiber (i.e., solid phase microextraction (SPME) fiber). The focus of this subsection is primarily on LDPE and PDMS-coated SPME given their prevalence and current use compared to POM samplers. Solid phase microextraction (SPME) is a sampling technique that usually uses a glass fiber coated with an extracting phase such as organic polymer and extract/concentrates target chemicals from a bulk phase such as water and air. 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.

Both LDPE and PDMS-coated SPME samplers typically require a deployment time of 30 days. However, deployment times can vary depending on sampling conditions, in situ versus ex situ exposure parameters, and the target analytes being measured. More hydrophobic compounds, such as PCBs and dioxin/furans, typically require the full exposure period, along with potential corrections to account for analytes that don't 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 US EPA published a 2017 User's Manual along with calculator tools for data analysis available on the US EPA's website. Regulatory acceptance of integrating passive samplers into site characterization and monitoring has increased in recent years. While no published standard methods are currently available for polymeric passive samplers, numerous studies have been conducted to standardize the preparation and analysis.

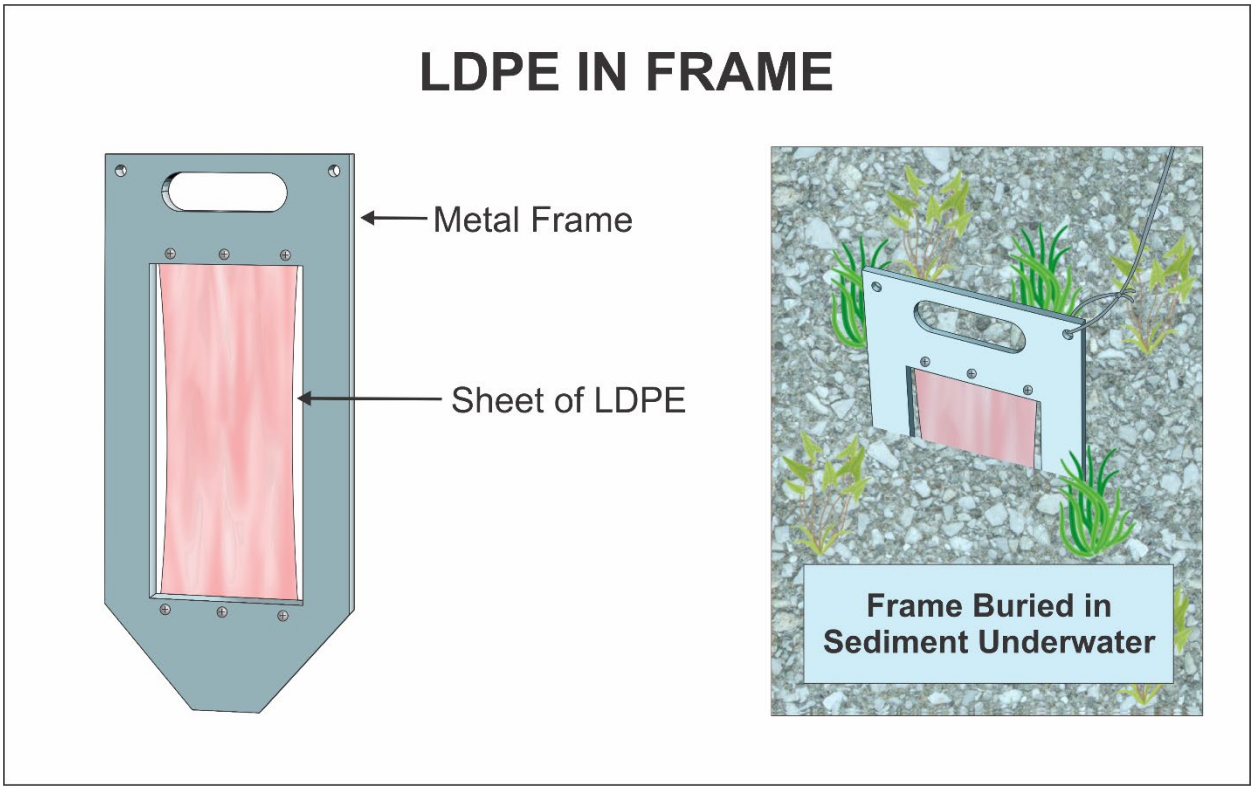
POM samplers are pieces of plastic sheeting ranging from 10 to 100 µm in thickness (U.S. EPA/SERDP/ESTCP 2017) (U.S. EPA, SERDP, and ESTCP 2017). PDMS samplers are fibers any they can also range in size, from 10 to 100 µm. The most common thickness frequently used for PDMS is 35 µm. For PDMS-coated SPMEs, the PDMS coating the glass fiber SPME rods is generally around 30 to100 µm thick, with a typical thickness of 35 µm (Michalsen, et.al., 2020). Multiple PDMS coated rods are typically deployed within the same sampler unit to increase the absorptive capacity and decrease analytical detection limits. Perforated metal rods, plates, or similar enclosures are typically utilized to ensure the samplers are protected while maintaining contact with the surrounding media.

Figure 5- 19: Illustration of a PDMS coated SMPE Samplers. *Figure used with permission from NJDEP.*



The LDPE samplers consist of a clean, uncoated sheet of LDPE, which can vary in thickness but generally from 13 to 76 µm (U.S. EPA/SERDP/ESTCP 2017) (U.S. EPA, SERDP, and ESTCP 2017). The dimensions of the LDPE can be developed to meet specific project conditions and deployment requirements. They are most typically deployed within an open frame or a metal mesh envelope.

Figure 5- 20: used with permission from NJDEP.



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 in such a way that also captures the near bottom surface water.

These passive samplers can be used for both ex situ and in situ sampling of sediment porewater, 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 logistical challenges that accompany in situ deployments, including loss of samplers. For ex situ sampling, exposure conditions can be controlled and time to equilibrium can also 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 porewater 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.

Compound Specific Information:

- Most commonly used for PCBs and PAHs.
- Also available for other organic chemicals including dioxins, polybrominated diphenyl ethers, chlorinated pesticides, pyrethroids.
- Recent research in passive sampler technology has provided a form of polymeric sampling that can measure PFAS. However, this sampler currently has limited commercial availability.

5.2.7.3 Advantages

- Polymeric 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.
- Can be performed in situ or ex situ.
- Use of PRCs allows for correction to equilibrium for more hydrophobic contaminants or time constricted deployments.
- Combines water sampling, extraction, and concentration
- Measures time-averaged concentrations
- Low detection limits for more hydrophobic compounds
- Minimal impact on sampling matrix and interferences with dissolved organic matter
- High resolution profiling of sediment porewater concentrations

5.2.7.4 Limitations

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

5.2.8 PASSIVE IN-SITU CONCENTRATION EXTRACTION SAMPLER (PISCES)

5.2.8.1 Description and Application

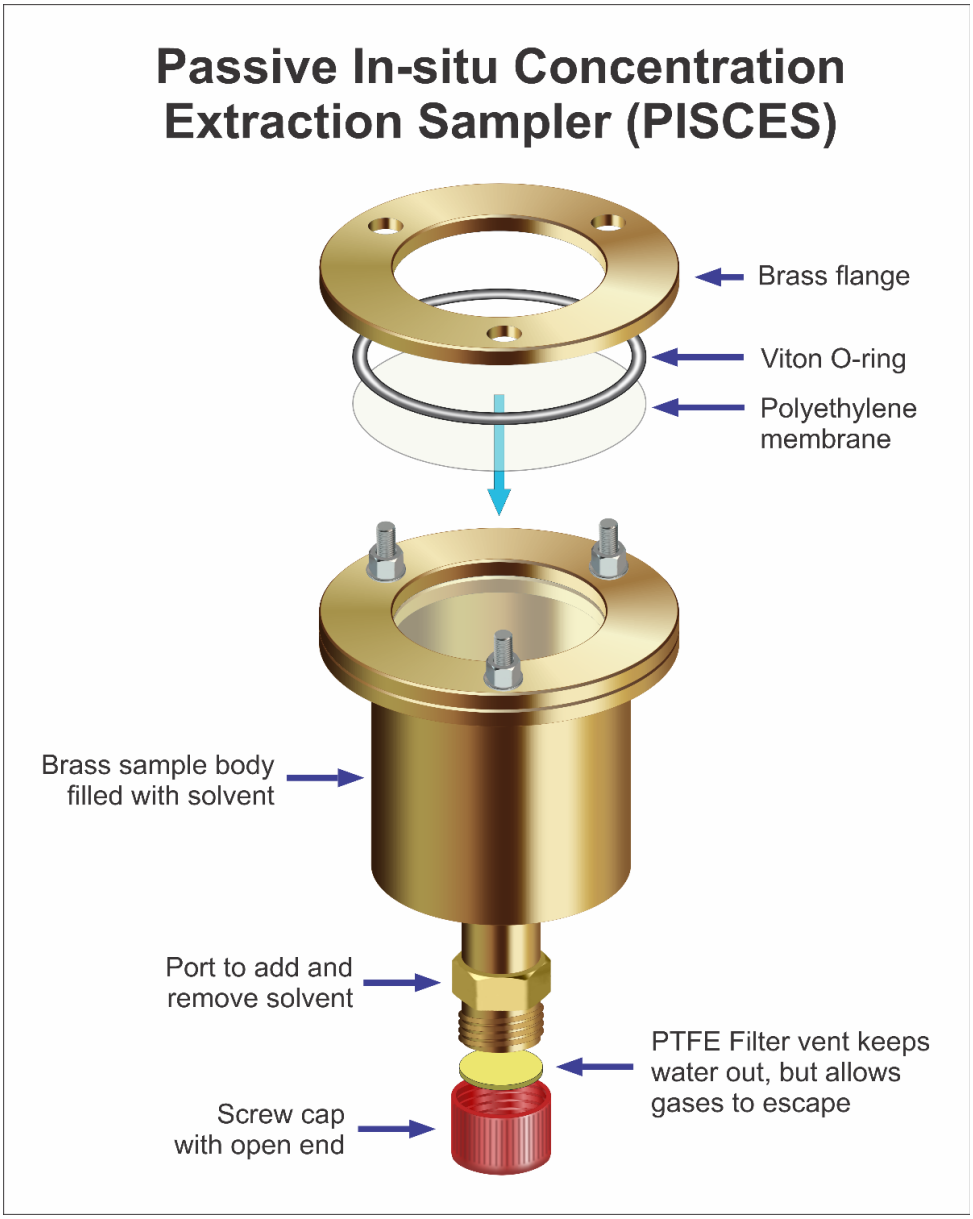
The Passive In Situ Concentration Extraction Sampler (PISCES) is intended to sample non-polar or hydrophobic organic chemicals in surface water (Belluomini et al. 1995). The sampler relies on diffusion and absorption to accumulate the target chemicals in the sampling medium (Belluomini et al. 1995). 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.

PISCES consist of a membrane, typically low-density polyethylene (LDPE), covering one end of a metal container filled with an organic solvent, typically hexane or isooctane (2,2,4- trimethylpentane) (Belluomini et al. 1995). Other solvents such as alcohols (methanol, ethanol, propanol) are currently being 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. 1995). For hydrophobic compounds, partition coefficients are large (greater than 1,000), and sampling continues at a constant rate for weeks to months without approaching equilibrium between the solvent and the water. Sampling rates do not vary from compound to compound, so relative distribution of chemicals in the solvent reflect the relative distribution of these compounds dissolved in the water. The solvent is analyzed by conventional analytical methods. The membrane excludes ionic, high molecular-weight natural organic matter, and particulates, thereby simplifying, and in some cases eliminating, the need for cleanup of samples before analysis.

PISCES are reusable and allow the easy addition and retrieval of the selected organic solvent. The device consists of a brass body where the selected organic solvent is placed. 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. The PISCES is manufactured in two sizes: a 7.6 cm (3 inches) flange diameter (has a membrane area of 21 cm^2 and can hold 100 mL of solvent), and a 10 cm (4 inches) flange diameter (has a membrane area of 50 cm^2 and can hold 200 mL of solvent). Both samplers are approximately 9.5 cm (3.75 inches) long.

LDPE membranes typically are between 150 and 700 µm thick (Szlachetka et al. 2021). The solvents pass through the membrane at an appreciable rate as long as the membrane is properly mounted and not damaged. Sampling rate does not differ between these two solvents. Hexane extracts are more easily concentrated by evaporation, and more volatile compounds can be separated from hexane and analyzed by gas chromatography; however, hexane is more flammable than isooctane, presenting a greater hazard to field crews and individuals who might tamper with samplers in the field. Isooctane extracts are more difficult to concentrate by evaporation, requiring vacuum distillation if a boiling water bath is used as the heat source. Because of the lower fire hazard, isooctane is the recommended solvent unless volatile chemicals such as xylenes are to be analyzed.

Figure 5- 21: used with permission from NJDEP.



5.2.8.2 Installation and Use

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

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, over 100 L of water is sampled for a one-month exposure. This yields a 100-fold decrease in detection limit relative to the traditional approach of grab-sampling and extraction of a 1-liter water sample.

5.2.8.3 Advantages

- Samplers can be redeployed without decontamination to same sample location
- Lightweight
- Reusable
- Improved laboratory detection limits
- Allow easy addition and retrieval of solvent

5.2.8.4 Limitations

- 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
- Samplers are not widely accepted by laboratories for analysis.

5.2.9 Ceramic Dosimeter / Ceramic Diffusion Sampler

5.2.9.1 Description and Application

The Ceramic dosimeter is a time-integrative passive sampler designed to measure VOCs, PAHs, and other organic chemicals in groundwater, surface water, and porewater (Martin et al., 2003; Bopp et al., 2005; Bopp et al., 2007; and Bonifacio et al., 2017). Ceramic dosimeter is made of a ceramic tube and solid adsorbent beads or resins enclosed inside of the tube. A ceramic tube acts as diffusive-controlling barrier

for target organic compounds. Enclosed solid adsorbent inside of the tube can uptake target organic compounds. The Ceramic dosimeter continuously accumulates target organic compounds during deployment in water. 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 et al., 2003). The ceramic tube is inert, water-wet, and does not adsorb or swell in contact with target organic compounds. Polytetrafluoroethylene (PTFE) caps are used to close a ceramic tube to minimize sorption of target organic compounds, and those caps are fixed in a stainless-steel holder.

