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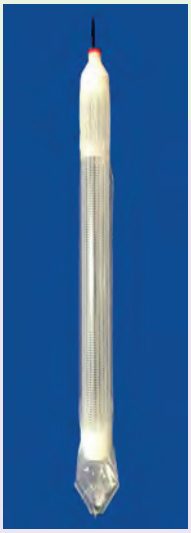
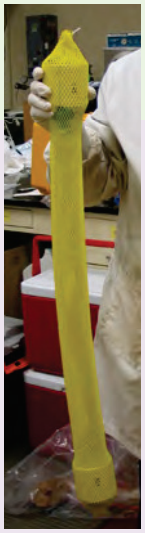
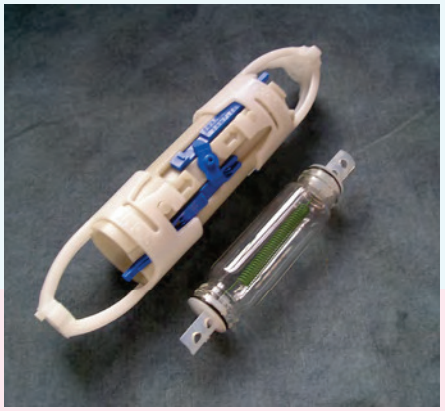
Passive Sampling of Groundwater Wells for Determination of Water Chemistry

Chapter 8 of
Section D. Water Quality
Book 1. Collection of Water Data by Direct Measurement



Techniques and Methods 1–D8

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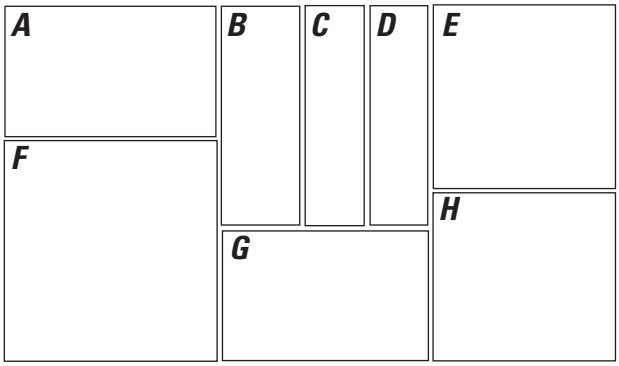

Cover. (*A*) Figure 15 from report, AGI Sample Module®. Photograph from Mark Arnold, Amplified Geophysical Imaging, LLC. (*B*) Figure 11*A* from report, an EON Products, Inc. Dual Membrane (DM) sampler®. Photograph by Bradley P. Varhol, EON Products, Inc. (*C*) Figure 7*B* from report a 2.5-inch-diameter regenerated cellulose dialysis membrane sampler with external supports after assembly. Photograph by Thomas E. Imbrigiotta, U.S. Geological Survey. (*D*) Figure 17*A* from report, A downhole semi-permeable membrane device (SPMD) sampler. Photograph and diagram by David A. Alvarez, U.S. Geological Survey. (*E*) A series of nylon screen samplers retrieved from a profile of the water column of a well showing capped bottles and the removed tops. The variation of iron-staining on the removed tops indicates stratified flow with different redox conditions occurs under ambient flow conditions in the well. Photograph by Philip T. Harte, U.S. Geological Survey. (*F*) Figure 5*A* from report, a polyethylene diffusion bag sampler. Photograph by Bradley P. Varhol, EON Products, Inc. (*G*) Figure 9 from report, a rigid porous polyethylene sampler, without protective mesh and with protective mesh, in a water-filled tube for shipment. Photographs by Leslie Venegas, ALS Global. (*H*) Figure 13*A* from report, QED Environmental Systems, Inc. Snap Sampler® with volatile organic compound bottle (40-milliliter vial). Photograph by Sanford Britt, QED Environmental Systems, Inc.

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U.S. Department of the Interior
DAVID BERNHARDT, Secretary

U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2020

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Contents

Figures

Tables

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
inch (in.)	25,400	micron (μm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square foot (ft^2)	929.0	square centimeter (cm^2)
square foot (ft^2)	0.09290	square meter (m^2)
square inch (in^2)	6.452	square centimeter (cm^2)
	Volume	
gallon (gal)	3,785	milliliter (mL)
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
cubic inch (in^3)	0.01639	liter (L)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per day (ft^3/d)	0.02832	cubic meter per day (m^3/d)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
	Density	
pound per cubic foot (lb/ft^3)	16.02	kilogram per cubic meter (kg/m^3)
pound per cubic foot (lb/ft^3)	0.01602	gram per cubic centimeter (g/cm^3)
	Transmissivity	
foot squared per day (ft^2/d)	0.09290	meter squared per day (m^2/d)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C = (°F - 32) / 1.8.$$

Datum

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L), micrograms per liter (µg/L), or nanograms per liter (ng/L).

Abbreviations

ASTM	American Society for Testing and Materials
cisDCE	cis-1,2-dichloroethene
D	Diffusion coefficient
DM	Dual membrane
DO	Dissolved oxygen
DQO	Data-quality objective
EM	Electromagnetic
IDW	Investigation derived wastewater
ITRC	Interstate Technology and Regulatory Council
LDPE	Low-density polyethylene
NS	Nylon screen
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCE	Tetrachloroethene
PDB	Polyethylene diffusion bag
PFASs	Poly- and perfluoroalkyl substances
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
QA/QC	Quality assurance/quality control

RCDM	Regenerated cellulose dialysis membrane
RPD	Relative percent difference
RPP	Rigid porous polyethylene
SC	Specific conductance
SPMD	Semi-permeable membrane device
SVOCs	Semi-volatile organic compounds
TCE	Trichloroethene
VOCs	Volatile organic compounds
USGS	U.S. Geological Survey

Passive Sampling of Groundwater Wells for Determination of Water Chemistry

By Thomas E. Imbrigiotta and Philip T. Harte

1.0 Introduction

Passive groundwater sampling is defined as the collection of a water sample from a well without the use of purging by a pump or retrieval by a bailer (Interstate Technology and Regulatory Council [ITRC], 2006; American Society for Testing and Materials [ASTM], 2014). No purging means that advection of water is not involved in collecting the water sample from the well. Passive samplers rely on diffusion as the primary process that drives their collection of chemical constituents. Diffusion is the transport of chemicals caused by the presence of a chemical gradient. Chemicals tend to move or diffuse from areas of higher concentration to areas of lower concentration to reach an average or equilibrium concentration.

Passive sampling of groundwater relies on the ambient exchange of groundwater in the formation with water in the screened or open interval of a well. In this report, the term formation is used to describe all saturated hydrogeologic units that yield water to a well. If the well opening is unclogged and free of a film of deposits from physical turbidity or chemical precipitation, then the exchange of groundwater is likely adequate, and the water in the open interval will be representative of water in the formation. In some cases, the passive sample from the well opening can be more representative of groundwater from the formation than a sample collected by pumping if pumping induces mixing of water in the open interval with stagnant casing water that has undergone chemical alteration (Harte and others, 2018). In most cases, passive sampling will better represent the ambient groundwater chemistry flowing through the open interval of a well because pumping may capture water of different chemistry from downgradient or lateral areas that would not normally pass through the well.

Three basic types of passive samplers are discussed in this report. The first type of passive sampler is the equilibrium-membrane type, which includes a semi-permeable membrane through which chemicals diffuse or permeate. Permeation is simply the process of water or chemicals moving through openings in the membrane. The authors contend that permeation is dominated by diffusion for many of the passive samplers discussed in this report. Some passive equilibrium-membrane-type samplers allow most types of chemical constituents through, whereas others allow the diffusion of only selected groups of chemicals. Once the chemical constituents are inside the membrane, they are retained by the equilibration of concentrations inside the sampler with those outside the sampler.

The second type of passive sampler is an equilibrium-thief type, which has no semi-permeable membrane. Chemical constituents simply move through the openings in the body of the sampler either initially through advection and dispersion or over time primarily by diffusion. Chemical constituents reach equilibrium between the water in the sampler and the water in the well and are captured in the sampler when the sampler is closed.

The third type of passive sampler is an accumulation-type sampler that contains sorptive media. Selected chemical constituents are sorbed onto the media that the sampler contains for later extraction and analysis.

Although passive samplers have been available for more than 15 years (from present [2020]), their use by U.S. Geological Survey (USGS) hydrologists and hydrologic technicians to monitor groundwater quality largely has been limited to selected research studies. The authors believe that this may be the result of (1) a lack of exposure of most USGS personnel to passive samplers and the uses of these samplers and (2) the lack of a USGS-approved protocol for the proper use of these samplers by USGS personnel. This report is an effort to fill those two needs.

The focus of this report is on hydraulic, hydrologic, and chemical considerations in the application of passive samplers and interpretation of groundwater chemistry results obtained using passive samplers in wells. This report describes the differences between purging and passive sampling methods in groundwater and explains how and why passive samplers work. The report points out the advantages and limitations of passive samplers in general and for each particular type of passive sampler. Important considerations to be taken into account prior to the use of passive samplers are discussed, such as defining the data-quality objectives, the water-quality constituents to be sampled, sample volumes required for analysis, well construction of the sampling network, and the geologic formations that will be sampled. Potential applications of passive samplers also are discussed, such as chemical-vertical profiling of wells. A general field protocol

for the deployment, recovery, and sample collection using these devices is described, and some overall guidance for the practitioner with application examples is given. Comparison methods used to evaluate results from passive sampling versus purge sampling also are discussed.

2.0 Overview of Groundwater Sampling

Over the past 51 years (1970–2020), knowledge of groundwater flow and transport processes has increased along with the development of innovative tools, techniques, and methods. Groundwater sampling has changed from simple bailing and standard purging methods to low-flow purging and passive sampling. In this section, we discuss the principle differences between purge and passive sampling to help qualify sample results from passive sampling.

Purge and grab sampling can be categorized as the collection of instantaneous samples, whereas passive sampling is a time-integrated sampling method. There are differences also in the volume of the formation interrogated, degree of mixing, and flow conditions.