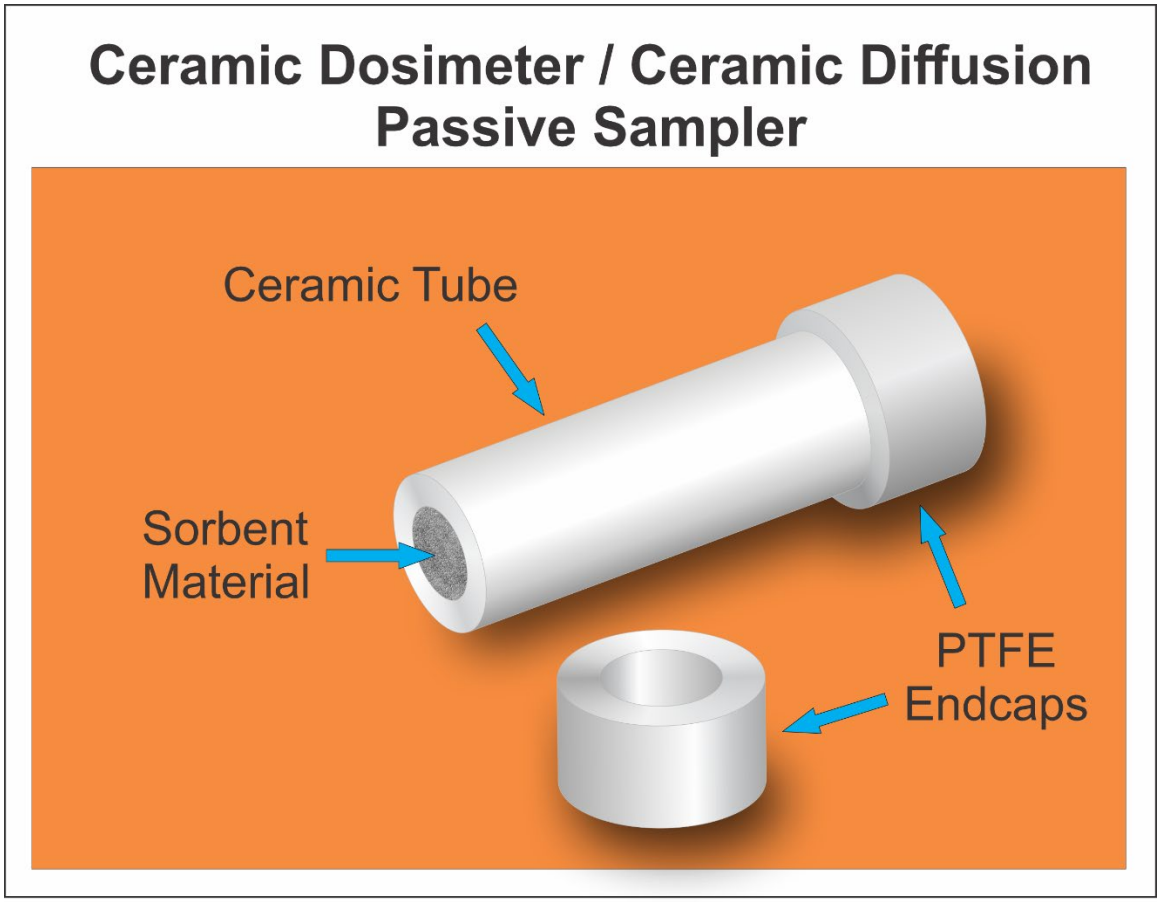
Martin et al. (2003) showed that the relationship between the time-weighted average concentration of a target chemical and the accumulated mass on the solid adsorbent beads is based on Fick's first law as follows:

$$M = F \cdot A \cdot t = D_e \frac{\Delta C}{\Delta x} \cdot A \cdot t \cong D_e \cdot C_W \cdot A \cdot t$$

where M is the accumulated mass of a target chemical [M], F is the mass flux of a target chemical through the ceramic tube [M t^{-1} L^{-2}], A is the ceramic tube surface area [L^2], t is the deployment time [t], D_e is the effective diffusion coefficient of a target chemical, and $\Delta C/\Delta x$ is the concentration gradient across the ceramic tube. 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.

As an example, solid adsorbent beads made of Amberlite IRA-743 from Sigma-Aldrich and showed its applicability to measure benzene, toluene, ethylbenzene, and xylenes (BTEX) in groundwater. The comparison between the concentrations derived from ceramic dosimeters and average concentrations determined by frequent conventional snap-shot active sampling showed that ceramic dosimeters perform well over up to 90 days of deployment in a contaminated aquifer (Martin et al., 2003).

Figure 5- 22: used with permission from NJDEP.



5.2.9.2 Installation and Use

Research is still in progress for this technology. Different solid adsorbent beads have been used in ceramic dosimeters to measure a variety of organic compounds. This technique has been applied and tested for dioxins (Addeck et al. 2012), flame retardants (Cristale et al., 2013), pharmaceutical compounds (Franquet-Griell et al., 2017), and per- and polyfluoroalkyl substances (PFAS) (Kaserzon et al., 2019) as long as the PTFE end caps are replaced with a PFAS-free material. Ceramic dosimeter can be combined with bioassay and biomonitoring by using a unique solid adsorbent material, which is specifically called a Ceramic Toximeter (Bopp et al., 2007; Addeck et al., 2012). Bonifacio et al. (2017) used a non-porous ceramic tube that excludes the permeation of water but allows only gas-phase diffusion of VOCs to the dry resin inside the ceramic tube and showed its effectiveness to measure VOC concentrations in water.

Ceramic dosimeter without solid adsorbent beads or resin can be used as an equilibrium passive sampler. Gefell et al (2018) used a ceramic porous cup saturated and filled with reagent water as a diffusion-based equilibrium passive sampler to measure SVOC and PAH concentrations in porewater containing non-aqueous phase liquid (NAPL). A ceramic porous cup is resistant to NAPL entry because of small pore sizes (i.e., a few micrometers) and the non-wetting behavior of NAPL; a ceramic porous cup acts as a

capillary barrier and excludes NAPL from water samples. A ceramic diffusion sampler can be placed into sediment or groundwater wells to equilibrate by diffusion to measure SVOCs and PAHs without NAPL impacts. This is a unique feature of this technology as NAPL exclusion is quite difficult for other passive samplers. For example, polymeric passive samplers such as LDPE and SPME fibers are preferentially coated and fouled with NAPL. NAPL surface coating onto polymeric passive samplers can result in overestimation of freely dissolved concentrations of a target chemical.

5.2.9.3 Advantages

- Ceramic porous cups and tubes are commercially available.
- Ceramic materials can exclude NAPL from water samples.
- 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 a ceramic tube.

5.2.9.4 Limitations

- Ceramic dosimeter and ceramic equilibrium sampler cannot be used for inorganic compounds because of uptake by ceramic materials.
- Ceramic dosimeter is still in development phase and requires extra steps to determine aqueous phase concentrations compared to grab or equilibrium passive samplers.

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 absorbent 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 absorptive granular solid material, like granular activated carbon, in the device. Alternatively, the collecting medium may be contained within a semipermeable membrane so that only certain molecules are able to 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 allows diffusion of specific contaminant molecules through the membrane so that 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 the temperature, pressure, flow rate past the sampler, and turbulence of the sampled environment. The target molecules continue to accumulate on the collecting medium until the medium reaches saturation; therefore, the collecting medium does not come to

2640 concentration equilibration with the surrounding medium. If the target medium becomes
2641 saturated before removal and analysis, the calculation of concentration will be understated.

2642 After the sampler has been recovered, the target molecules are de-sorbed from the collecting
2643 medium at a lab to produce a result of mass of accumulated target molecules. The resulting
2644 sample chemical mass, or flux, is used to calculate a time-weighted average (TWA)
2645 concentration of target compounds chemicals over the exposure period (Huckins, Petty, and
2646 Booji 2006) (Taylor et al. 2021[2559]).

2647 Table 5 – 4 below lists chemical families that can be analyzed using the noted passive
2648 sampling technologies (USGS, 2020).

2649 *Table 5 – 4 (see separate excel to for a user-friendly view)*

Passive Accumulation Sampling Technologies	AGI	POCIS	Sentinel	SPMD	Ceramic Dosimeter	DGT	Min Trap	Radiello	Waterloo	Beacon	Dart	Fossil Fuel	Bio-Trap
Chemical Constituents and Characteristics													
Field physiochemical characteristics (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	N/A
Major cation and anions (Ca, Mg, Na, K, HCO_3, Cl, SO_4, F, Br)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Nutrients (NO_3, NO_2, NH_4, PO_4)	N/A	N/A	N/A	N/A	N/A	Some (NO3, PO4)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Trace Elements (Metals) (Fe, Mn, Al, Ag, Zn and others)	N/A	N/A	N/A	N/A	N/A	ALL	N/A	N/A	Some (Hg)	Hg	N/A	N/A	N/A
Perchlorate (ClO_4)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Organic Carbon (dissolved or total)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	petrogenic CO2 in soil (via measurements of total and modern (based on 14C))	N/A
Dissolved Hydrocarbon Gases (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	N/A
Volatile Organic Compounds (Chlorinated solvents, BTEX)	All	N/A	N/A	N/A	All	N/A	N/A	ALL	ALL	All	N/A	N/A	N/A
Semi-volatile Oranics (1,4-Dioxane, BN, Phenols, PAH, PCB, dioxins, furans)	Some	N/A	N/A	Some	Some (PAH)		N/A	N/A	Some	Some	Some (PAH)	N/A	N/A
Pesticides, Herbicides, and Fungicides (organoCl, organoPO_4)	Some	ALL	N/A	Some	NT	Some (organoc PO4)	N/A	N/A	N/A	Some	N/A	N/A	N/A
Explosive Compounds (RDX, HMX, TNT)	Some	N/A	N/A	NT	NT	NT	N/A	N/A	N/A	Some	N/A	N/A	N/A
Poly- and perfluoroalkyl substances (PFASs)	NT	Some	Some	NT	Some	Some	N/A	N/A	N/A	Some	N/A	N/A	N/A
Pharmaceuticals (Drugs, fragrances, hormones)	N/A	ALL	N/A	Some	N/A	Some	N/A	N/A	N/A	NT	N/A	N/A	N/A
Minerals (pyrite, mackinawite, iron compounds)	N/A	N/A	N/A	N/A	N/A	N/A	ALL	N/A	N/A	N/A	N/A	N/A	N/A
Microbial Population sampling (e.g. Dehalococcoides)	N/A	N/A	N/A	N/A	N/A	N/A	Some	N/A	N/A	N/A	N/A	N/A	ALL

2650

Table Key	
ALL	All 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

Acronym Key:
[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO3, bicarbonate; Cl, chloride; SO4, sulfate; F, fluoride; Br, bromide; NO3, nitrate, NO2, nitrite; NH4, ammonium; PO4, phosphate; Fe, iron; Mn, manganese; Al, aluminum; Ag, silver; Zn, zinc; BTEX, benzene, toluene, ethylbenzene and xylene; RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane; TNT, trinitrotoluene; organoCl, organo-chlorine; organoP04, organo-phosphate; PAH, polycyclic aromatic hydrocarbons; BN, base-neutral organics; PCB, polychlorinated biphenyls; ClO4, perchlorate; PFOS, perfluorooctane sulfonic acid; PFOA, perfluorooctanoic acid; PFNA, perfluorononanoic acid, NT, not tested]

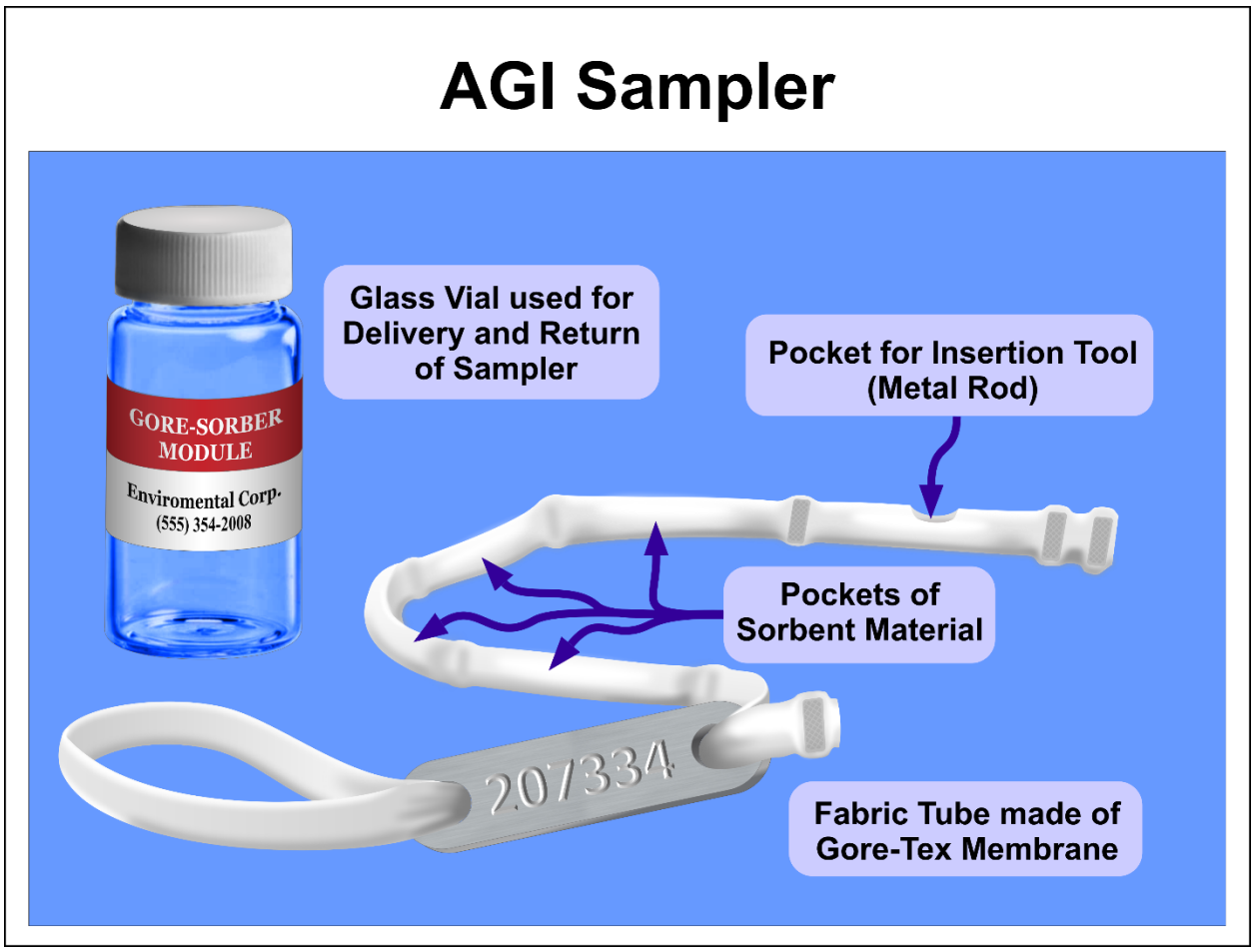
5.3.1 AGI Universal Sampler (formerly the Gore Sorber)

5.3.1.1 Description and Application

The Amplified Geochemical Imaging (AGI) Universal Sampler is a device that relies on diffusion and adsorption to accumulate chemicals on the "passive sorbent collection units ('sorbers')" contained within the sampler (or module). These modules yield a chemical mass that can then be correlated with concentrations of said chemicals in water or air. This device can be utilized 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. 1995).