2.1 Purge Methods

Groundwater flow in the open interval of a well will differ under ambient and pumping conditions (Crisma and others, 2001; Elci and others, 2001). Flow differences are likely more pronounced in wells with long open intervals (>10 feet [ft]) because of the potential to intercept either differences in hydraulic head vertically across the well opening or in hydraulic conductivity (referred to as permeability in this report). In the case of the former, ambient flow will be dominated by inflow from the layer with the highest hydraulic head. In the case of the latter, pumping will induce flow from the layer with the highest permeability. If the layer with the highest hydraulic head and the layer with the highest permeability are not coincident, then the water sources differ, which may have implications for water chemistry.

In some cases, there may be little difference in water under ambient and pumped conditions. Elci and others (2001) found that ambient flow in one well at the Savannah Test Site in Aiken, South Carolina, had a maximum upward flow of 0.28 liter per minute (L/min) from a bottom inflowing layer to an upper outflowing layer. Under this scenario, the passive and the purge samples collected from this well would produce similar results for two reasons. The first reason is that in both the passive and the pumped samples, the water chemistry in the open interval will be dominated by the inflowing bottom layer. The second reason is that strong vertical flow may produce altered water chemistry in the aquifer in the outflow zone of the well such that even when a pump is drawing water into the well from the outflow zone, thereby reversing flow, that water likely represents the inflowing water from the bottom layer of the well. Thus, with both methods samples would be exposed to the same water chemistry.

2.1.1 Three-Well-Volume Purge

The relatively high volume, active purge method called the three-well-volume method or volumetric purge is a benchmark sampling procedure used for many water-quality studies, including the USGS National Water Quality Assessment Project (Koterba and others, 1995), and is one of the methods presented in the USGS National Field Manual (USGS, 2017). In this method, a portable or installed pump is set at the bottom of the casing directly above the well opening if the saturated water column extends to that depth. Purging is initiated and continues until a predetermined equivalent volume of water, typically equal to three volumes of the water column in the well, is evacuated or until stabilization of field physical and chemical characteristics (pH, specific conductance [SC], temperature, dissolved oxygen [DO], and turbidity) occurs within acceptable limits over three successive measurements.

Purging the well is done to reduce or eliminate the inclusion of stagnant water in the well casing (Koterba and others, 1995). Purging also helps reduce the turbidity in the well caused by the deployment of a portable pump in the well (if one is used). The consequence of a volumetric purge is that the collected sample represents a flow-weighted, mixed, integrated sample dominated by groundwater from the more permeable hydrogeologic units with some contribution from the lower permeability units (Britt and Tunks, 2003).

Barber and Davis (1987) incorporated well hydraulics with water chemistry differences between the well and formation to derive purge/volume times associated with achieving representative samples from wells. As expected, the aquifer permeability and storage play important roles in the time a particular well needs to be purged to ensure a representative sample. The initial water chemistry conditions of the well also played a role in that it took longer to achieve a representative value if the SC of the well water was initially higher than the SC of the formation water. In some cases, Barber and Davis (1987) found that more than three well-casing volumes of water were needed to ensure a representative sample, and in some low-permeability formations, as many as nine borehole volumes were needed.

Several pitfalls can result from volumetric purging that can alter the chemistry of the formation water in the well. These include the potential for in-well degassing from excessive withdrawals and pressure decreases (Roy and Ryan, 2010), the need to extract and sometimes collect and treat large volumes of contaminated water, long purge times to achieve representative conditions, and unrepresentative mixing either in the well or formation. Mixing can alter the water chemistry from that of the groundwater in the formation. However, mixing in the well can be problematic for many sampling methods. Several of these processes are discussed in more detail in Section 10.2.

2.1.2 Low-Flow Purge

A primary goal of low-flow purge sampling of groundwater (pumping at low rates, 0.1–0.5 L/min) is to minimize the amount of water pumped from in-well storage by avoiding drawdown in the well; consequently, in-well vertical flow from the stagnant water column in the well casing above the screened or open interval is minimized (Puls and Barcelona, 1989; Barcelona and others, 1994; Pohlmann and others, 1994; Kearl and others, 1994; Shanklin and others, 1995; Puls and Barcelona, 1996; Barcelona and others, 2005). Hence, water within the screened or open interval typically is more representative of formation water than water in the casing (Kearl and others, 1992).

Additional benefits of low-flow sampling include small purge volumes, which minimizes the production of investigation-derived waste (IDW) caused by pumping contaminated water, and the collection of groundwater samples with low turbidity, which decreases the need for filtration. However, there are associated hydraulic and chemical concerns when purging and sampling using low rates of flow. According to the State of New Jersey sampling guidance (http://www.state.nj.us/dep/srp/news/1997/9711_04.htm):

> "The zone sampled within the well by low-flow methods is conceptually limited. If the contaminant distribution in the screened section of the aquifer is heterogeneous, which may be the case in most wells, the sample results obtained by low-flow sampling may be significantly biased low if the sampling device intake is not placed at the same depth as that of the highest contaminant concentration entering the well."

A common assumption for low-flow groundwater sampling was that low purge rates capture primarily lateral inflow (horizontal laminar flow) through the screened interval from the formation at depths coincident with the pump intake (Stone, 1997). However, because even low-flow sampling causes some drawdown in the well, convergent, in-well, vertical flow is induced toward the pump intake from inflow across the entire well screen (Harte, 2017). Varljen and others (2006) show that the entire well screen is sampled during low flow with preferential sampling of high permeability layers under steady-state transport. Flow convergence toward the pump promotes mixing that is biased toward the capture of formation water from layers with the highest head and permeability that intersect the well screen (Divine and others 2005). Because low-flow purge sampling uses lower rates of pumping and less volume is extracted from the well than for the three-well-volume purge method, the resultant low-flow sample tends to be more affected by the ambient flow (pre-purged) and initial-head distribution than three-well-volume purge samples. Nevertheless, the low-flow sample can approximate either (1) a flow-weighted sample dominated by transmissive layers of the formation (similar to volumetric purge methods) or (2) a flux-averaged sample dominated by chemical mixing and averaging of chemical concentrations along the open interval or screen of a well. The former sample is called a flow-weighted sample, and the latter is called a volume-integrated sample.

2.1.3 Field Physical and Chemical Characteristics Stabilization

Inherent in many active/purge sampling methods (volumetric and low-flow) is the requirement that, prior to collecting a sample, field physical and chemical characteristics such as pH, DO, SC, temperature, and turbidity achieve some degree of stability as an indicator of formation water recharging the well water. Harte (2017) found that stabilization of field physical and chemical characteristics monitored during purging was useful in diagnosing the contribution of in-well vertical flow and transport to the pump intake location. However, stabilization of field physical and chemical characteristics during purging may not always be a reliable indicator of the chemical stability for other chemical constituents. For example, during purging at sites in the Coastal Plain sediments of New Jersey, field physical and chemical characteristics at 10 wells typically achieved stabilization before 2 casing volumes were purged. However, the aromatic organic compounds being sampled took slightly more than 3 casing volumes of purging to stabilize (Gibs and Imbrigiotta, 1990). Researchers hypothesize that the primary factors affecting the difference between field physical- and chemical-characteristic stability and target-constituent stability include the physical and chemical heterogeneity of the formation, mixing of groundwater in the well, reactions within the wellbore external to the formation, and the presence of a well-skin effect that may alter flow and chemistry (Church and Granato, 1996; Reilly and LeBlanc, 1998). Therefore, relying on the stability of field physical and chemical characteristics alone may provide a false measure of success during purge sampling. Rather, knowledge of well and formation hydraulic characteristics with either purge or passive sampling will increase the likelihood of obtaining a representative groundwater sample from the formation. A coupled hydraulic and chemical monitoring approach is discussed in Harte (2017), and an analytical model is provided in Harte and others (2019) for such an analysis.

2.2 Passive Sampling

Field application of passive sampling started in the late 1980s when passive sampling methods were first developed to sample organic vapors from air and soil gas (Vroblesky and others, 1991; Vrana and others, 2005). Soon thereafter, these methods were applied to sampling groundwater in wells. Accumulation-type and equilibration-type passive samplers were developed in the 1990s (Petty and others, 1995; Ellis and others, 1995; Vroblesky and others, 1996; Vroblesky and Hyde, 1997; Einfield and Koglin, 2000). Today (2020),

several different passive samplers are available that can be used to sample a wide variety of different chemical constituents in wells. These samplers are discussed in more detail in Section 4.

The idea behind passive sampling is simple; rather than purging a well and actively drawing water into a well, a passive sampler is lowered into the screened or open interval to sample the water flowing through it owing to natural groundwater gradients. Driven by the process of diffusion, chemical constituents in the passing groundwater can be collected in the sampler. This has benefits in that pumps requiring power are not needed; pumps and hoses do not have to be decontaminated between wells; and, at sites with contamination, large volumes of IDW water do not have to be collected and treated.

Passive samplers collect samples that are representative of the water adjacent to the sampler, which in most cases represents water in the screened or open interval of a well. Because passive samplers do not induce flow into the well from the formation, they do not collect instantaneous samples. They also do not collect samples that are necessarily representative of a finite volume of water from the aquifer around the well, unlike purge samples.

Because passive samplers function primarily by diffusion, they require a specified minimum deployment period in the well. The deployment period depends on the inflow and outflow patterns of a well, the degree of mixing of groundwater in a screened or open interval, the rate of groundwater flow through the screened or open interval, and the diffusion rates of constituents of interest. In general, samples obtained with a passive sampler will probably represent the time-weighted average concentration found in water flowing through the well over the most recent 3–4 days prior to sample collection (Vroblesky, 2001a, 2001b; ITRC, 2006).

The general theory and principles of how and why passive samplers work, and their primary advantages and limitations, are discussed in Section 3. Individual types of passive samplers that have been developed for use in wells are discussed in Section 4.

3.0 Theory and Principles of Passive Sampling

Although many passive samplers appear simplistic in appearance, understanding the principles of operation will help ensure appropriate sample collection procedures are used. This section provides an overview of the physical and chemical principles of passive sampler operation.

3.1 Kinetic and Equilibrium Sampling Regimes

When a passive sampler is placed in a well, it encounters two primary sampling regimes. Initially, the mass of chemical taken up by the sampler increases somewhat linearly with time, and maximum relative change occurs during this time (fig. 1). This is known as the kinetic sampling regime. In the kinetic sampling regime, the longer the sampler is in the well, the more the chemical constituent of interest will diffuse or permeate into the sampler. This process can be represented by the first-order, one-compartment, mathematical model described by Vrana and others (2005):

$$C_s(t) = C_w (k_1/k_2)(1-e^{-k_2 t}) \quad (1)$$

where

$C_s(t)$ is the concentration of the constituent/analyte in the sampler at exposure time (t),

C_w is the constituent/analyte concentration in the well, and

k_1 and k_2 are uptake and offload rate constants, respectively.

The period of deployment for accumulation-type passive diffusion samplers that contain sorptive material to collect samples is restricted to the kinetic sampling regime.

Once the passive-sampler-deployment time exceeds the time period associated with the kinetic sampling regime, the relative rate of solute uptake of the constituent/analyte into the sampler decreases. Once the concentrations within the sampler are at equilibrium with the concentrations outside the sampler, the rate of uptake becomes essentially zero. This is referred to as the equilibrium sampling regime. In this regime, solutes may move into or out of the sampler in an attempt to maintain equilibrium with changes that may occur in water outside the sampler. During this period, equilibrium-type passive samplers rely on either diffusion of chemical constituents across a membrane (equilibrium-membrane type) or into a sample container (equilibrium-thief type) to collect samples that are equal to the concentrations of chemical constituents of interest in the well.

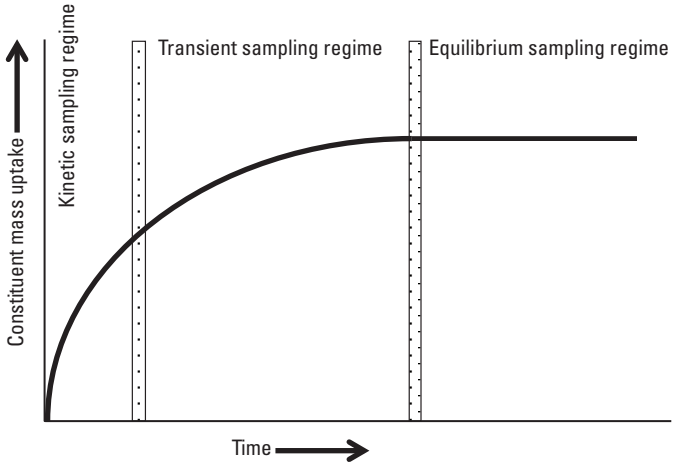

Figure 1. Passive sampling regimes. Modified from figure 1 of Seethapathy and others (2008).

3.2 Diffusive Chemical Exchange

All equilibrium-type passive samplers rely primarily on the process of diffusion to collect samples of the constituents of interest from the well. Diffusion is governed by Fick's Law (Seethapathy and others, 2008), which briefly stated says that solutes diffuse from areas of high concentration to areas of low concentration. For equilibrium-type passive samplers, the gradient that drives diffusion is the difference between the concentration of a chemical outside the sampler and the concentration of a chemical inside the sampler (fig. 2). At the initial time of deployment (t_i=0), the concentration of the constituent to be sampled is essentially negligible (c_i=0) inside the sampler because it is filled with deionized water free of the constituent of interest. After deployment for some time (t>0), chemical exchange occurs according to Fick's First Law of Diffusion, which states

$$M/t = D\ (A/L)\ (C_w - C_s) \qquad (2)$$

where

M is the mass of the constituent collected by the sampler per unit time (t),
D is the diffusion coefficient (area/time),
A is the surface area of the diffusion path,
L is the diffusive path length,
C_w is the constituent concentration (mass/volume) in the well, and
C_s is the constituent concentration in the sampler.

In a passive sampler with a semi-permeable membrane, A is the surface area of the membrane through which diffusion occurs, and L is the membrane thickness. Sample collection is complete when the concentration inside the sampler equals the concentration outside the sampler. This is shown graphically in figure 2.

Equation 2 can be rearranged to describe the relative uptake potential for water-filled passive samplers (Divine and others, 2005; Sanford and others, 1996). In this case, the rate of equilibrium between the concentration of the constituent of interest in the passive sampler and that of the well water can be expressed as

$$C_s(t) = 1 - e^{(-D_m At/VL_m)} \qquad (3)$$

where

$C_s(t)$ is the ratio of the concentration inside the passive sampler to the concentration in the well water in contact with the sampler,
D_m is the diffusion coefficient of the constituent of interest across the membrane (solved),
A is the diffusive surface area of membrane,
t is the time of deployment,
V is the volume of sampler, and
L_m is the thickness of membrane.

For accumulation-type passive samplers, the concentration gradient that drives sample collection is between the concentration of a chemical in water outside the sampler and the concentration on the surface of the sorptive media. The net rate of uptake is controlled by the slower of the two processes: permeation through the membrane and diffusion through the boundary layer (Seethapathy and others, 2008). The two boundary layers are formed between the aqueous side of the membrane (well water) and the receiving side of the membrane (fig. 3). The sorptive media remove a constituent from solution, which creates a low-concentration zone on the receiving phase side of the boundary layer (fig. 3). Deployment time must be short enough that all the sorptive sites on the sampler are not saturated with the constituent of interest by the end of the deployment.

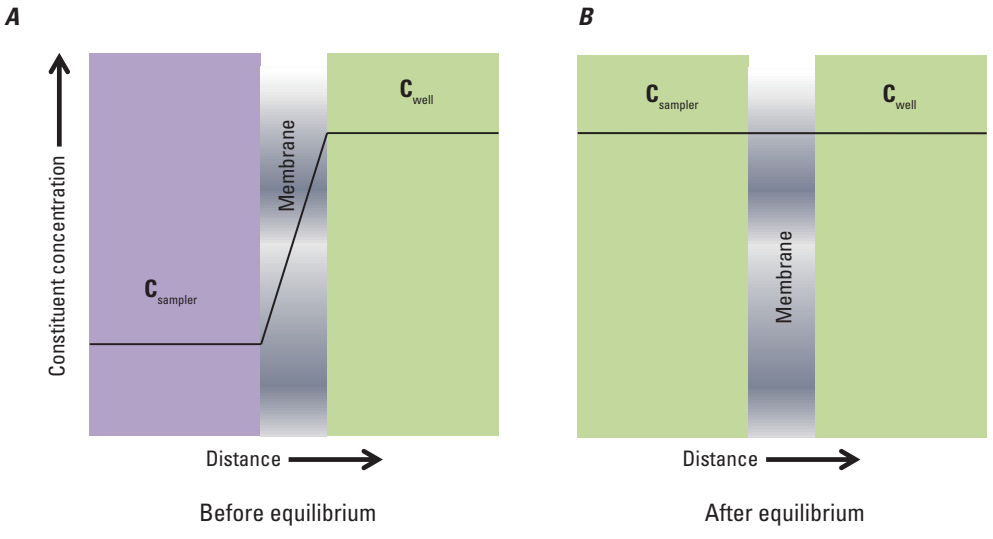

Figure 2. The chemical gradient across a membrane *A*, before equilibrium and *B*, after equilibrium. Modified from Interstate Technology and Regulatory Council (2004). [C, concentration]

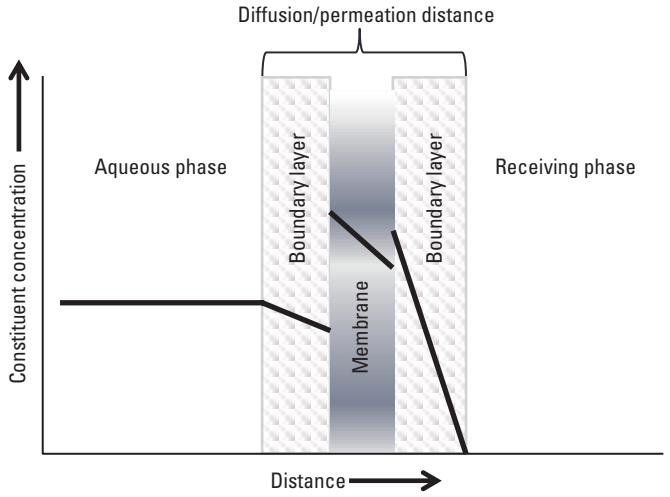

Figure 3. Chemical gradient from the groundwater to the receiving phase of the accumulation-type passive sampler. Modified from Seethapathy and others (2008).

3.3 Well Communication and Hydraulics

The hydraulic connection between the screened or open interval of a well and the formation is an important factor that affects a well's ability to collect water representative of the water chemistry in the formation without the need to induce flow into the well by pumping. The ambient flow through the open interval of a well is dependent on well communication (ability to exchange groundwater with the formation); well construction (length of well opening in particular); formation characteristics, including physical and chemical heterogeneity; and position of the well relative to hydrologic boundary conditions, which affects horizontal and vertical hydraulic-head gradients. All of these topics are discussed in more detail in Section 5.

Wells that are open to the formation distort the groundwater flow field because of the permeability contrast between the well (more permeable) and formation (less permeable). This distortion facilitates flushing or exchange of water in the well with the groundwater in the formation under ambient-flow conditions. Drost and others (1968) utilized tracers coupled with point-dilution theory to demonstrate the ambient flushing of water into a well. Mathematically, the distortion of groundwater flow is expressed as

$$q_o = q/\alpha \quad (4)$$

where α is the convergence/divergence (distortion factor) of the groundwater flow in the vicinity of a well, water flux (q_o) in the formation, and water flux (q) through the well (Basu and others, 2006). A distortion factor of 0.9–2.4 was measured in wells by Verreydt and others (2015), indicating that flow through the well generally exceeded flow through the formation by as much as 2.4 times.

3.4 Sampler Materials and Constituents Sampled

Passive samplers are constructed of a variety of materials. The material type depends on the type of sampler and the constituents to be collected. Passive samplers have been developed that can sample for a wide range of constituents, including major cations and anions, trace metals, nutrients, dissolved gases, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), explosive compounds, poly- and perfluoroalkyl substances (PFASs), and pesticides. Different types of passive samplers vary in their ability to sample each of these categories of chemical constituents.