Each module is approximately ¼ inches in diameter, 13 inches in length, and consists of a polytetrafluoroethylene (GORE-TEX ™) membrane tube that contains four connected sorber pockets that contain engineered sorbent material. The Gore-Tex ™ membrane is microporous, expandable, and is relatively chemically inert (Imbrigiotta and Harte 2020). A typical sorber pocket is about 25 mm in length, 3 mm in diameter, and contains a 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). The end of the module has a loop with a unique serial number label. For deployment to groundwater monitoring wells, the module can be suspended on a line within the groundwater. A weight must be added to the end of the module in order to keep the module suspended at the desired depth. For the best results, the sampler should be suspended in the screened interval of the well or at the desired sample interval in an open borehole. The modules size also allows deployment to smaller diameter wells (half-inch ID and larger).

Figure 5- 23: used with permission from NJDEP.



5.3.1.2 Installation and Use

The AGI Universal Sampler 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. Ensure that the field personnel wear gloves (nitrile or latex) when both installing and retrieving the samplers in all media. Additionally, for all media, it is important to ensure that the serial numbers on the samplers match their glass vials both before deployment and upon retrieval. Medium-specific installation and use is as follows:

Soil Gas Sampling

First, the field personnel must drill a vertical boring. This can be completed 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 assuming a 36-inch vertical hole with a 1.2-inch diameter. Should a project's DQO's require deeper

samples, AGI should be consulted during the planning phase of the investigation. Once the boring is drilled, the field personnel must 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 photos below) is placed into the pocket of the sampler and both the rod and sampler are inserted into the boring. Note that the insertion rod is only used 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 retrieved. Once the sampler is placed at the target depth interval, the string, which extends up from the sampler, is tied to the bottom of the cork, which is then used to seal/plug the boring. The cork is designed to plug a ½-inch diameter hole. Once the sampler is deployed, and the installation date and time is recorded. The samplers are then left to passively collect for seven to ten days. To retrieve, the field personnel must remove the cork (by hand or with a screwdriver) and remove the sampler from the ground using the 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 the modules do not have to be kept cold for shipment (AGI 2016). Therefore, the modules can be kept in glass vials (without refrigeration) until they are analyzed by the laboratory (typically within four to seven days).

Figure 5- 24: Used with permission.

Figure 5- 25: Used with permission.

Figure 5- 26: Used with permission.

Indoor/Outdoor Sampling

When using this device to collect indoor/outdoor air, the field personnel should decide on the appropriate method for installing the samplers in their desired locations, and have the appropriate supplies ready (i.e., pre-cut pieces of string nails, or pushpins) 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 (can range from several days to multiple months), each sampler is retrieved, the retrieval date and time recorded, the attachment material disposed of, and the samplers returned to their appropriate vials. The vials are placed

back into the sample box, the samples logged on the chain-of-custody, and the box shipped to AGI's laboratory for analysis. The modules do not have to keep cold (typically 4° C) for shipment to the laboratory. Therefore, the modules can be kept in glass vials (without refrigeration) until they are analyzed by the laboratory (typically within four to seven days).

Figure 5- 27: Used with permission.

Groundwater Sampling

After removing the module from the vial, it is placed down a groundwater well to 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 (i.e., trip blanks, equipment blanks, and/or duplicates), and Chain-of-Custody (COC) forms are shipped to AGI's laboratory, typically via overnight courier. AGI's internal research has determined that the modules do not have to be kept cold for shipment (AGI 2016). Therefore, the modules can be kept in glass vials (without refrigeration) until they are analyzed by the laboratory (typically within four to seven days).

5.3.1.3 Advantages

- Simple to install and retrieve, thereby decreasing field labor costs
- When sampling groundwater, there is no purge water generated
- When sampling soil gas, there is no need for pumps or purging
- Applicable to a wide range VOC and SVOC compounds

- Can be placed in NAPL to sample
- Sensitive to parts per trillion levels
- Minimal handling is required, reducing possible field sampling errors
- Single use, no material decontamination needed (the sampling kit provides enough supplies for single use)
- Can be used in monitoring wells, sediments, surface water, springs, and other aqueous settings, regardless of their flow or turbidity
- Can be used in small-diameter monitoring wells and piezometers
- Minimal shipping requirements (do not require ice or coolers) and reduced shipping costs
- Short residence period for groundwater
- Modules contain duplicate samples
- Commercially available
- Excellent for evaluating lateral delineation in less mobilizations, primarily for soil gas

5.3.1.4 Limitations

- When used to measure dissolved gases in groundwater, gives total mass desorbed, therefore requiring calibration with measured concentration in wells.
- Single source supplier and laboratory
- This technology cannot be used to measure field parameters
- This technology cannot be used for inorganics
- Compound detection is limited by vapor pressure
- Not particularly feasible for vertical delineation in soil gas
- Soil gas data may not be accepted for risk assessment purposes in some states

5.3.2 Polar Organic Chemical Integrative Sampler

5.3.2.1 Description and Application

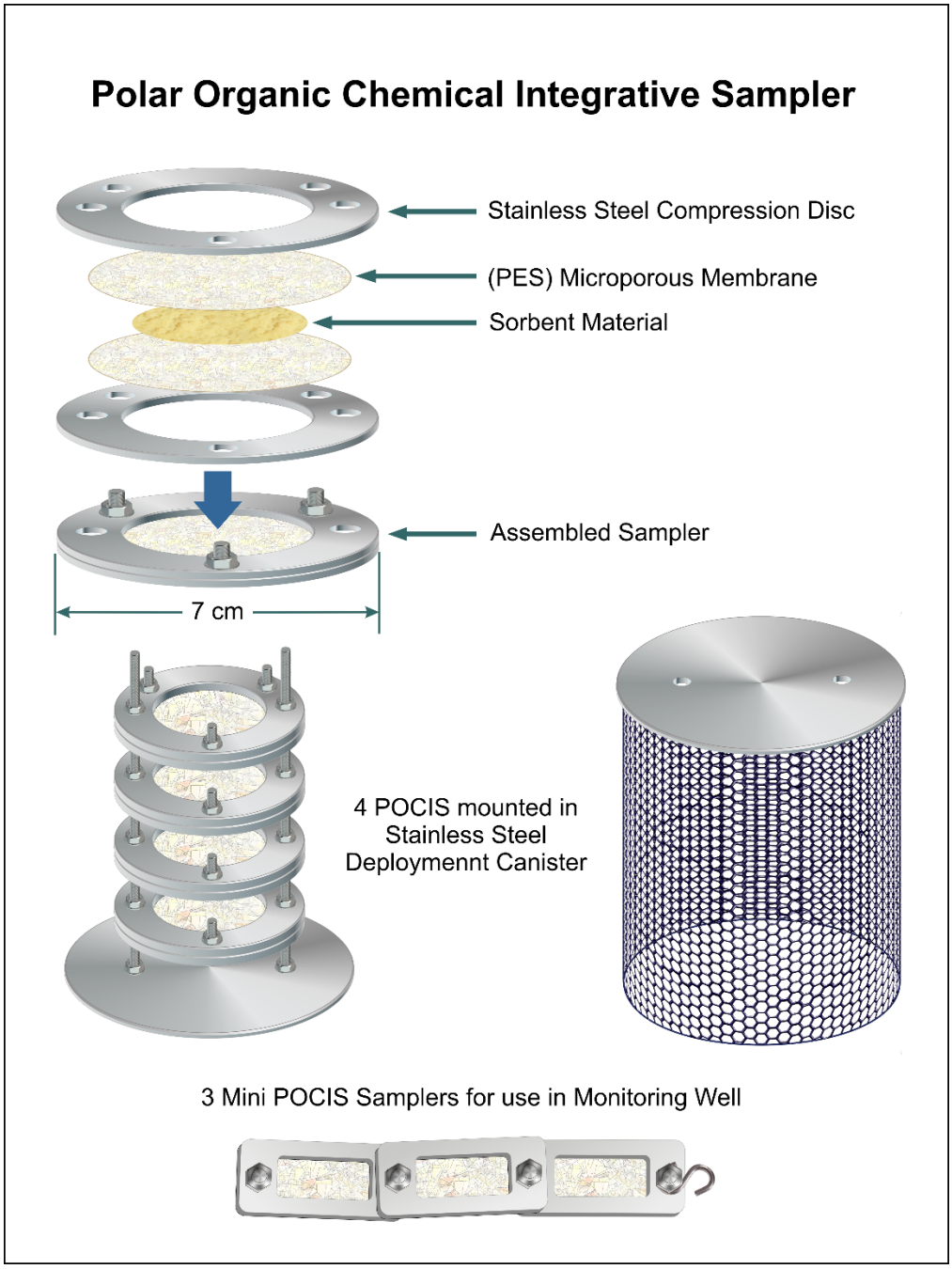
The Polar Organic Chemical Integrative Sampler (POCIS) is designed to sample water-soluble (polar or hydrophilic) organic chemicals from aqueous environments. This device relies on diffusion and sorption to accumulate a total mass of chemicals. The residence period ranges from weeks to months. This device 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 (TIE) approaches.

The POCIS consists of a solid material (sorbent) contained between two microporous polyethersulfone (PES) membranes. The membranes have a pore size of 0.1 µm, which allows for water and dissolved chemicals to pass through to the sorbent where the chemicals are trapped (MacKeown et al. 2022). Larger materials, such as sediment and

particulate matter, do not pass through the membrane(D. Alvarez and Huckins 2004). The build-up 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 build-up 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 @ 180 cm^2/g (D. Alvarez and Huckins 2004). Typically when deployed, POCIS can effectively sample a surface area of 41 cm^2 (D. Alvarez and Huckins 2004). Figure 12-1 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 as they are not compatible with standard sealing techniques (i.e., 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- 28: used with permission from NJDEP.



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. After retrieval, the sorbent is transferred into a chromatography column. 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), GC, GC/MS, and liquid chromatograph/mass spectrometer (LC/MS) (D. Alvarez and Huckins 2004). Additionally, bio-indicator tests, such as Microtox® and the Yeast Estrogen Screen (YES) , 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 (D. Alvarez and Huckins 2004). A listing of some of the chemicals identified in POCIS extracts is shown in Table 5 – 4.

5.3.2.3 Advantages

- Easily deployable to a variety of different water bodies

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 porewater 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 5-27) is a thin tag-like shape (approximately 2.5 cm wide by 5.0 cm long) constructed of either high-density polyethylene (HDPE) for water sampling or stainless steel for sediment porewater 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. 2023a). The resin is emplaced between HDPE mesh screens and is in direct contact with the environmental water being sampled. The sorbent comes pre-wetted with glycerol from the manufacturer, which allows the samplers to be placed directly into the environmental water without pre-treatment steps ("FAQ: Sentinel^{TM} PFAS Passive Samplers," n.d.). 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.

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 modified EPA Method 537.1 or modified Draft EPA Method 1633.