Accumulation-type passive samplers are made of inert structural materials, such as stainless steel and Teflon, and organic media that adsorb organic compounds of interest. The sorbent media used include polymeric resins and triolein (ITRC, 2007). The accumulation-type passive samplers discussed in this report collect only organic compounds, such as VOCs, pesticides, and SVOCs and cannot be used to sample for inorganic constituents.

Equilibrium-thief-type samplers are constructed of relatively inert materials, such as stainless steel and Teflon. The sample collection containers are made of either glass or polyethylene. Equilibrium-thief-type passive samplers theoretically can collect any type of chemical that moves into them. The only constraint is that the material of the sample container cannot adsorb or leach the constituents of interest. This is important because the sample is not transferred: the collection container is submitted to the laboratory. Glass sample containers are used to collect samples for organic compounds, whereas polyethylene containers are used to collect samples for inorganic constituents and trace metals (Britt and others, 2010).

Equilibrium-membrane-type samplers are constructed with many materials, the most important of which is the membrane material. Membranes have been made of polymers such as polyethylene, regenerated cellulose, cellulose acetate, nylon, polydimethylsiloxane, polysulfone, silicone-polycarbonate, polytetrafluoroethylene (PTFE), polypropylene, and polyvinyl chloride (PVC) (Seethapathy and others, 2008; ITRC, 2007). The function of the membrane is to act as a semi-permeable barrier that allows the diffusion of selective groups of chemical constituents into the passive sampler.

Equilibrium-membrane-type samplers are constructed with valves, mesh, and connectors, as well as membranes. All these components may sorb the constituents of interest. In general, however, such sorption or exchange is considered to not affect the sample quality as long as they do not add to the concentration of the constituents of interest and equilibration is reached during the deployment period.

Equilibrium-membrane-type passive samplers have been developed that can sample for VOCs, major cations and anions, most trace metals, nutrients, perchlorate, dissolved organic carbon, PFASs, and most explosive compounds. The constituents that these samplers collect depend

on the membrane material. Some equilibrium samplers have been developed that sample only for certain types of organic compounds, whereas others allow for the collection of inorganic cation and anions and trace metals, as well as organic compounds.

The selectivity of a semi-permeable membrane is due to several factors, such as its chemical characteristics, pore size, or hydrophobicity. The size of the pores of the membrane in relation to the size of the inorganic cation and anions or organic compounds can be a physical factor that prevents or allows constituents to diffuse through the membrane. The hydrophobic or hydrophilic characteristics of a membrane will allow some constituents to pass through and repel others. Characteristics of the constituents being sampled, such as solubility, volatility, diffusion coefficient, and partition coefficient, in relation to the chemical composition of the membrane will also affect whether a membrane will allow constituents to diffuse through it.

3.5 Equilibration and Exposure Time

Passive samplers must be deployed in a well for a predetermined length of time prior to their removal and sampling. Equilibrium-type samplers must be left in the well long enough to equilibrate to within at least 95 percent of the actual concentrations in the groundwater, yet not long enough for membrane degradation or clogging to occur. Accumulation-type samplers must be exposed to groundwater long enough to sorb detectable concentrations, yet not long enough to oversaturate all the sorption sites on the sampler. A general rule of thumb is that for most passive samplers, reasonable deployment times range from a few days to a few weeks for chemicals with diffusion coefficients greater than 10^{-8} square centimeters per second (cm^2/s). Factors affecting equilibration and exposure time are discussed in more detail in Section 5.

3.6 Common Advantages and Limitations of Passive Samplers

The use of passive samplers has general advantages and limitations compared to the use of conventional pumps or bailers in sampling groundwater wells. Advantages and limitations that are common to most passive samplers are given below.

3.6.1 Advantages

This section lists the common advantages that most passive samplers have over purging methods. Advantages specific to each type of passive sampler are provided where each sampler is discussed in Section 4.

No pump required: One of the advantages of using passive samplers is that they eliminate the need to purge water from the well during active sampling. This means that no pump or power source is needed to sample the well. This can save on equipment costs and operational costs.

Time in the field reduced: Purging a well prior to sampling frequently represents the largest amount of time spent in the field to collect a groundwater sample. Use of passive samplers can eliminate most of this field sampling cost. For example, Imbrigiotta and others (2007) found the typical time for low-flow purging of a well less than 100 ft deep to reach stabilization of field physical and chemical characteristics was 45–60 minutes (min). In comparison, passive samplers typically took 15 min to deploy and 15 min to retrieve from a well of this depth, so the field time and costs saved were substantial.

The savings in time and costs when using passive samplers rather than the three-well-volume purge method become more substantial as wells are deeper, well diameters are larger, and well volumes are greater. For wells where a three-well-volume purge is required prior to sampling, typical evacuation times on the order of 30–400 min for a 100-ft, 4-inch (in.) -diameter saturated column of water to 200–2,200 min for a 500-ft, 4-in.-diameter saturated column of water are needed for a 1-gallon-per-minute (gal/min) to 10-gal/min pumping rate (fig. 4).

No purge water produced: Another advantage to using passive samplers instead of purging is that passive samplers produce very little leftover water or IDW. This is particularly important at groundwater hazardous waste sites where purge water must be drummed, transported, and treated. Passive sampling saves time and costs by eliminating the need to collect, transport, and treat the IDW.

No cleaning required: Most passive samplers are disposable and are constructed or purchased clean and ready for use. This is an important advantage over non-dedicated pumps that require cleaning or decontamination between wells.

Ease of use: Most passive samplers are easily deployed in a well by lowering them on a weighted suspension line to a selected depth in the open interval and tying off the line. Recovery is just the opposite; the sampler is untied and pulled up. Once the passive sampler is at the surface, minimal training is required for the field sampling personnel on the correct way to transfer the water from the sampler to the sample containers.

No filtration required: For equilibrium-type passive samplers, several do not require filtration because the membranes have very small openings (some smaller than 0.45 micron [µm]), which act as filters. This intrinsic filtering process can have the analytical advantage of reducing matrix interference from turbidity.

One field trip to deploy and recover: Some equilibrium-type passive samplers that are constructed of non-biodegradable materials can stay in the well from one sampling event to the next for wells that are periodically sampled. Therefore, these passive samplers are not constrained by a maximum deployment period. Field personnel can retrieve and collect a sample from the equilibrated passive sampler, and then deploy a new

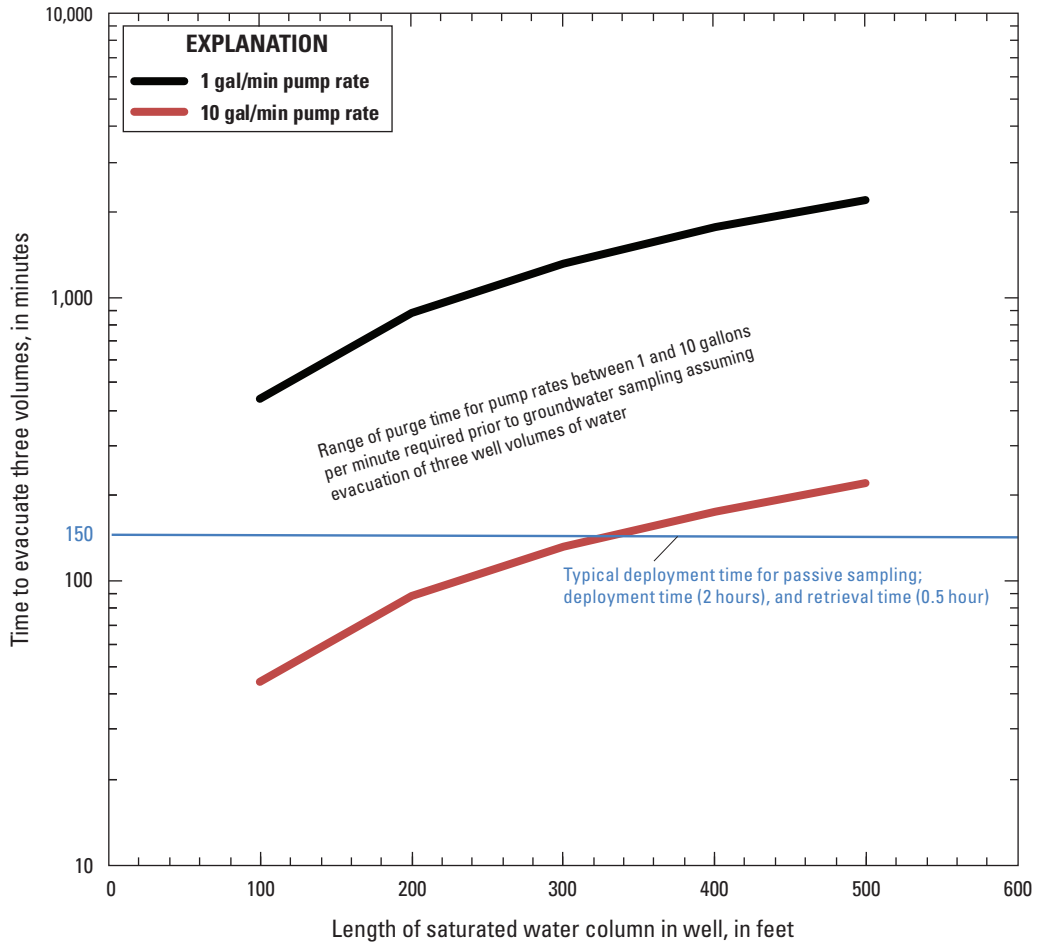

Figure 4. Purge duration for 1- and 10-gallon-per-minute rates of pumping for a 4-inch-diameter well. (gal/min, gallon per minute)

passive sampler during the same field trip. The new passive sampler is then allowed to equilibrate until the next scheduled sampling event.

Easily adapted to long-term monitoring plans: In many cases, passive samplers are easily incorporated into long-term monitoring plans. As long as the results obtained with the passive sampler are accepted as being comparable to the purging results, wells can simply be switched from purging to passive samplers.

Use to sample low-yield wells: Many passive samplers can be used to sample low-yield wells using long-term deployments to allow the chemical concentrations to come to equilibrium. Passive samplers save time in the field when field personnel otherwise would have to purge a low-yield well, wait for it to recover, and then pump it again to sample it.

No depth limitations: Passive samplers can be used to sample at any depth in a well. The only depth restriction is the length of the suspension line. This is an advantage over some pumps that are limited by the depth they are able to lift water.

Well sampling in high-traffic areas: Because the deployment and recovery times are usually short for passive samplers, they can be used to sample wells in high-traffic areas, such as wells in roadways or near airport runways provided proper safety procedures and conditions are met.

Integration of water-quality results: Equilibrium-membrane-type and equilibrium-thief-type passive samplers integrate a time-weighted average of the concentrations they are exposed to over the last 3–4 days of deployment. Accumulation-type passive samplers can integrate the concentrations of constituents they are exposed to during the entire time of their deployment. If the sorption sites are not saturated during the deployment period of an accumulation-type sampler, then the sampler will have the ability to measure episodic events. Therefore, passive sampling allows for a more cost-effective alternative to some active sampling methods, which are inherently instantaneous in operation.

Use in vertical profiling: Passive samplers can be used to provide an approximate vertical profile of the concentrations in the open or screened interval of a well for purposes of determining constituent input depths or chemical stratification in a formation because of their ability to interrogate a relatively small volume of water from a discrete depth (Vroblesky and Peterson, 2004; Divine and others, 2005). This differs from the purging method, which induces convergent flow to the pump intake and interrogates larger volumes of water. However, the ability of the passive sampler chemical profile to represent the chemical profile in the formation is a function of well-flow dynamics and the degree of in-well mixing under ambient conditions.

3.6.2 Limitations

Limitations common to the use of many passive samplers are discussed in this section. Limitations for individual types of passive samplers are discussed in Section 4.

Two field trips to deploy and recover: Passive samplers that are made with biodegradable materials and some accumulation-type samplers have limited deployment periods. Therefore, it is likely these types of samplers will require two trips to the field, one to deploy and one to retrieve, regardless of whether they are part of a periodic monitoring program. These samplers must be recovered before microbes perforate their membranes or before their sorptive media are saturated with the constituents of interest.

Sample volume restrictions: A primary limitation to equilibrium-type passive samplers is the restricted volume most samplers can contain, particularly samplers utilizing water as an uptake medium (receiving phase). Some chemical constituents require a liter or more of water for analysis, and several passive samplers can only collect samples of 0.1 to 0.5 liter in volume. Volume requirements using some types of samplers can be met by deploying multiple samplers in a well at closely spaced vertical intervals.

Flux versus concentration results: Accumulation-type passive samplers produce flux results (mass/time) rather than concentration results (mass/volume). This can be considered a slight limitation because concentration results are used more commonly than flux results.

Extraction required prior to analysis: Accumulation-type passive samplers with unique receiving-phase media, such as lipids, carbon, or resins, require extraction or desorption of the target chemical constituent from the sorptive media into a liquid or gas phase prior to analysis. This extra step can be a limitation because it requires more preparation work in the laboratory and may restrict the number of laboratories that can do these analyses.

Potential difficulty in accurately measuring field physical and chemical characteristics: Measurements of common field physical and chemical characteristics, such as water temperature, DO, and redox potential, that typically are made using an in-line flow cell during well purging are likely to be more representative of field physical and chemical characteristics than measurements made in aliquots of water from a passive sampler. This is because chemical changes can easily take place in the sample when a passive sampler is exposed to oxygen or increased or decreased temperatures when it is removed from the water column in a well. However, pH and SC may be measured in water collected with some equilibrium-type samplers that allow the collection of dissolved ions. Accumulation-type samplers cannot be used to measure field physical and chemical characteristics.

Samplers must be kept hydrated: Several equilibrium-membrane-type passive samplers must be kept hydrated or submerged in water between their construction and installation in a well.

Chemical constituent limitations: Some passive samplers work only for a specific type or class of chemical constituents. For example, some samplers collect organic compounds but not inorganic constituents, whereas others cannot collect VOCs or dissolved hydrocarbons.

Deployment time limitations: Some passive samplers have deployment time restrictions owing to biological degradation or chemical clogging of the membrane. In addition, some samplers have time restrictions owing to water loss through the membrane. Deployment times for accumulation-type samplers are uptake and sorption dependent. Deployment of several samplers that are retrieved at different durations may be required to ensure sorption sites are not saturated. Equilibrium-membrane-type samplers usually require deployment times of a couple weeks to minimize hydraulic disturbance during deployment and allow for chemical equilibration across the membrane.

4.0 Types of Passive Samplers

The main types of passive samplers developed and used over the past decade (2010–20) have included 5 equilibrium-membrane-type samplers (polyethylene diffusion bag [PDB] sampler, regenerated cellulose dialysis membrane [RCDM] sampler, rigid porous polyethylene [RPP] sampler, nylon screen [NS] sampler, and EON Dual-Membrane [DM] Sampler®), 1 equilibrium-thief-type sampler (QED Snap Sampler®), and 2 accumulation-type samplers (AGI Sample Module® [formerly GORE-SORBER® Module] and a semi-permeable membrane device [SPMD] sampler). Each of these samplers is discussed in detail below. Other types of passive samplers are discussed briefly in Sections 4.9–4.10.

Equilibrium-membrane-type passive samplers rely on diffusion of chemicals across a semi-permeable membrane to collect samples. The basic design for these samplers consists of a tube of semi-permeable membrane filled with distilled or deionized water. The sampler is deployed in the screened or open interval of a well for a sufficient length of time to reach chemical equilibrium. Once equilibrium has been reached, the constituent concentrations inside the sampler will be equal to those outside the sampler. The equilibrium sampler is retrieved, and water inside the membrane is collected in sample containers and sent for analysis of the chemical constituents of interest. This type of sampler results in a direct measurement of concentrations of chemicals (mass per volume) in the groundwater in a well.

Equilibrium-thief-type passive samplers rely on diffusion or permeation of solutes into the open ends of the device. The basic design for equilibrium-thief-type samplers consists of a container, a container holder, and a closing mechanism made of mostly inert non-sorptive materials that will not interact with the groundwater sample. The sampler is deployed in the open position in the screened or open interval of a well for a sufficient length of time to reach chemical equilibrium. Once

equilibrium is reached, the sampler is remotely triggered to close and brought to the surface. The closed sample container is then sent directly to the laboratory for analysis. This type of sampler also results in a direct measurement of chemical concentrations (mass per volume) in the groundwater in a well.

Accumulation-type passive samplers rely on the diffusion and permeation of chemicals to reach the sorbent material of the sampler and sorb to it. The basic design for all accumulation-type samplers consists of a tube containing a material that is highly sorptive for the chemical constituents of interest. The sampler is deployed in the screened or open interval of a well for a length of time shorter than the time needed to completely saturate all the sorption sites on the sampler. The sampler is then recovered and sent to the laboratory for extraction and analysis. This type of sampler results in a direct measurement of the flux (mass per time) of chemicals in the groundwater coming into the well. Separate concentration comparison measurements may be made during the initial sampling to correlate the measured fluxes with chemical concentrations or an algorithm may be applied that approximates the concentrations on the basis of the measured fluxes and the estimated groundwater flow through the open interval of a well over the time of deployment of the sampler.

4.1 Polyethylene Diffusion Bag (PDB) Sampler

The PDB sampler is an equilibrium-membrane-type passive sampler. Polyethylene diffusion bag samplers were one of the first types of passive samplers developed in the late 1990s for groundwater sampling. They are directly descended from polyethylene vapor diffusion samplers, which were initially developed to determine where VOCs in shallow groundwater were discharging to streams (Vroblesky and others, 1991; Vroblesky and others, 1996; Church and others, 2002). Instead of having VOCs equilibrate with the headspace inside a glass vial with a low-density (LDPE) polyethylene membrane over the mouth, a tube-shaped LDPE membrane was filled with deionized water, installed in a well, and the VOCs in the groundwater were allowed to equilibrate with the water inside the membrane (Vroblesky and Hyde, 1997). Since then, PDB samplers have been extensively tested against purge sampling techniques and are now a widely accepted sampling method for VOCs in groundwater wells (Vroblesky and others, 2000; Vrobesky and Petkewich, 2000; Vroblesky and Peters, 2000; Harte and others, 2000; Vroblesky, 2001a; Vroblesky 2001b; Vroblesky and Campbell, 2001; Vroblesky and others, 2001; Vroblesky and Pravecek, 2002; Parker and Clark, 2002; ITRC, 2004; Archfield and LeBlanc, 2005; ITRC, 2006; Huffman, 2015).

PDB samplers can be used to collect samples for most VOCs, some SVOCs (naphthalene), and some dissolved hydrocarbon gases (methane, ethane, ethene). Several soluble polar VOCs, such as acetone, take a longer time to consistently diffuse through the LDPE membrane, so PDB samplers are not recommended for sampling of these VOCs (Vroblesky and Campbell, 2001). The small pore size (10 angstroms) of the LPDE membrane reduces matrix interference from turbidity and reduces volatilization loss from the possible formation of alkaline foams in alkaline waters (ITRC, 2006). Water samples collected with PDB samplers are shipped to the laboratory for direct analysis of concentrations of VOCs and dissolved hydrocarbon gases. An example of a study utilizing PDB samplers is given in Appendix A, Case Study A1.

4.1.1 Description and Operation

PDB samplers consist of a deionized water-filled tube made of LDPE membrane material (typically 2–4 mils thick; fig. 5). A sampler is constructed by heat-sealing a length of LDPE tubing, filling with a volume of deionized water, and then heat-sealing the other end to form a water-filled tube. These samplers are commercially available pre-filled or with a port on one end to fill in the field or laboratory, and usually come in a protective polyethylene mesh sleeve to prevent abrasion during installation and recovery. Most PDB samplers are made of 1.25-in.- or 2.5-in.-diameter LDPE tubing and are 1–2 ft in length, depending on the diameter of the well and the volume of the bottles to be filled. A 1.25-in.-diameter by 12 in.-long PDB sampler filled with target analyte-free water has enough volume to easily fill four 40-milliliter (mL) vials for sampling of VOCs.