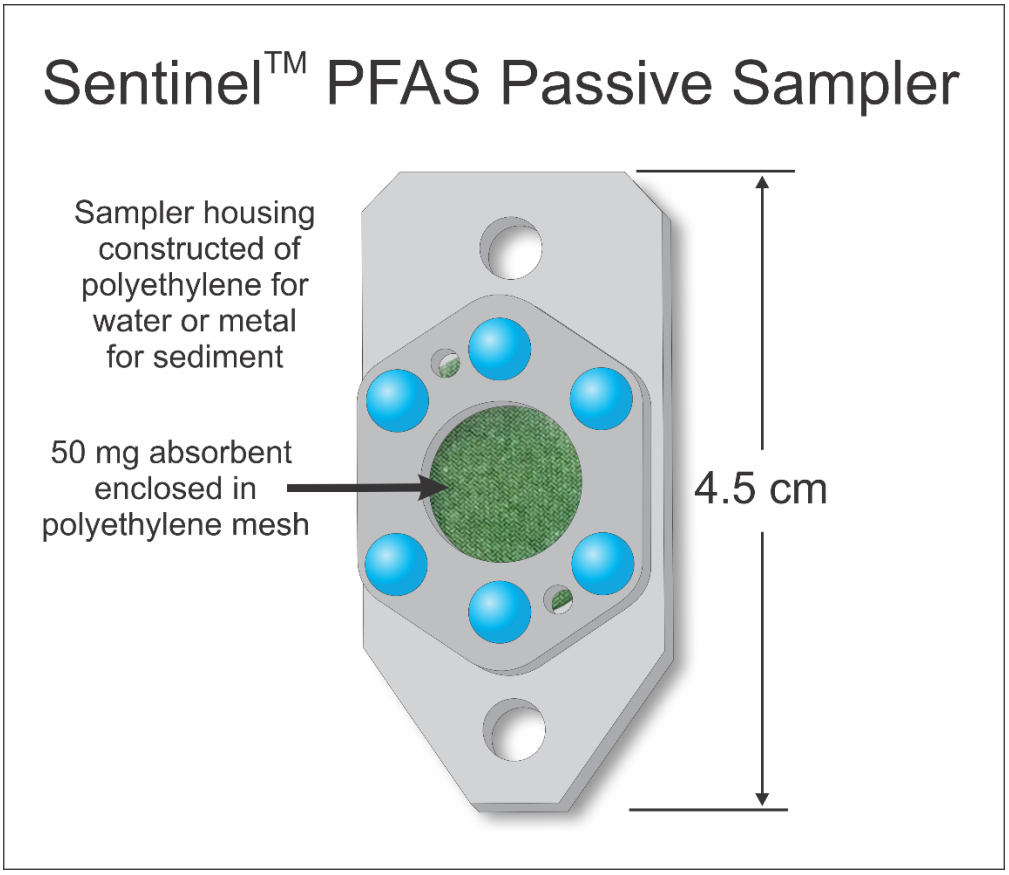
The accumulated mass (ng) recovered from the Sentinel passive sampler is converted to the aqueous phase concentration, C_w (ng/L), using the following equation:

$$Cw = accumulated\ mass\ /\ (Rs \times t)$$

where R_s is the sampling rate (L/day), and t is the sampling time in 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 Draft EPA 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). The Sentinel passive sampler was demonstrated in the field at deployment durations of several days to several weeks (Edmiston et al. 2023a). 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. 2023b).

Figure 5- 29: used with permission from NJDEP.



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 porewater applications). Guidance for groundwater and surface water field applications are available from the SERDP project website (SERDP 2023, ER20-1127). For groundwater applications, the passive sampler may be attached to a deployment line (e.g., 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 (e.g., 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 (Environmental Security Technology Certification Program [ESTCP] ER23-7696; Lotufo et al. 2023) . 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 deionized 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.
- Single-use device limits potential for cross-contamination.
- Time-integrative sampler provides average concentration over entire period of deployment, capturing both spikes and low concentrations.
- 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

- New to 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 EPA Draft Method 1633.)
- Samplers must remain submerged during deployment.

5.3.4 Semipermeable Membrane Devices (SPMDs)

5.3.4.1 Description and Application

Semipermeable Membrane Devices (SPMDs) were developed in the mid-1990s by personnel at the USGS Columbia Environmental Research Laboratory and designed to sample hydrophobic organic chemicals in surface water, mimicking the accumulation of hydrophobic organic contaminants (HOCs) and pesticides into the fatty tissues of organisms (Huckins et al., 2006). 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). SPMDs have been used to determine freely-dissolved (bioavailable) concentrations of HOCs with log octanol-water partition coefficients (log K_{OW}) greater than 3 such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (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).

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) non-porous lay-flat polyethylene membrane tube. The tube allows the nonpolar chemicals to pass through to the lipid where the chemicals are concentrated. Larger molecules (> 600 Daltons) and materials such as particulate matter and microorganisms are excluded by the tube.

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). The calculated amount of PRC lost during deployment is used to adjust the laboratory sampling rates at each sampling location.

Figure 5- 30: used with permission from NJDEP.

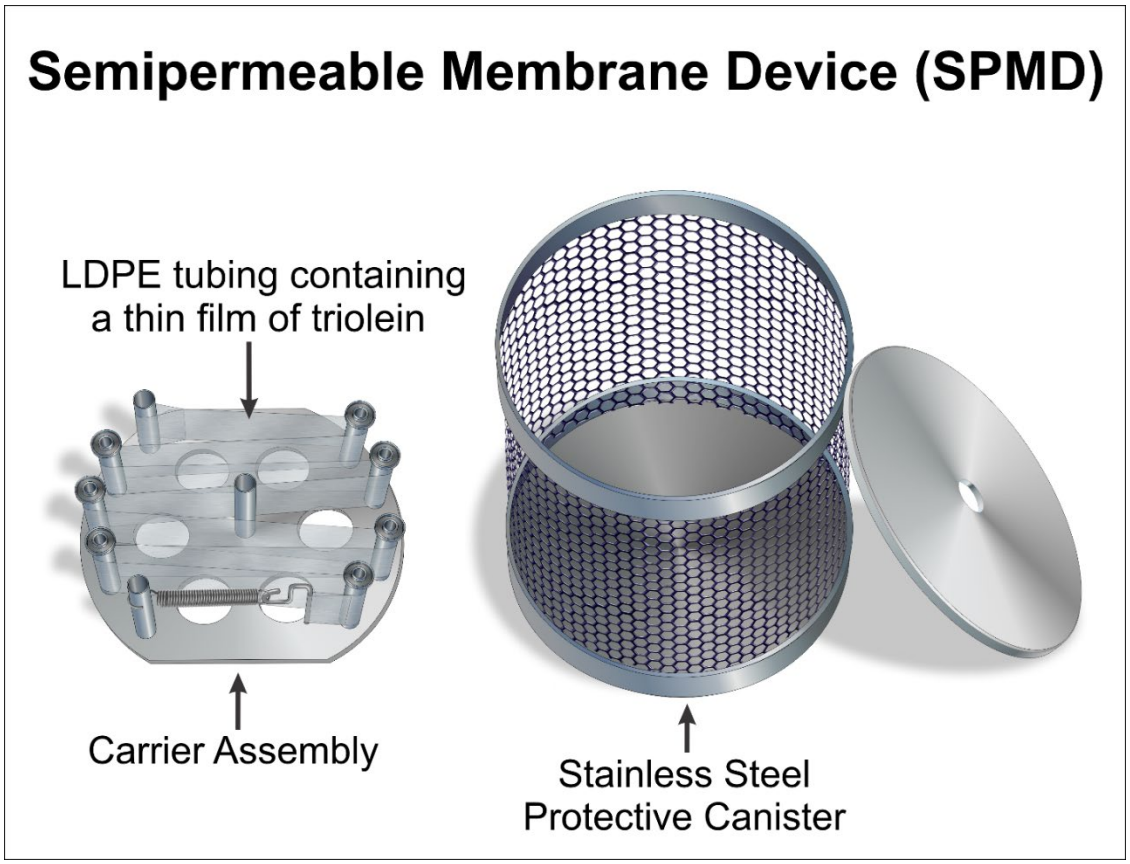


Figure 5- 31 shows the SPMD carrier assembly and triolein film. Photo obtained from Masa Kanematsu, used with permission.

Figure 5- 32 shows the SPMD carrier assembly inside the protective cannister. Photo obtained from Masa Kanematsu, used with permission.

Figure 5- 33 shows a SPMD device put together before deployment. Photo obtained from Masa Kanematsu, used with permission.

5.3.4.2 Installation and Use

Compound Specific Information

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

- SPMDs must remain submerged in water, but not buried in the sediment during the whole deployment period. It is important to keep SPMDs shaded to prevent photodegradation of some light-sensitive chemicals such as PAHs.

5.3.4.3 Advantages

- SPMDs provide data as a time-weighted average concentration of a chemical within the whole deployment period (D. A. Alvarez 2010).
- 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 low-density polyethylene (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), and 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.

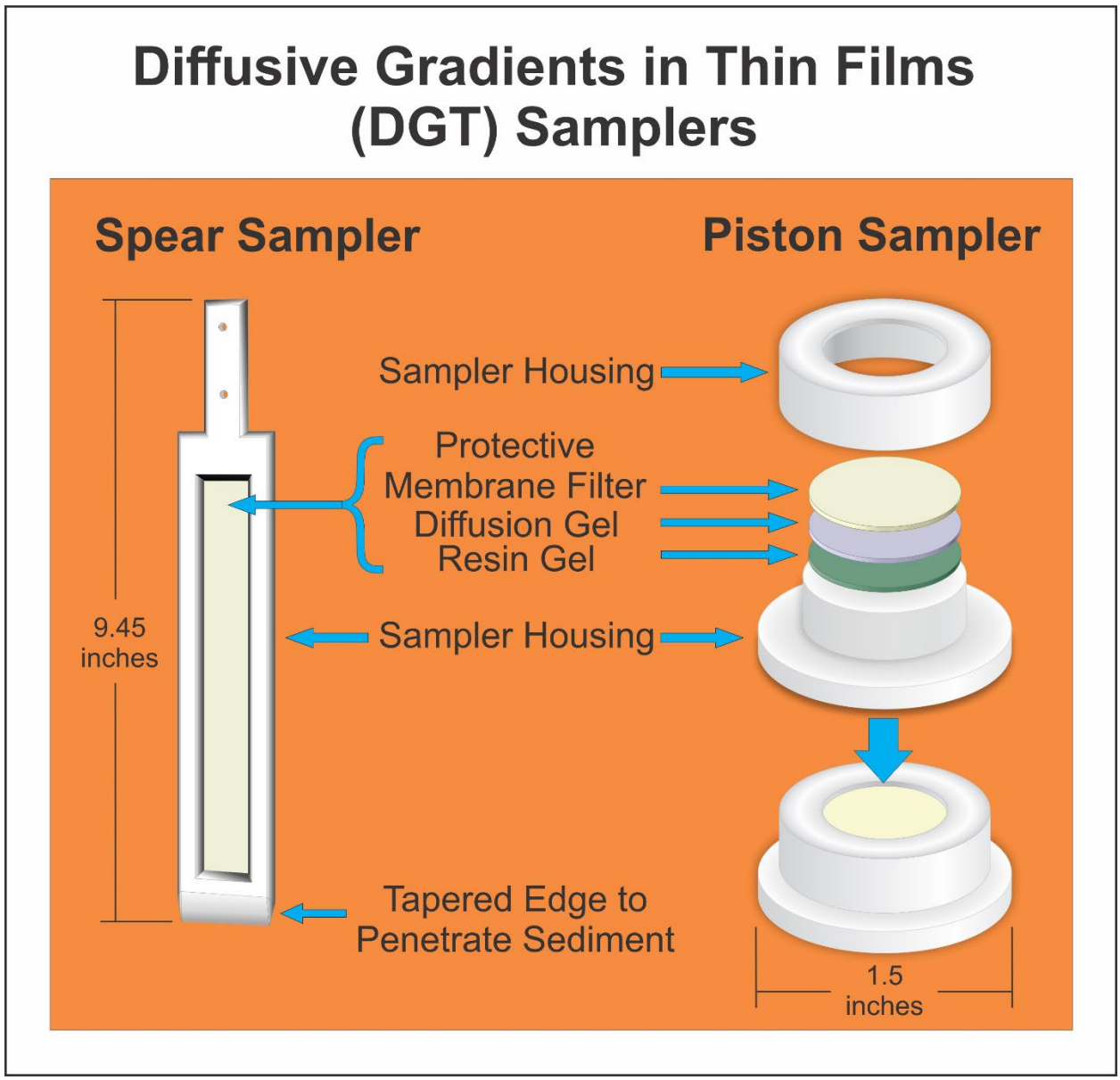
5.3.5 Diffusive Gradient in Thin Films (DGT) Sampler

5.3.5.1 Description and Application

Diffusive Gradient in Thin Films (DGT) are designed to sample dissolved inorganic species in aqueous environments, including sediment/soil porewater, surface water, and groundwater. Since the first development by the researchers at Lancaster University in 1994, the DGT technique has been altered and expanded to include a large number of chemicals including heavy metals, inorganic nutrients, oxyanions, and radionuclides. The DGT usually comprises three successive layers of material held together by a plastic housing. The outer layer is an organic membrane filter that permits only dissolved inorganic species to interact with the gels and protects the gels inside, while also preventing influence from surrounding hydrodynamic fluctuations. Below the organic membrane filter is a diffusion polyacrylamide hydrogel of a known thickness, through which the inorganic species diffuse at a known rate. Below the diffusion gel is a binding gel that reacts with the inorganic species diffused through the diffusion gel and serves as a solute sink. Because the binding gel accumulates a target solute over time, DGTs can achieve better detection limits after longer deployment times (greater than 24 hours). Diffusion kinetics in the diffusion hydrogel are well established for many inorganic species, and a concentration of a target chemical at the surface of the DGT can be calculated from the mass of the solute accumulated to the binding gel (U.S. EPA/SERDP/ESTCP 2017). The pore sizes of both the organic membrane filter (typically 0.45 μm) and the hydrogel effectively exclude inorganic species associated with particulates and colloids. Therefore, DGT is a suitable technique for in-situ evaluation of labile fractions and by approximation, bioavailability of inorganic species in aqueous environments.

DGT binding gel can be saturated when deployed for long duration, which does not allow use of the linear diffusion assumption and once saturated, no longer to be used for a quantitative sampling.

Figure 5- 34: used with permission from NJDEP.



5.3.5.2 Installation and Use

DGT sampler use, and construction can vary by media including deployment in solid phase (dry soils, sediment) and liquid phase (groundwater/surface water). The device configuration and type (examples include piston-type samplers for dry soils and flat-type probes for sediment) will depend on the environment, deployment strategy, and properties of the monitored media. Inserting a DGT sampler by hand into solid material

(pressing) may alter soil characteristics such as density and soil layer thickness, which may result in altered results (Li et. al. 2019). The use of 'flat-type' and dual-mode DGT devices can reduce the effects induced by traditional DGT samplers and have been utilized for measurement of solutes including metals (Li et al. 2019). Liquid-phase units are most similar to the 'piston-type' arrangement, with the binding agent and diffusion membrane housed on a base, similar to the diagram above.