For the deployment of PDB samplers (and many other passive samplers), either a dedicated/disposable polypropylene line or a re-useable Teflon-coated line is used to suspend the sampler in a well at the desired depth. The PDB sampler is deployed in the open interval or screen of a well for about 2 weeks to equilibrate (figs. 5 and 6). During this time, VOCs in groundwater passing by the sampler adsorb to the LDPE material, diffuse across the thin membrane, and re-equilibrate with the deionized water inside. The LDPE membranes are hydrophobic, so no actual physical transport of water occurs between the outside and the inside of the sampler. At the end of the equilibration period, the concentrations of VOCs inside the PDB sampler are equivalent to the concentrations of VOCs outside the sampler. The sampler is then retrieved, the contents transferred to standard VOC vials, and the samples are sent to the laboratory for analysis. VOC concentrations determined from PDB samplers represent average VOC concentrations present in the open interval of the well over the 3–4 days prior to sample collection.

A simplistic conceptualization of a string of passive samplers deployed in a well is shown in figure 6*A*, which depicts stratified horizontal flow into the well. In this case, water well chemistry varies with depth, and samplers will reflect the chemistry of the inflowing groundwater at the same depth. A more complex conceptualization is shown in figure 6*B* that depicts a number of flow processes in the well. In the latter case, the water well chemistry may not be reflective of the inflowing groundwater at that same depth given processes such as vertical flow, dispersion, well mixing, and diffusion.

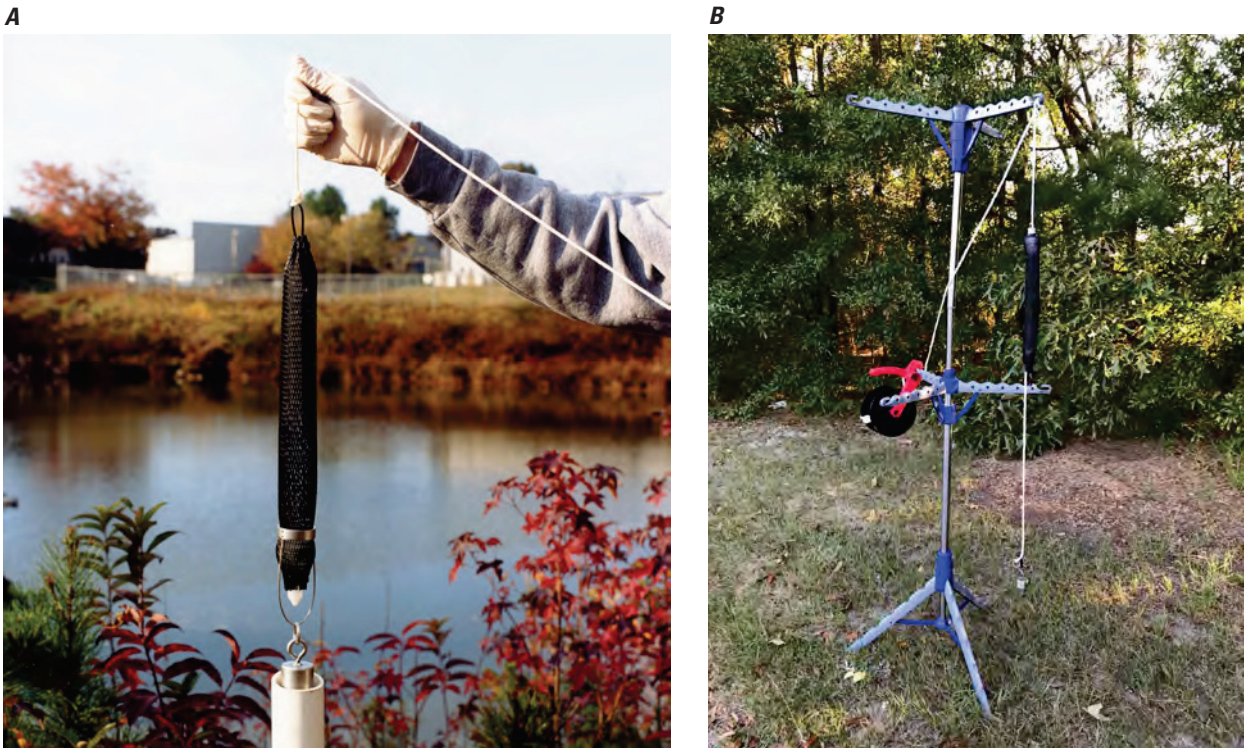

Figure 5. *A*, A polyethylene diffusion bag (PDB) sampler and *B*, a tripod used for installation of PDB samplers in a well. Photographs by Bradley P. Varhol, EON Products, Inc.

4.1.2 Advantages and Limitations

The main advantages of using PDB samplers are that they are low cost to construct or purchase, they are disposable, they can be left in wells indefinitely without degrading, and they have an extensive track record of proven performance in VOC sampling that is based on years of comparison to low-flow purging and other sampling methods. Because PDB samplers will not biodegrade, they can be left in a well between long-term-monitoring sampling events. This allows the field technician to collect a sample from an equilibrated PDB sampler and install another new PDB sampler during one field trip. From that point on, only one field trip is necessary to collect samples using this passive sampler. The main limitation of PDB samplers is that they are unable to sample for inorganic constituents and most SVOCs.

4.2 Regenerated Cellulose Dialysis Membrane (RCDM) Sampler

The RCDM sampler is an equilibrium-membrane-type passive sampler. The earliest version of a downhole dialysis sampler was developed by Ronen and others (1986), Ronen and others (1987), and Magaritz and others (1989), but it was limited to 20-mL sample volumes at each sampled depth. The current version of the RCDM sampler was developed in the early 2000s specifically to meet the need to sample for more than just VOCs using a passive sampler. RCDM samplers were developed to sample for inorganic constituents and non-volatile organic compounds, in addition to VOCs, particularly at groundwater contamination sites where monitored natural attenuation potential was being evaluated, which required the collection of ferrous and ferric iron, sulfate and sulfide, and carbon dioxide and methane. RCDM samplers have been used successfully to sample wells for a wide variety of organic and inorganic chemical constituents (VOCs, major cations and anions, trace metals, nutrients, dissolved organic carbon, dissolved hydrocarbon gases, perchlorate, some PFASs, and selected explosive compounds) (Vroblesky and others, 2002a, 2002b; Vroblesky and Pravecek, 2002; Imbrigiotta and others, 2002; Vroblesky and others, 2003; LeBlanc, 2003; Ehlke and others, 2004; Harter and Talozi, 2004; Parsons, 2005; Imbrigiotta and others, 2007; Imbrigiotta and others, 2008; Imbrigiotta and Trotsky, 2011). Water samples collected with RCDM samplers are shipped to the laboratory for direct analysis of concentrations of organic compounds and inorganic constituents. Examples of studies utilizing RCDM samplers are given in Appendix A, Case Studies A3 and A4.

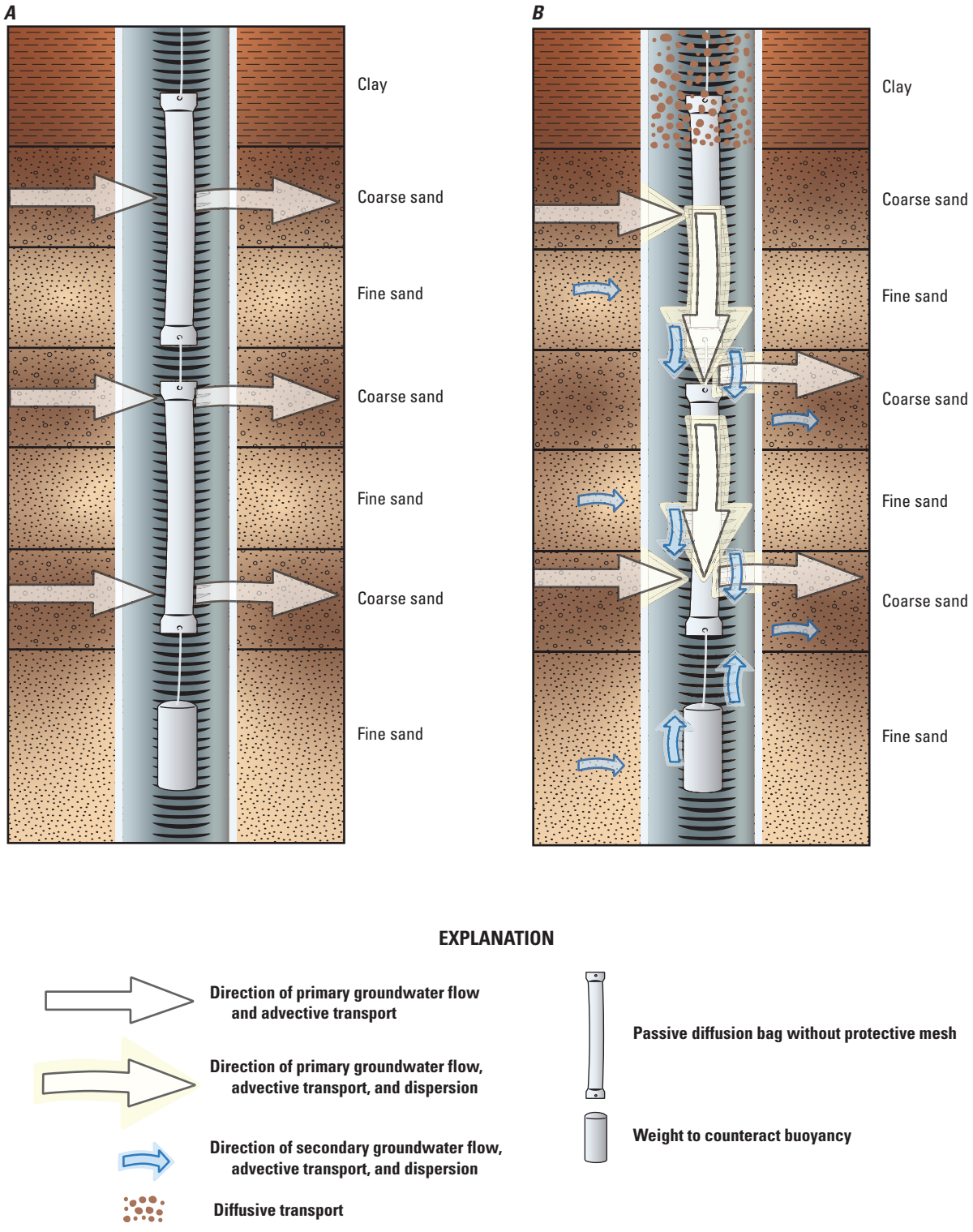

Figure 6. Multiple polyethylene diffusion bag samplers *A*, deployed in a well screen under horizontal flow conditions, and *B*, multiple PDBs deployed under complex vertical and horizontal groundwater flow conditions. Modified from Vroblesky and others (2001). [Arrows indicate direction of groundwater flow.]