More than two dozen binding agents have been documented (Li et al. 2019) for various target chemicals including metals, radionuclides, nutrients, pesticides, PFAS, antibiotics, and other organic chemicals. Diffusive phase agents also vary by application. Each deployment configuration shares the general components of a binding agent and diffusion layer housed within a protective casing that may be constructed of plastic, metal, or other materials.

Sulfide measurement in sediment porewater by the DGT technique has been shown to be very effective in contrast to active porewater collection, in which oxygen may be introduced.

The DGT techniques have been well used in academic research to measure "bioavailable" fraction of dissolved inorganic compounds such as metal and nutrients. The DGT technique has been well established for hydrophobic organic chemicals. The DGT techniques have been recently studied to measure PFAS in the aqueous phase.

5.3.5.3 Advantages

- Low detection limits can be achieved since the binding gel accumulates solute over time.
- Allows in situ evaluation of labile fractions and by approximation, bioavailability of inorganic species in aqueous environments.
- A probe-type DGT can be inserted into the sediment or soil vertically to assess the vertical profile of a target chemical with sub-mm high resolution.

5.3.5.4 Limitations

- The diffusion kinetics of a chemical can be influenced by competing solutes and biofilm development after longer deployment.
- Laminar flow can influence the diffusive boundary layer in fast-flowing waters.

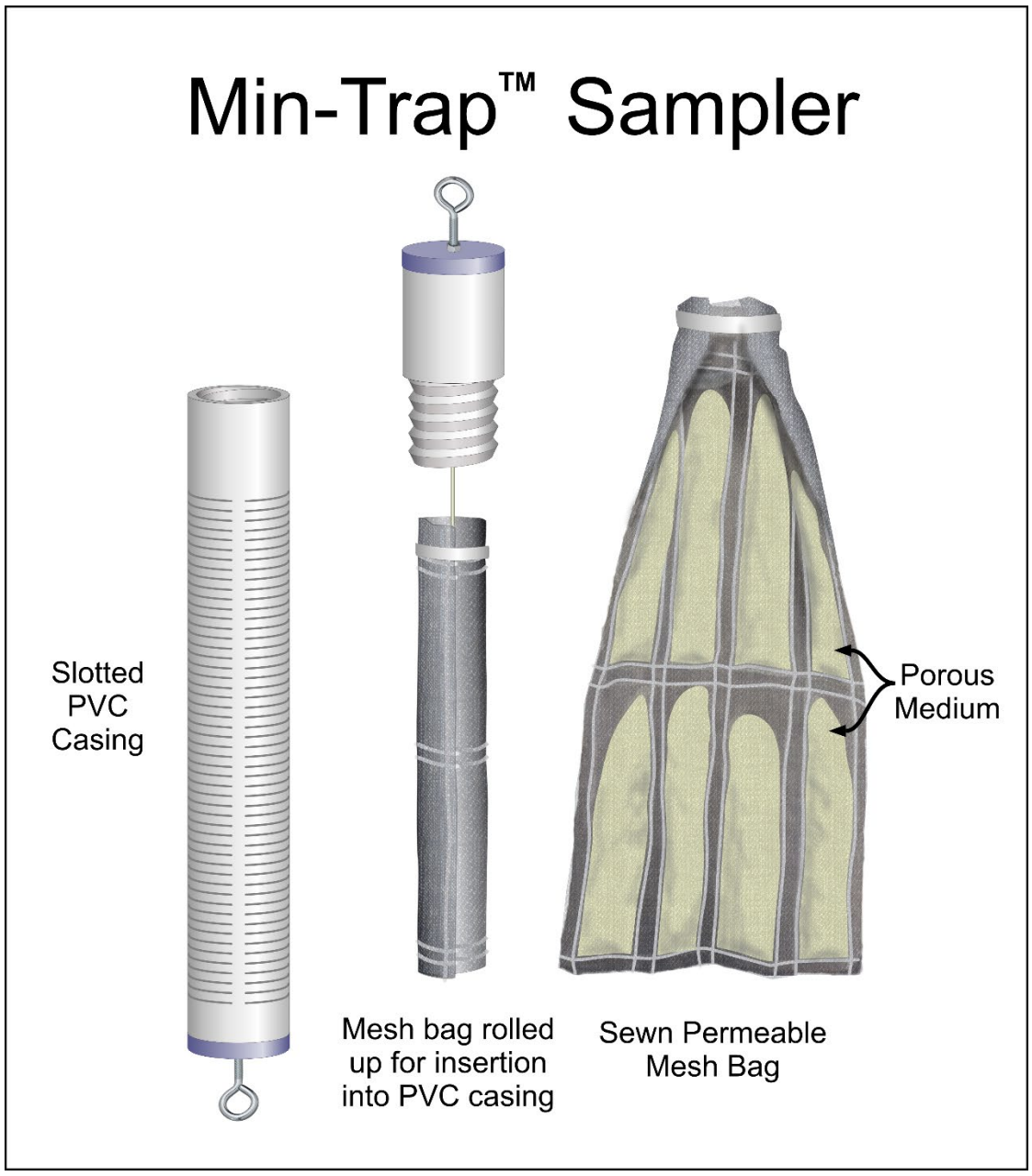
5.3.6 Mineral Sampler (Min Traps ®)

5.3.6.1 Description and Application

The Min-Trap® 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 non-reactive medium (e.g., silica sand), a reactive medium (e.g., 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 slotted polyvinyl chloride (PVC) casing. The standard Min-Trap has a non-reactive medium that provides a carrier substrate where target minerals can form passively (Tilton and Gentile 2019). 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 (Divine et al. 2020a). 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 (e.g., 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).

Figure 5- 35: used with permission from NJDEP.



5.3.6.2 Installation and Use:

Virtually any in-situ remediation strategy that results in either 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 chlorinated volatile organic compounds (CVOCs), which is often a target mechanism for in situ chemical reduction (ISCR) and enhanced reductive dichlorination (ERD) 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. (2023a,b) 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.

At the conclusion of the deployment period, the Min-Trap is retrieved from the well, the housing opened, and the media "pillows" 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 (e.g., 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. (2023a).

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, FeS2) minerals using the Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) suite [Kennedy et al. 2004]); 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 weight percent).

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 (e.g., FeS, FeS2) 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 an MNA 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 (i.e., "false negative") is the most likely limitation and could be the result of inadequate deployment times and/or elevated mineral detection limits (e.g., typically >1 weight percent 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 through the use of 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 (i.e., iron sulfides) during sampling and short-term storage (Ulrich et al. 2021).

5.3.7 Radiello Sampler

5.3.7.1 Description and Application

Radiello are a trade name of cylindrical, concentration gradient-reliant samplers originally developed by Fondazione Salvatore Maugeri (Padova, Italy) and distributed by Supelco Analytical (Atlanta, Georgia, 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 (cartridge adsorbent) inserted into a protective housing that allows for air diffusion (diffusive body). Several different cartridge adsorbents are available for different classes of compounds. Compounds that can be sampled include over 70 VOCs, including BTEX, aldehydes, 1,3-butadine and isoprene, phenols, ozone, ammonia, nitrogen and sulfur dioxides, hydrogen sulfide, hydrochloric acid and hydrofluoric acid.

Figure 5- 36: used with permission from NJDEP.

5.3.7.2 Installation and Use

The minimum requirements of the system include cartridge adsorbent, diffusive body, adhesive labels for sample tracking, 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 pre-assembled adaptor and support plate. Available optional accessories include outdoor shelter and in-field thermometer and reader.

Prior to sampling, the adsorbent cartridge is transferred from storage container into an appropriate diffusive body, then it is screwed onto the 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 table below, from product manual) and can comprise of a pure adsorbent material or a chemically coated support. 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 (shown in figure above). 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 4-5 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 polyethylene bag after sampling before desorption/analysis. The cartridges are desorbed for analysis by chemical (solvent) or thermal extraction, depending on the specific cartridge. While 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

- These sampling systems are relatively cost effective. At the time of this guidance development, a package of 20 cartridges specific for detection of BTEX and VOCs detection with thermal desorption (RAD 130) cost $1490 while a package of 20 cartridges for detection of BTEX and VOCs for carbon disulfide desorption (RAD145) cost $391. The hardware is reusable (e.g., triangular support plate).
- These sampling systems are convenient to use, compact in size, lightweight, and portable. The system requires no supervision, limited technical training to set up and deploy samplers, are non-flammable, require no energy input for operation, and are noiseless.
- The radial design of the Radiello allows air-borne analytes 360° access to the diffusive surface and adsorbent material, resulting in a significantly higher uptake rate and faster sampling compared to traditional 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 protects the sampler from unfavorable weather conditions.

- Different adsorbents may be used to broaden the application scope of the Radiello system. Higher sampling volumes, greater adsorbent capacity, and higher uptake rate contribute to minimal reverse diffusion and greater uptake rate consistency, which results in highly reproducible results.
- Uptake rates are the amount of a chemical absorbed 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, along with lower detection limits, allow sampling time from 15 minutes to weeks or months (1ppb – 1000 ppm). The time-integrated nature of passive sampling gives an average concentration over a specific sampling period, for example, over a 24 hour or 2-week period.
- The Radiello system predominantly uses solvent/chemical desorption, and therefore does not require thermal desorption equipment. Thermal desorption and Gas chromatography/Mass Spectrometry (GC/MS) systems are also available for precise and very sensitive measurements.

5.3.7.4 Limitations

- Uptake rates can also be obtained by comparison to experimental measurements by other sampling methods (e.g., active sampling or real-time monitoring instruments) or to theoretical models. In a review study, Lutes et al. (2010) compared both thermal 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. They also reported poor agreement between Radiello samplers and TO-15 samples for polar compounds.
- 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, precise 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 Saborit and Cano (2007) 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. 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.

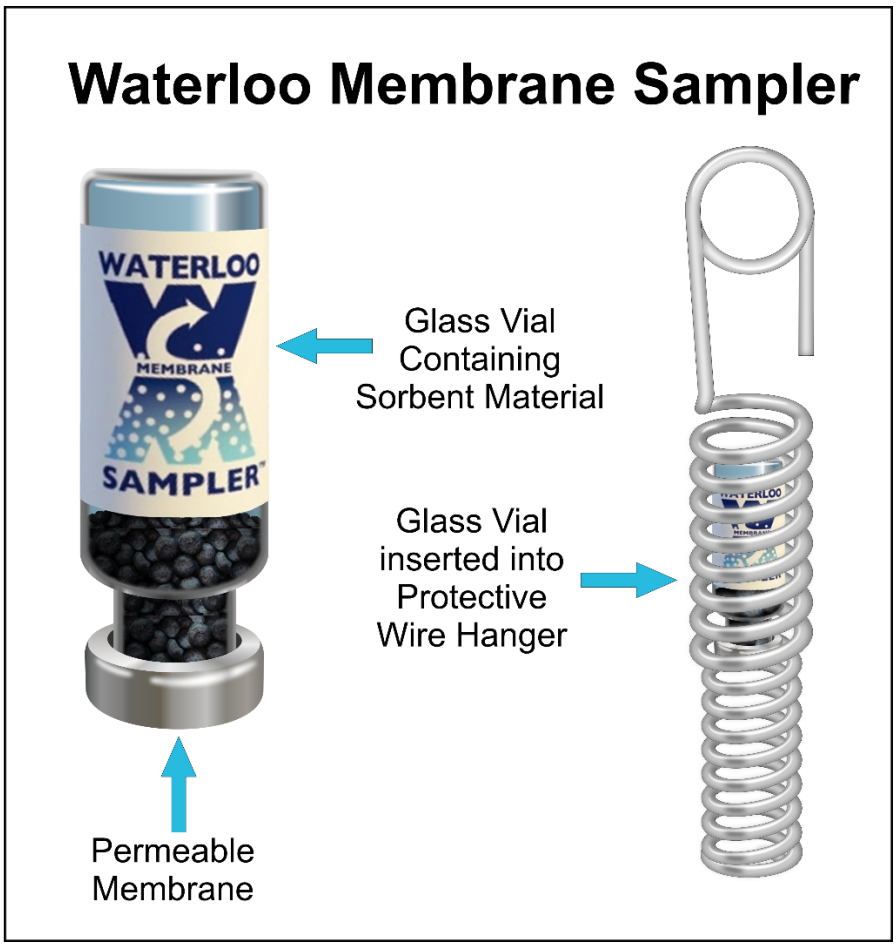
- Passive uptake of a chemical from media is only linear (constant uptake rate) when the concentration of the chemical on the sampler is low. The uptake rate slows as the chemical concentration on the sampler increases and approaches equilibrium. There is no net uptake onto the passive sampler when the sampler reaches equilibrium.
- Another review (Wania and Shunthirasingham, 2020) of passive air sampling of semi-volatile organic compounds (SVOCs) suggested that the Radiello diffusive bodies made of polyethylene is itself capable of adsorbing SVOCs and interfere 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.
- Overall, the smaller air volumes sampled by passive sampling results in higher detection limits compared to active sampling methods.

5.3.8 Waterloo Membrane Sampler (Solvent-extracted)

5.3.8.1 Description and Application

The Waterloo Membrane Sampler™ (WMS™) is a "tube-syle 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 (EPA 2014). 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). Solvent extraction laboratory preparation methods result in lower analytical sensitivity but longer sample duration than thermal desorption methods with higher analytical sensitivity but shorter sample duration. Volatile organic compound (VOC) vapors permeate through the PDMS membrane and are trapped by the sorbent medium. 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 uptake rates for many common VOCs.

Figure 5- 37: used with permission from NJDEP.



5.3.8.2 Installation and Use

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

The sampler is shipped in a thermally sealed polycoated aluminum pouch and should not be opened until the sampler is ready for use (Figure 5-37(Fig. 1)) 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 ten feet) to help with deployment (c), and Teflon™ tape for re-sealing the glass vial once the sample has been collected (c) (Figure 5-37(Fig. 2)) (SiREM Lab, n.d.).

Figure 5- 38 obtained from SiREM Labs, used with permission.

Figure 1: WMS™ sampler shipping pouch

Figure 2: Contents of sampler shipping pouch

Do not store/use WMS™ samplers near volatile chemical sources including perfume, felt markers, etc. and avoid touching the WMS™ sampler membrane (Fig 3).

Figure 5- 39 obtained from SiREM Labs, used with permission.

Figure 4: WMS™ sampler inside 20 mL glass vial

Figure 5: Aligning WMS™ sampler in wire hanger

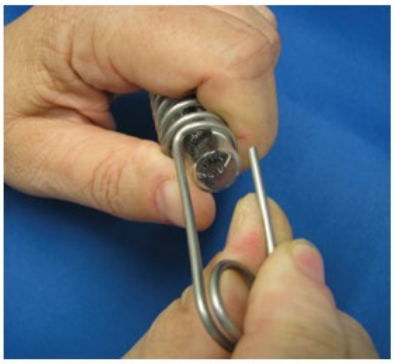


Figure 6: Bending wire to insert WMS™ sampler

After removing the sampler from the glass vial (Figure 5-38$_{(Fig. 4)}$), position the sampler upside down (Figure 5-38$_{(Fig. 6)}$) and insert into the wire hanger (Figure 5-38$_{(Fig. 6)}$). 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 downwards (Figure 5-38$_{(Fig. 7)}$) (SiREM Lab, n.d.). Once sampling is complete, remove the sampler from the wire hanger (Figure 5-38$_{(Fig. 8)}$). 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 5-38$_{(Fig. 9)}$) (SiREM Lab, n.d.).

Figure 5- 40 obtained from SiREM Labs, used with permission.

Figure 7: Deployed WMS™ sampler with line

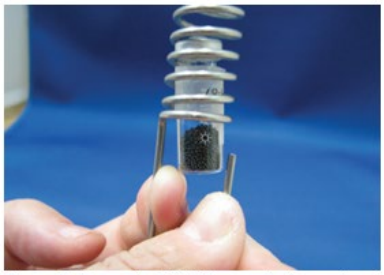


Figure 8: Removing WMS™ sampler from wire hanger

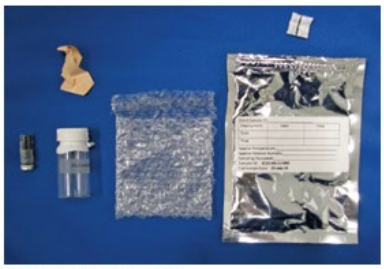


Figure 9: Re-packaging

5.3.8.3 Advantages

- Easy to use with simple sampling protocols without specialized training.
- Very small size (discrete to deploy and easy to ship).
- Leaks in sampling train not a concern compared to active sampling methods.
- Can effectively handle ranges of moisture and VOC concentrations commonly found in the subsurface.
- Insensitive to wind velocity (beneficial for outdoor and vent-pipe monitoring).
- Ability to modify configurations to lower uptake rates to avoid the "starvation effect" when collecting soil gas samples, and to allow for quantitative soil gas sampling in a range of subsurface soil moisture or permeability conditions.
- Better analytical sensitivity to provide lower reporting limits then conventional canister samples.
- Longer time-integrated samples (several days to weeks) to provide more representative results.

- Ability to measure a broader range of VOCs than conventional canisters.

5.3.8.4 Limitations

- Starvation effect where the sampler removes VOC vapors from the subsurface soil gas faster than they are replenished due to low soil air permeability.
- Saturation of sampler due to exposure to high chemical concentrations over extended period of time.
- Competition between strongly adsorbing VOCs displacing less strongly absorbed VOCs.
- Poor retention from use of weak sorbents resulting in back-diffusion losses.
- Poor recovery from use of strong sorbent with strongly sorbed compounds that are not completely released from the sorbent during analysis (McAlary 2015)
- Unplanned uptake of chemicals during shipping and storage.
- Requires calculations to convert sample concentrations from mass to volume to report to a regulatory agency.

5.3.9 Beacon Sampler

5.3.9.1 Description and Application

Beacon Samplers 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, including sewer gas. 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 (EPA 2014). The concentration gradient from the surroundings to the sorbent provides the driving force for diffusion of VOC vapors into the sampler.

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 states in EPA 2014, the average concentration over the sampling period can be calculated as follows:

Equation 3

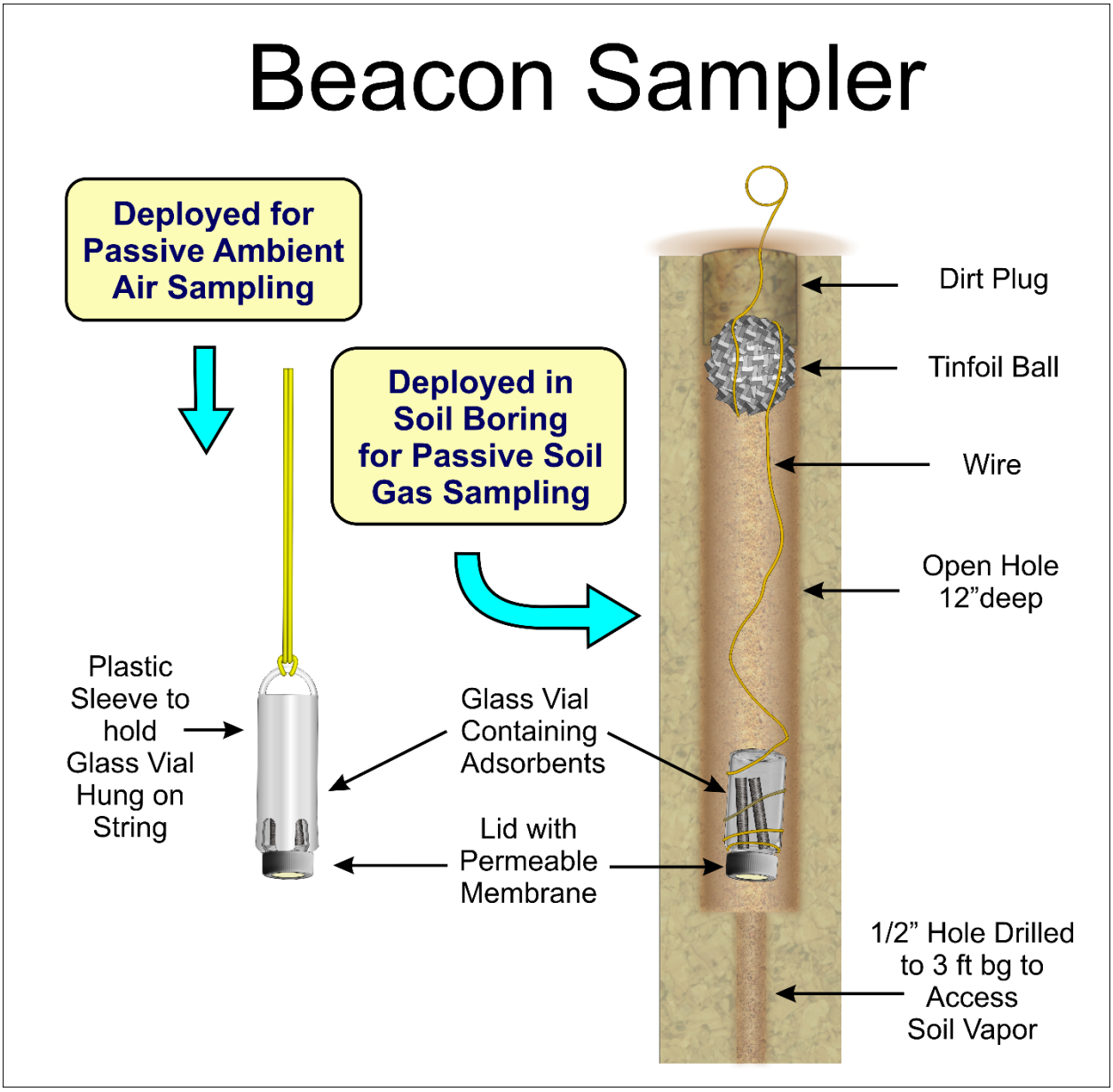
$$C = M / (UR \times t)$$

Where:
C = time-weighted average air concentration (µg/m3)
M = mass of VOC retained by passive sampler (pg)
UR = uptake rate (mL/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 EPA Method 8260D, TO-17, 325B, or TO-15 (O'Neil 2019). Accordingly, the uptake rate (sampling rate) is the most critical variable for accurately determining air concentrations when using any passive samplers (EPA 2014).

Uptake rate has units of volume/time, but it is not a flow rate. It is however equivalent to the flow rate that would be necessary for a pumped adsorptive sample to sorb the equal mass of a target chemical, with equal sample duration times, when exposed to the similar chemical concentration (U.S.EPA, 2014).

Figure 5- 41: used with permission from NJDEP.



5.3.9.2 Installation and Use

Passive soil gas (PSG) sampler

Beacon PSG samplers can be installed to various depths depending on the project objectives. A standard approach involves drilling a 1 ½-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 ¼ inch concrete patch. As an option, a mechanical plug can be used

to seal the hole through impervious surfacing during the sampling period and between sampling events.

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) one of the Beacon samplers (a glass vial containing two sets of hydrophobic absorbent 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.

Chlorosorber passive sampler

The ChloroSorber sampler targets a range of chlorinated compounds from vinyl chloride to tetrachloroethene with low-level detection limits in air or sewer gas. Follow the installation instructions on Beacon website. 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 absorbed 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. 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 sampler is returned to Beacon for analysis following analytical procedures described in U.S. EPA Method TO-17 and TO-15. The holding time from sample collection until analysis is 30 days.

5.3.9.3 Advantages

- Time-weighted average (TWA) concentrations of VOCs are collected over days or weeks to provide time intergraded measurement and provide an average measurement over an extended sampling period. There are no pumps or vacuums used so the reported measurement represents a concentration under ambient conditions. The sampling protocols are simpler than the traditional sampling methods, which reduces the cost of sampling and risk of operator error.
- Quantitative uptake rates were experimentally determined and validated for the Beacon Sampler and ChloroSorber in a third-party study which included other passive samplers with known uptake rates as a reference and were 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 (MDHS) are the source of most of the published uptake rates in the relevant international standard methods (e.g., ISO 16017-2)3. 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.
- Simple application and installation. All materials for sampling procedures are provided in a well-organized sampling kit.

- Analyses of all samples is completed by Beacon Environmental following US EPA Methods and DoD ELAP and/or NELAP accredited procedures.

5.3.9.4 Limitations

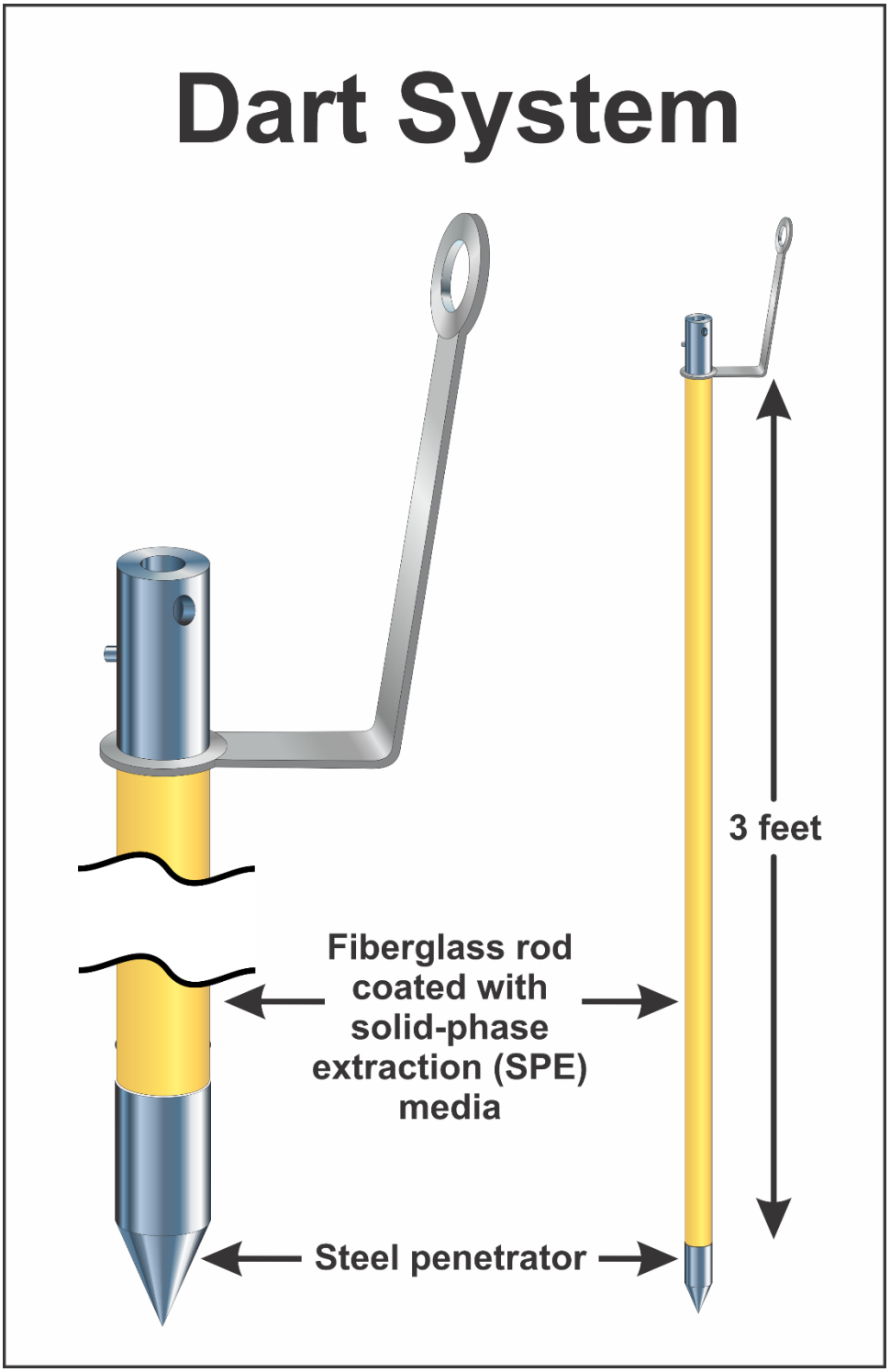
- The detection limits are based on the sampling duration and extended sampling periods may be required (e.g., 14 days)
- Only 13 chlorinated VOCs were tested in the laboratory for validated uptake rates, and Graham's Law of gas diffusion is used to calculate the uptake rates for other VOCs. However, all chlorinated compounds targeted by the ChloroSorber were included in the uptake rate study.
- Sample analysis is performed exclusively by Beacon Environmental's accredited laboratory. Third party analysis is not available.