4.2.1 Description and Operation

The RCDM sampler consists of a deionized water-filled tube of high-grade regenerated cellulose dialysis membrane (fig. 7). The regenerated cellulose membrane is tied in a knot at one end, and a valve is attached to the other end. The membrane is then inserted into a protective LDPE mesh, the tube is filled with deionized water, and the valve is closed. The protective LDPE mesh is then cable-tied shut at both ends. Weights are attached at the bottom to overcome buoyancy, and a dedicated polypropylene line is used to suspend the sampler in the well. The sampler may have protective PVC supports external to the dialysis membrane to prevent leakage or an internal perforated PVC pipe or rigid polypropylene mesh to support the membrane in high ionic strength waters (fig. 8).

The sampler is deployed in a well at the chosen depth for 1–2 weeks to reach equilibrium. Because the dialysis membrane is hydrophilic, water can diffuse through the membrane. While the sampler is deployed in the open or screened interval, higher inorganic constituent or organic compound concentrations in the well water will diffuse through the membrane into the sampler in response to the concentration gradient with the enclosed deionized water. At the end of the deployment period, the concentrations of constituents inside the sampler are equivalent to the concentrations of constituents outside the sampler. The sampler is retrieved from the well, and the water sample is drained through the valve into the sample containers required for analysis. The sampler diameter and length can be adjusted to fit down the well and to collect the volume of water required for the chosen analyses.

Regenerated cellulose dialysis membranes can be purchased in different widths. The filled diameters and volumes of the two most commonly used dialysis membrane widths used to construct samplers for 2- and 4-in.-diameter wells are listed in table 1. For example, RCDM samplers made to fit in 2-in.- and 4-in.-diameter wells that are 63 centimeters (cm; 24.8 in.) long will contain volumes of approximately 500 mL and 2,000 mL, respectively.

Fully constructed RCDM samplers are not currently available from any commercial vendor. Dialysis membranes can be ordered from various material vendors. Purchase of pre-cleaned regenerated cellulose dialysis membrane material is recommended, particularly if trace metals and sulfides are to be sampled, because these constituents will be present in the dry, uncleaned dialysis membrane material. The dialysis membrane should have a nominal molecular weight cut-off of 8,000 Daltons with an average pore size of 0.0018 µm. The regenerated cellulose dialysis membrane remains useable for 3–5 years if kept refrigerated in its preservative solution.

Figure 7. A 2.5-inch diameter regenerated cellulose dialysis membrane sampler with external supports, *A*, prior to assembly, and *B*, after assembly. Photographs by Thomas E. Imbrigiotta, U.S. Geological Survey.

Figure 8. Internal supports for regenerated cellulose dialysis membrane samplers. Photographs by Thomas E. Imbrigiotta and Donald A. Vroblesky, U.S. Geological Survey.

Table 1. Dialysis membrane flat widths, filled diameters, and filled volumes for regenerated cellulose dialysis membrane passive samplers. From Imbrigiotta and others (2007).

[mm, millimeter; cm, centimeter; mL milliliter; ft, foot]

Well diameter (inches)	Lay-flat width (mm)	Filled diameter (mm)	Filled diameter (inch)	Filled volume (mL/cm)	Filled volume (mL/ft)
2	50	31.8	1.25	7.94	242
4	100	63.7	2.5	31.87	971

4.2.2 Advantages and Limitations

The main advantages of RCDM samplers are that they can be used to collect samples for analysis for a wide variety of organic and inorganic chemical constituents, they are relatively low cost to construct, the samples they collect require no field filtration, and they are disposable. Their limitations are primarily that they must be filled and kept immersed in deionized water between construction and deployment, they can biodegrade in groundwater systems after 4–6 weeks so they cannot be left in a well for extended periods, and the process of dialysis causes these samplers to lose a small percentage of their water volume with time (<3 percent per week) until equilibrium is achieved. RCDM samplers need to be filled with oxygen-free deionized water if redox-sensitive constituents are to be measured.

4.3 Rigid Porous Polyethylene (RPP) Sampler

The RPP sampler is an equilibrium-membrane-type passive diffusion sampler. The RPP sampler was developed in the mid-2000s to meet the need for a polyethylene non-biodegradable diffusion sampler that could be used to sample for inorganic constituents and non-volatile organic compounds, in addition to VOCs, at groundwater contamination sites where monitored natural attenuation potential was being evaluated.

The RPP samplers have been successfully used to sample groundwater for a wide variety of organic compounds and inorganic constituents (VOCs, major cations and anions, most trace metals, nutrients, dissolved hydrocarbon gases, perchlorate, hexavalent chromium, 1,4-dioxane, explosives, and phenols; Vroblesky, 2004; Parsons, 2005; LeBlanc and Vroblesky, 2008; Savoie and LeBlanc, 2012). Water samples collected with RPP samplers are shipped to the laboratory for direct analysis of organic compound and inorganic constituent concentrations.

4.3.1 Description and Operation

The RPP samplers consist of a 1.5-in.-outside-diameter by 6-in.-long, rigid porous polyethylene tube with a cap at one end and a plug at the other end (fig. 9). The tube is constructed from thin sheets of foam-like porous polyethylene with pore

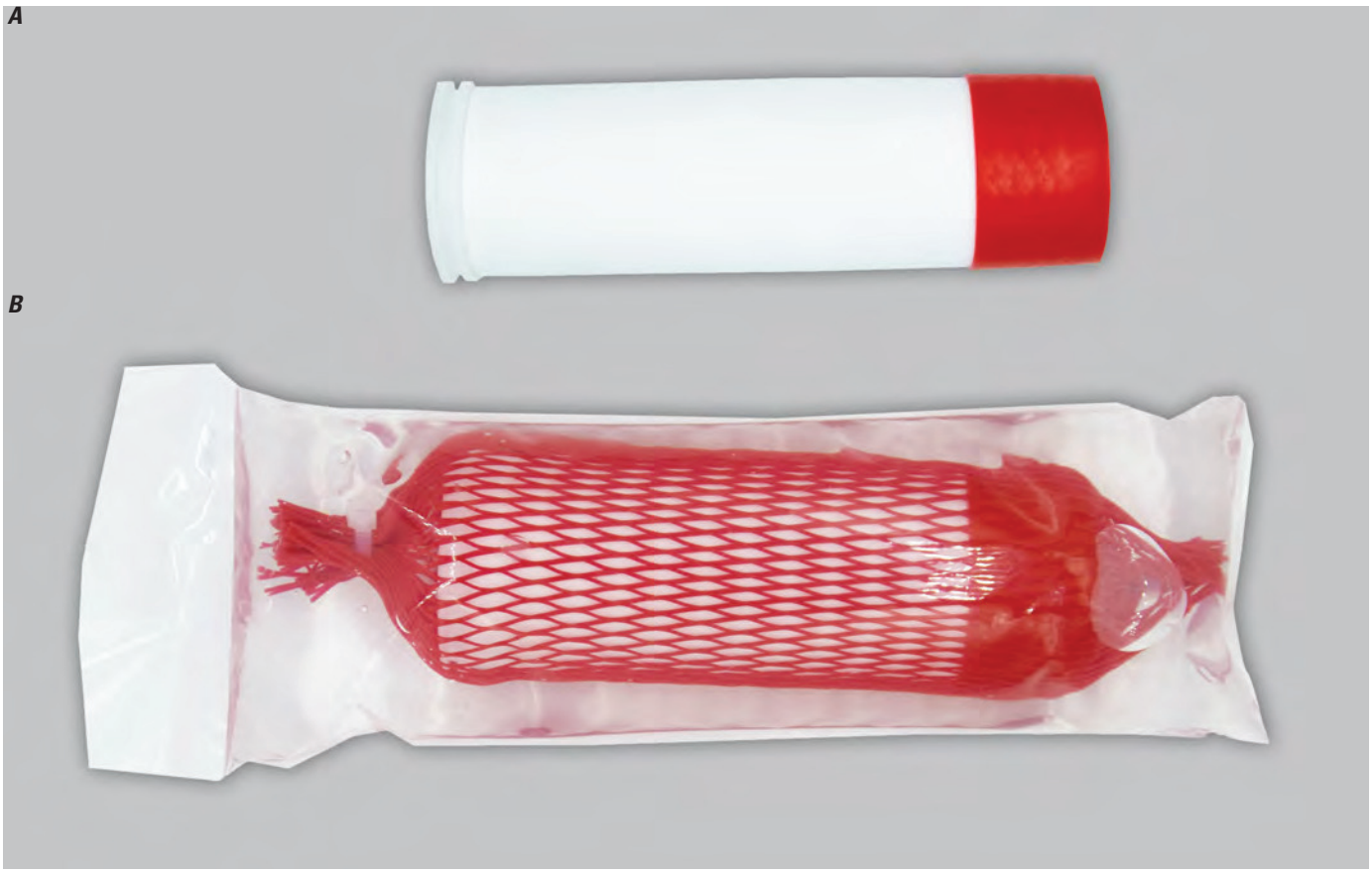

Figure 9. A rigid porous polyethylene sampler *A*, without the protective mesh, and *B*, with the protective mesh in a water-filled tube for shipment. Photographs by Leslie Venegas, ALS Global.

sizes of 6–15 µm. The sampler is filled with deionized water; closed at both ends; placed inside a mesh sleeve, which is subsequently attached to a deployment rope using cable-ties; and lowered into a well. This size sampler holds 90–100 mL of water.