5.3.10 Dart Sampler

5.3.10.1 Description and Application

The Dart sampler is used to delineate an area of interest for polycyclic aromatic hydrocarbons (PAHs) in sediments and similar soft soils. The technology is deployed when traditional mechanized sampling (like laser-induced fluorescence (LIF), traditional soil borings, etc.) are limited by site constraints, potentially unsafe or impactable for mechanized sampling. This technique applies to PAHs that exist as a component of non-aqueous phase liquids (NAPL) in sediments, not the dissolved phase. Accordingly, the Dart sampler is especially useful for high-resolution NAPL characterization at sites that can generally be difficult and expensive to profile NAPLs, like shorelines, marshes, shallow bodies of water adjacent to refineries, or former MGP or creosote sites. The Dart sampler contains a rod coated with a non-fluorescing solid-phase extraction (SPE) media, which is also used in labs for EPA-approved cleanup and pre-concentration of PAHs in traditional grab samples ("Darts," n.d.). The technique relies on the fluorescing property of PAHs that have sorbed into the SPE material under excitation by ultraviolet laser light.

Figure 5- 42: used with permission from NJDEP.



5.3.10.2 Installation and Use

The Darts are driven 1 to 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 to 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're stored in solid solution and remain contained there almost indefinitely without the need for refrigeration.

The Darts are processed through an LIF reader by Technicians at Dakota. The LIF and Dakota's ultraviolet optical screening tool (UVOST) are very similar ("Darts," n.d.). 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) vs. depth, typically at very high resolution (>100 readings/ft) to "read" the sorbed PAHs' fluorescence along the Darts entire length and circumference ("Darts," n.d.). 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 of the graphical log and high-resolution data files.

5.3.10.3 Advantages

- Samples don't require ice or low temperature storage after collection.
- No waste disposal of soil or groundwater.
- Data is digitized.
- Provides location and depth specific NAPL verification and characterization.

5.3.10.4 Limitations

- Lighter end LNAPLs such as kerosene and gasoline don't 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 (%reference emitter)) cannot be directly converted to concentration levels unless a calibration study of site-specific NAPL on site-specific sediment is conducted.

5.3.11 Fossil Fuel (CO2) Traps

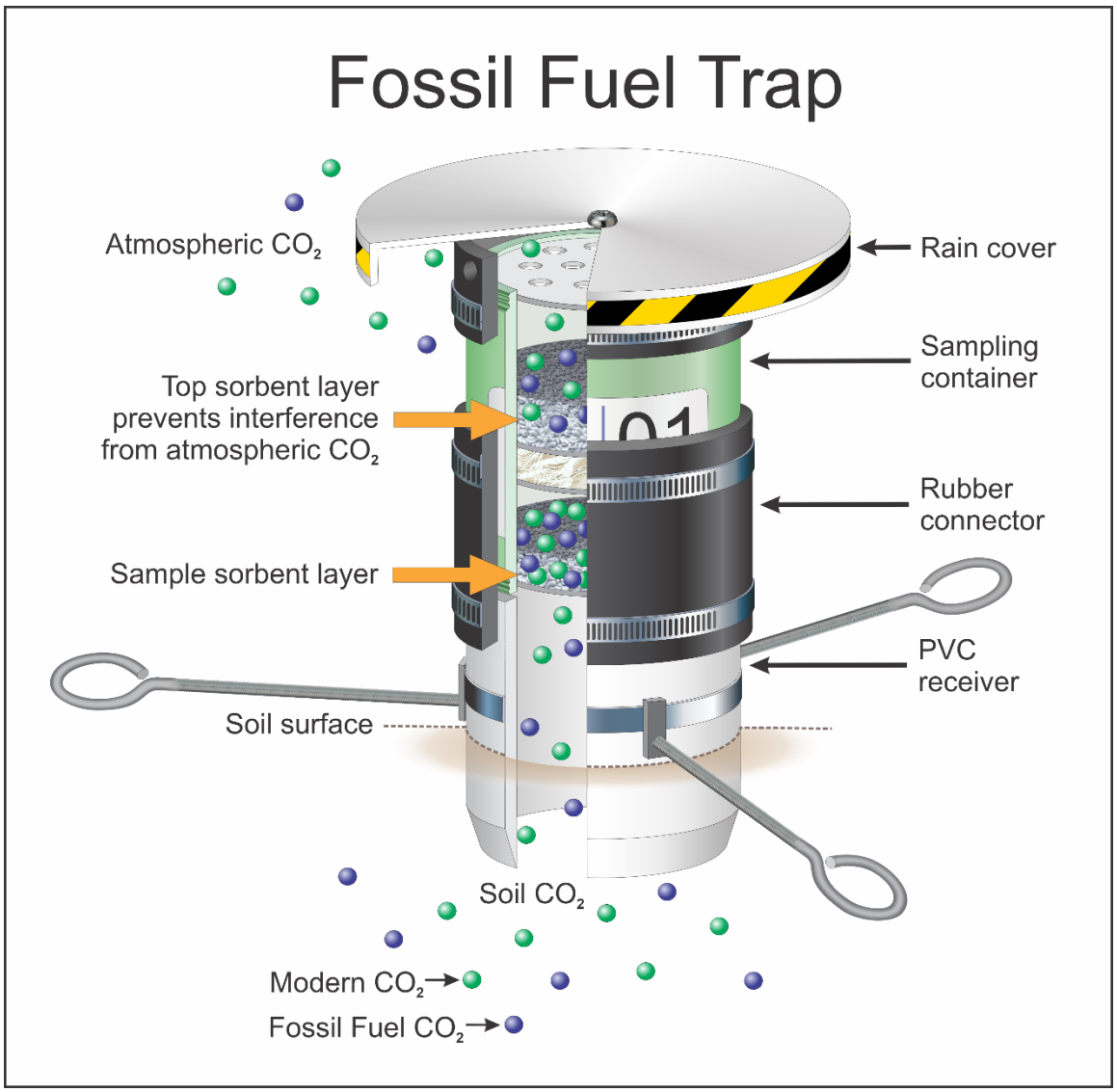
5.3.11.1 Description and Application

Fossil Fuel Traps (also known as CO2 Traps) are at-grade passive samplers that measure time-integrated CO_2 fluxes through the surface at petroleum-contaminated sites. CO2 Traps are patented cannisters that contain a strongly basic solid-state sorbent material, which converts the CO2 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 CO2 flux rates are then used to determine the rate of naturally occurring biodegradation of light non-aqueous phase liquid (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_2 traps have two layers of sorbent. The first layer, at the top, captures ambient CO_2, which eliminates ambient interference in the bottom sorbent. The second sorbent layer is at the bottom and absorbs CO_2 released from the soil. Since the fossil fuel trap is open to the atmosphere and the CO_2 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 (CO2 Traps) – a Passive Soil Gas Sampling Method.," n.d.). CO2 does not build up in the head space of the fossil fuel trap because it is open to the atmosphere and the CO2 absorbs into the sorbent. Consequently, gas flow and the diffusion gradient are unaffected. Modern CO_2 contributions (i.e., from natural soil respiration processes) can be significant and need to be subtracted from the net CO_2 flux measurement before an accurate biodegradation rate can be estimated. In some contexts, modern CO_2 contributions (i.e., from natural soil respiration processes) can be significant, requiring consideration for estimating an accurate biodegradation rate. Under these conditions, the modern CO_2 contributions would be subtracted from the net CO_2 flux measurement ("Fossil Fuel Traps (CO2 Traps) – a Passive Soil Gas Sampling Method.," n.d.). However, to eliminate this modern carbon interference, every bottom layer of the sorbent is precisely analyzed for its radiocarbon (^{14}C) content (ASTM D6866-18) ("Fossil Fuel Traps (CO2 Traps) – a Passive Soil Gas Sampling Method.," n.d.).

Figure 5- 43: used with permission from NJDEP.



5.3.11.2 Instillation and Use

The use of a CO2 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 (CO2 Traps) – a Passive Soil Gas Sampling Method.," n.d.).

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_2 and petrogenic CO_2 via unstable isotope analysis (14C radiocarbon dating). The unstable isotope 14C 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 CO2 flux estimation than can reasonably be accomplished via other CO_2 flux methods. The CO2 flux is then converted to a depletion rate by multiplying by an appropriate stoichiometric ratio, which describes the mass relationship between CO_2 and the specific LNAPL compound of interest. Measuring the total CO_2 flux over an extended period gives a time averaged estimate of the soil CO_2 flux. This extended period also accounts for temporal variability including atmospheric pressure fluctuations and weather changes.

5.3.11.3 Advantages

- Do not require power, so can be deployed in remote locations.
- Easy to use and can be installed by local site personnel without specialized training.
- Can produce time-integrated average flux measurements, accounting for diurnal and daily fluctuations.
- Capable of ^{14}C analysis to differentiate fossil fuel-generated CO_2 from modern CO_2 interference, providing location-specific background correction ("Fossil Fuel Traps (CO2 Traps) – a Passive Soil Gas Sampling Method.," n.d.).

5.3.11.4 Limitations

- Cannot be used in areas with impermeable surface cover that limits atmospheric-soil gas exchange (e.g., asphalt, concrete, or other liners).
- Saturated soil (due to recent high precipitation events) can hinder CO2 mobility to the surface, thus biasing the results from this method low.
- May not be valid at sites where 14C-enriched chemicals have been used or sites in the vicinity of nuclear reactors or waste.
- Higher cost than other CO2 flux methods, which may limit the number of traps used at a site.

5.3.12 Bio-Trap Samples

5.3.12.1 Description and Application

Bio-Trap® Samplers are passive samplers that collect microbes over time to better understand biodegradation potential ("Bio-Trap Samplers," n.d.). Bio-Sep® beads, a unique sampling matrix, are key to the technology's approach. The beads are 2–3 mm in diameter and are constructed from a composite of Nomex® and powdered activated carbon (PAC) ("Bio-Trap Samplers," n.d.).

Figure 5- 44: used with permission from NJDEP.

5.3.12.2 Instillation 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 m2/g) that is colonized by subsurface microorganisms ("Bio-Trap Samplers," n.d.).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 PLFA can be extracted from the beads for qPCR, QuantArray or PLFA assays to evaluate the microbial community ("Bio-Trap Samplers," n.d.). The Bio-Trap is able to produce results that can be integrated over time rather than from a single sampling event ("Bio-Trap Samplers," n.d.). Numerous Bio-Trap samplers can be confined from one another using a double seal cap assembly.

5.3.12.3 Advantages

- Integrated view rather than a snapshot.

- Organisms colonize the traps in situ selecting for active processes.
- Can be analyzed with any molecular tool.
- Strong adsorptive capability.
- Versatile

5.3.12.4 Limitations

- Organisms must actively colonize the trap so it may miss low concentration processes or organisms.
- Must leave in the monitoring well for at least 30 days. Need two trips to the field for deployment and retrieval.

6. NON-PASSIVE GRAB SAMPLING TECHNOLOGIES

The following technologies do not meet the technical definition of a passive sampler in this document. 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 since 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 data quality objectives are their respective projects, where a truly passive grab sample is not required.

Table 6- 1: Non-Passive 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		●							

6.1 Syringe Sampler

6.1.1 Description and Application

Syringe samplers 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. While 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 sample for dissolved metals analysis.

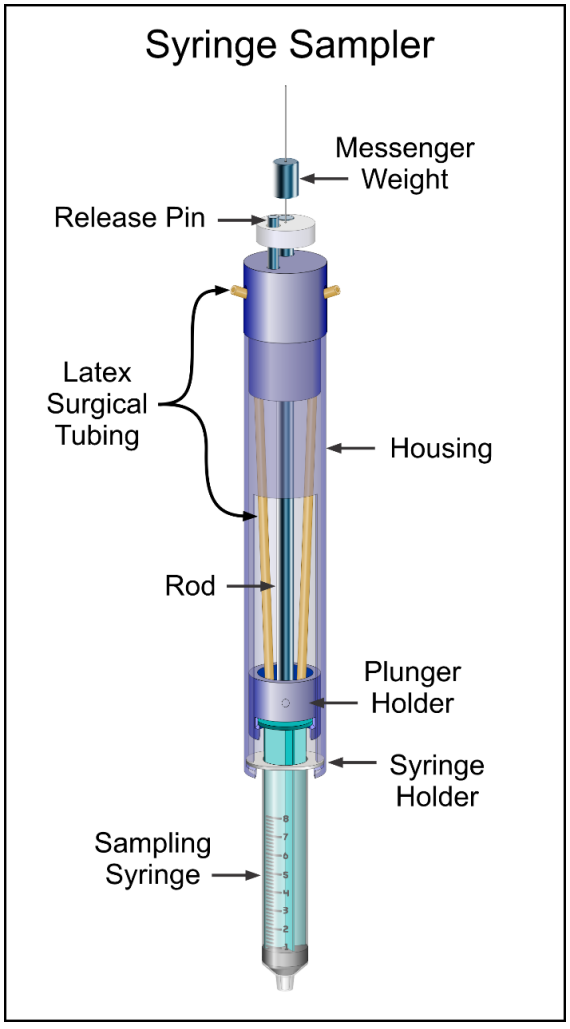
The device is constructed of different materials including stainless steel and glass components, or high-density polyethylene (HDPE). Devices constructed with those materials can be used multiple times following decontamination. Another sampler is of

polycarbonate material and can only be used once (NJDEP 2022). The samplers are designed to be compatible with standard off the shelf medical syringes of varying volumes (NJDEP 2022). 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 attempting to collect a discrete, non-purged sample (NJDEP 2005). This is markedly true when gathering an undisturbed aliquot of nonaqueous phase liquid (NAPL) from a well or targeting a zone for field analytical measurement (NJDEP 2005). 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.

Figure 6- 1: used with permission from NJDEP.



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 again to sample.

6.1.3 Advantages

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

6.1.4 Limitations

- Difficulty in collecting quality assurance samples.
- Use of this device might require regulatory guidance.

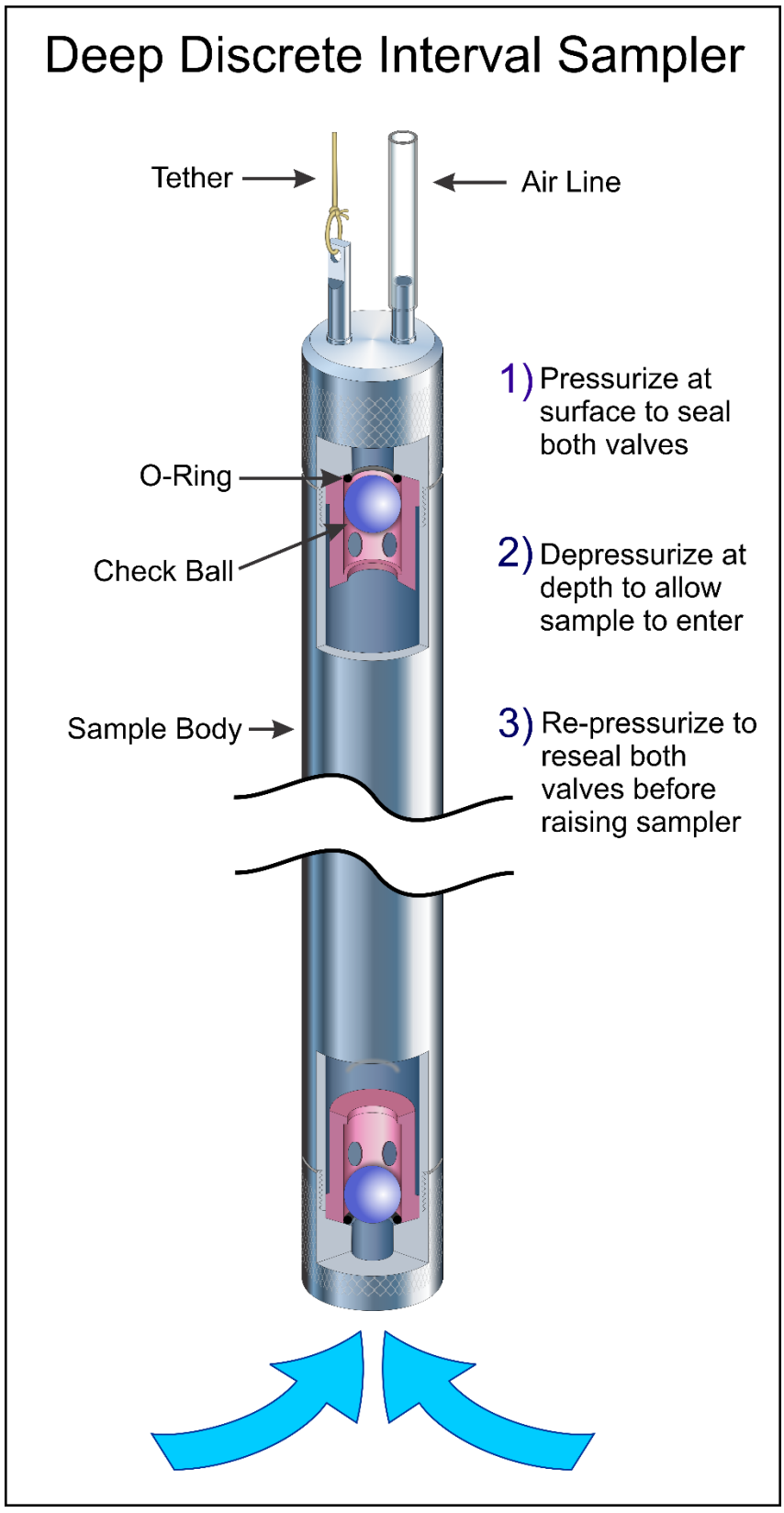
6.2 Deep Discrete Interval Sampler

6.2.1 Description and Application

The Model 425 Discrete Interval Sampler (DIS) 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 can is a no-purge sampler that samples all chemicals including (e.g., VOCs, metals, field parameters, etc.) and can also 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, which 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. There are three sampler diameters available, 1”, 1.66” and 2”, 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 over 100 feet.

Figure 6- 2: used with permission from NJDEP.



6.2.2 Installation and Use

The DIS is pressurized before being lowered, to prevent water from entering the sampler, in order to obtain a sample. 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. The DIS can be used to sample all common chemicals including but not limited to the following: VOCs, semi-volatile organics, metals, major cations and anions, dissolved trace metals, dissolved sulfide, dissolved gases (methane/ethene/carbon dioxide), field parameters, Hex Cr, Oxygenates, MTBE, explosives, and perchlorate.

6.2.3 Advantages

- Effective for collecting water samples of any type of chemicals.
- Discrete sampling in wells, boreholes, and open bodies of water.
- Collect samples from a narrow depth range with no movement of the sampler position during collection.
- Sample has not been pumped through tubing.
- Minimal water disturbance.
- Easy to disassemble for decontamination.
- Avoids purging and disposal of purge water.
- Reduced cost and time to retrieve samples.
- No gas or electricity required for operation.
- Easy operation and transportation.

6.2.4 Limitations

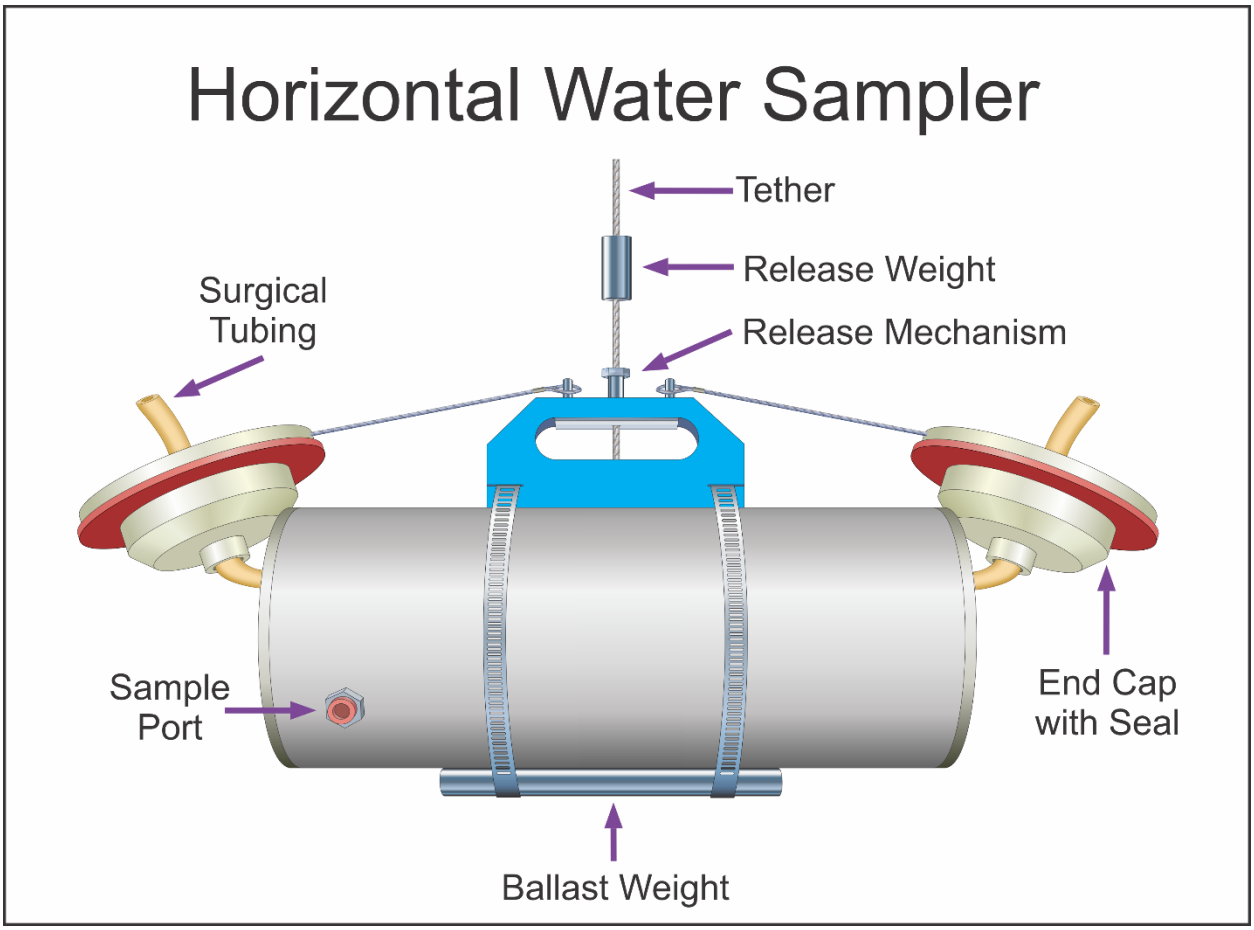
- Discrete interval Samplers are designed to sample in wells larger than 1” in diameter, with no upper limit to well diameter that can be sampled. DIS can also be used to sample from open bodies of water.
- Sampling depth may be a limitation. The Standard Model 425 Discrete Interval Samplers can sample to depths of 300 feet (90 meters) below water level, regardless of total depth from surface (“Discrete Interval Samplers: Model 425 & 425-D Data Sheet” 2021).
- Collects 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) 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 have a tube with varying diameter and lengths with a sealable end cap. The dimensions of the sampling device control the volume of water being sampled. The sampling devices can be made of varying materials that need to be considered based upon the chemicals 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: used with permission from NJDEP.



6.3.2 Installation and Use

Horizontal Surface Water Interval Sampler is a surface water no purge sampling device. The sampling devices have a water collection tube, sometimes referred to as a bottle or chamber by different manufacturers, with varying diameter and lengths with a sealable end cap(s). The dimensions of the sampling device control the volume of water being sampled. There are different options provided by different manufacturers on the materials that the bottle/tube is made of and some variation in sampling device sizes. In general, the sampling devices are cylindrical in shape and generally range between 30 and 45 centimeters in length and about 10 to 15 centimeters in diameter. This range of sizes

usually equate to sample volumes between 1.5 to 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. Depending on selected sampler materials, the samplers may be suitable for sampling for 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 and 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 need to 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 meters 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

- Can be redeployed multiple times after decontamination.
- Can collect "grab" sample from relatively thin (10 to 15 cm thick) water column, which may be desirable for stratified surface water bodies.

6.3.4 Limitations

- Can only be used in surface water
- Only collects a "grab" sample

7. GLOSSARY

Accumulation Sampler: a technology that concentrates the target chemical on a selective collecting medium such as an absorbent or absorbent solid, a solvent or chemical reagent.
Active Sampling: a method that relies on the mechanical action of sampling equipment to draw the medium and contaminants into the sampling device, causing deviations from the natural flow or ambient conditions.
Ambient Air: for the purpose of this document, ambient air is equivalent to outdoor air.
Chemical *(within the parameters of the document)*: a generic term referring to an element or compound that is the target for sampling with the technology in question. This term is used in place of other common terms such as analyte, constituent, compound, contaminant, or COC.
Dalton: The unit used for the molecular weight cutoff (MWCO) by the manufacturers of dialysis membranes. It is a measure of what sized molecules will go through or be excluded

by the membrane. 1 Dalton=1 gram/mole, but all dialysis membranes are sold by MWCO values in Daltons.

Data Quality Objective (DQO): a process that is used to systematically plan for collecting environmental data of a known quality and quantity to support decisions.

Equilibrium Sampler: a technology that functions in a selected medium where chemicals reach concentration equivalence between the medium and the sampler through diffusion.

Field Parameters: measurements that provide information about the state and surroundings of the media in question. Examples include, but are not limited to, pH, temperature, conductivity, turbidity, dissolved oxygen, etc.

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 or a period surrounding sample collection

Groundwater: water that can be found in the subsurface in the annular spaces between soil, sand, and rock and is accessed by monitoring wells.

Indoor Air: the air present within buildings and structures that may be closed or sealed from exterior air.

Media/Medium: soil, water, air, or any other parts of the environment that may contain contaminants.

Minimum Residence Time: the duration a sampling device remains in the medium for it to collect a representative sample. For groundwater, this includes well restabilization time.

Monitoring Well/Probe: A device constructed in accordance with state or local regulations to obtain access to media.

NAPL: the acronym for Non-Aqueous Phase Liquid and refers to typically organic liquids that are immiscible or not soluble in water. There are two types of NAPL: Light Non-aqueous Phase Liquids (LNAPL) which are less dense than water and Dense Non-aqueous Phase Liquids (DNAPL) which are denser than water.

Non-passive sampler: technologies that do not fully meet the definition of active or passive sampling in this document.

Outdoor Air: the air present exterior of the building or from within structures that cannot be sealed from external sources.

Passive Sampling: a method that acquires a sample from a discrete location without inducing active media transport.

Polymeric samplers: a technology that contains a hydrophobic polymer that absorbs organic compounds present in the media sampled.

Porewater: 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). This document primarily references sediment porewater, however the information may also apply to soil porewater.

Sediment: a medium consisting of primarily solid minerals and/or organic particles that are deposited as a result of water or wind transportation.

Soil: unconsolidated material that overlies bedrock.

Soil Gas (Soil Vapor): gaseous elements and chemicals that are located in the spaces between soil particles within the vadose zone.

Surface Water: permanent or reoccurring water open to the atmosphere under either high-flow (rivers or streams) or low-flow (ponds, oceans, or lakes) conditions.

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