While deployed in the open or screened interval of a well, solutes in the groundwater will diffuse through the pores of the porous polyethylene membrane, driven by the concentration gradient between the groundwater and the deionized water inside the sampler. After 2 weeks, the constituent concentrations in water inside the RPP sampler will equal the constituent concentrations outside the RPP sampler. Upon retrieval, the capped end is removed, and the contents of the sampler are poured immediately into sample containers. Water samples are then shipped to the laboratory for direct analysis of concentrations.

RPP are commercially available for purchase. The RPP samplers can be stacked to collect larger sample volumes. RPP samplers are restricted to a 6-in. length; if they are longer, they have a tendency to leak water as a result of the pressure of the fluid column inside the sampler exceeding atmospheric conditions. Even at 6 in., RPP samplers can leak if exposed to the atmosphere for several minutes.

4.3.2 Advantages and Limitations

The main advantages of RPP samplers are that they can be used to collect samples for analysis of a wide variety of organic compounds and inorganic constituents and that they are not biodegradable, so they may be left in a well between sampling events. Their primary limitations are that they must be filled and kept immersed in deionized water prior to deployment owing to the possibility of leakage, the sample volume is restricted, and relatively large pore sizes (6–15 µm) allow for sampling of larger-sized molecules but consequently may require 0.45-µm filtering of the water upon retrieval. The length of the sampler, which is constrained by the height of the water column inside the sampler and the membrane pore size, limits the volume to approximately 100 mL per sample. These samplers need to be filled with oxygen-free deionized water if redox-sensitive constituents are to be measured.

4.4 Nylon Screen (NS) Sampler

The NS sampler is an equilibrium-membrane-type passive sampler. The NS sampler was originally developed in the late 1990s to sample for trace metals in groundwater. These samplers were tested in the early 2000s for their ability to sample VOCs, trace metals, major cation and anions, dissolved oxygen, 1,4-dioxane, and perchlorate (Vroblesky and others, 2002a; Vroblesky and others, 2002b; Vroblesky and others, 2003; Parsons, 2005). In some cases, the NS sampler may take a longer time (at least 3 weeks) to equilibrate with concentrations in the well water. If sampled before equilibration, the constituent concentrations in samples may be underestimates of concentrations in well water. The volume of water inside the sampler (V) relative to the diffusion surface area (A) of the nylon screen may play a role in equilibration and may be constituent dependent. Further research is warranted for the ability of NS samplers to sample for trace metals (ITRC, 2006). Water samples collected with NS samplers are shipped to the laboratory for direct analysis of organic compound and inorganic constituent concentrations. An example of a study utilizing NS samplers is given in Appendix A, Case Study A2.

4.4.1 Description and Operation

Nylon screen samplers can vary in size but typically consist of a 175-mL polypropylene wide-mouth bottle (diameter of 62 millimeters [mm] at top, 58 mm at bottom, and a height of 58 mm) filled with deionized water, with a 125-µm mesh nylon screen placed across the opening, and covered with a cap that has an opening about 58 mm in diameter (fig. 10). The resulting V/A ratio is about 6:1 (Webster and others, 1998).

Different sizes of samplers and corresponding V/A ratios can be used as shown in figure 10. The sampler in figure 10*A* has a V/A ratio of 6:1, whereas the sample in figure 10*B* has a V/A ratio of 22:1. The NS sampler diffusion uptake can be calculated using equation 3 for constituents of interest.

For deployment in wells, the NS sampler is placed within a protective polyethylene mesh and attached to a weighted line. It is preferable to deploy the NS sideways in a well but owing to size restrictions it is usually necessary to deploy it facing downward to minimize mixing as the samplers are brought back to the surface. During deployment, chemicals in groundwater in the well diffuse through the nylon screen membrane and equilibrate with water inside the sampler. The sampler retains the water inside by a combination of surface tension between the water and the screen and the vacuum that develops in the inverted bottle. Once retrieved, the samplers are re-inverted and the contents of the sampler can be transferred to sample containers, or solid caps can be screwed over the membrane in place of the open caps, and the entire sampler can be sent to the laboratory.

Fully constructed NS samplers are not currently available from any commercial vendor. Nylon screen of varying mesh sizes can be ordered from a number of material vendors. The NS samplers can be stacked to collect larger volumes of water from a well.

4.4.2 Advantages and Limitations

The main advantages of NS samplers are that they can be used to collect samples for analysis for a wide variety of organic compounds and inorganic constituents, they are low cost to construct, and they are disposable. Their limitations are primarily related to the small volumes of sample collection, typically 175 mL per sample, and that samples may require filtration through a 0.45-mm filter if dissolved concentrations are needed. NS samplers must be filled and kept immersed in deionized water between the time of construction and deployment in a well. These samplers need to be filled with

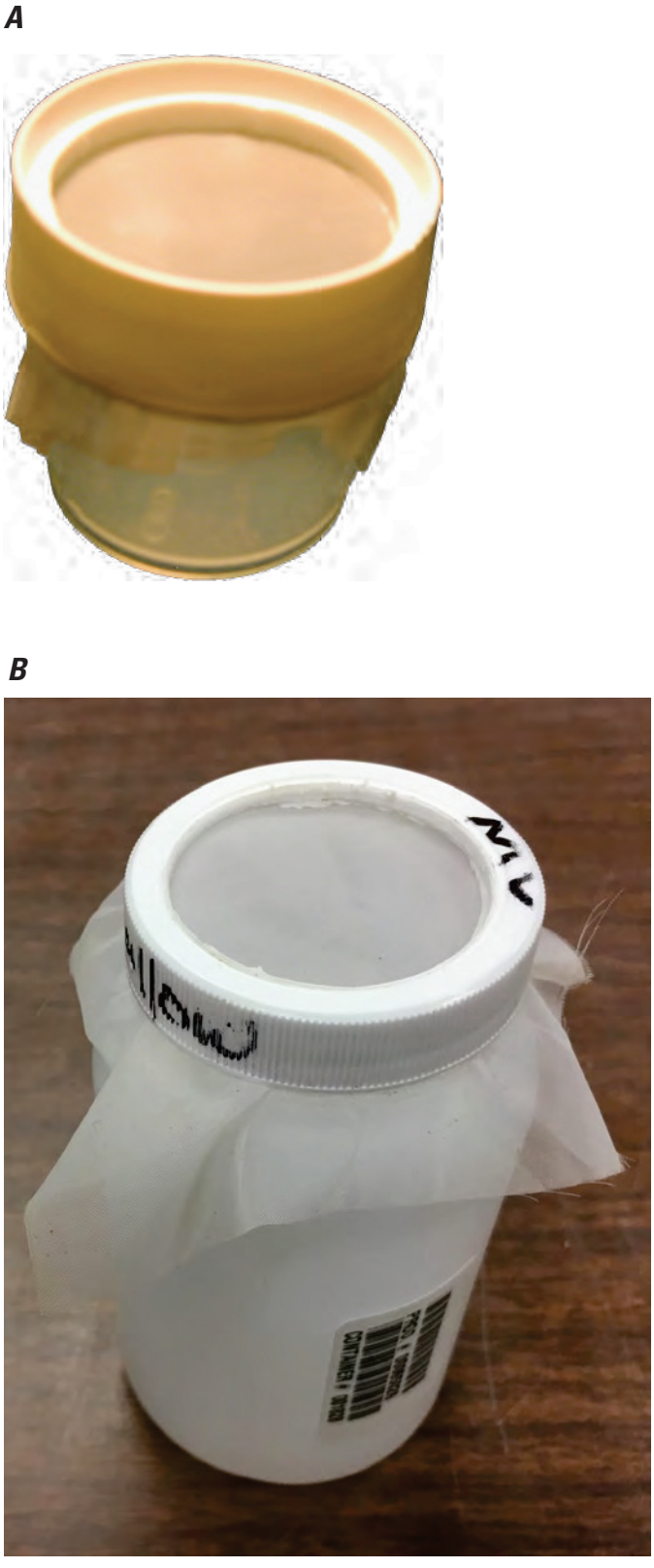

Figure 10. Two different sized nylon-screen passive samplers *A*, V/A ratio of 6:1 and *B*, V/A ratio of 22:1. Photographs by Donald A. Vroblesky and Philip T. Harte, U.S. Geological Survey. [V, volume of sampler; A, diffusion surface area of opening of sampler].

oxygen-free deionized water if redox-sensitive constituents are to be collected. Further, extended periods of deployment (>3 weeks) may be needed to achieve equilibration for some trace metals.

4.5 EON Dual Membrane (DM) Sampler®

The EON Products, Inc. Dual Membrane (DM) sampler® is an equilibrium-membrane-type passive sampler. It essentially combines a PDB sampler and a NS sampler using two semi-permeable membranes in one diffusion sampler. It was developed fairly recently (circa 2015; EON Products, Inc., 2016). Given its recent development, the sampler has not been used extensively. The DM sampler theoretically allows sampling of major cations and anions, some trace metals, nutrients, VOCs, and some PFASs.

A comparison study of the results of samples collected with DM samplers and with low-flow purging at Kirtland Air Force Base, Albuquerque, New Mexico, showed relatively good agreement between the concentrations of two VOCs (1, 2-dibromoethane and benzene), major cations and anions, and selected trace metals (EA Engineering, Science, and Technology, 2016, 2017). More than 90 percent of the comparisons made between the two sampling methods were within a relative percent difference (RPD) of 20 percent and were comparable to the RPD between duplicate samples (EA Engineering, Science, and Technology, 2016, 2017). Water samples collected with DM samplers are shipped to the laboratory for direct analysis of organic compound and inorganic constituent concentrations.

4.5.1 Description and Operation

The DM sampler consists of a 1.75-in.-diameter by 22-in.-long hollow cylindrical, perforated tube that forms a rigid sample chamber. The top 6 in. of the sample chamber is wrapped with a 125-µm mesh nylon screen material, whereas the bottom 16 in. of the sample chamber is wrapped with an LDPE membrane (fig. 11). Like many other passive samplers, they can be deployed in a vertical string to profile well chemistry (fig. 11). The large pores of the nylon screen in the top portion of the sampler allow diffusion of inorganic constituents and polar organic compounds into the sampler (fig. 12). The LDPE membrane in the lower part of the sampler allows diffusion of VOCs (fig. 12) and acts as a reservoir. The two membranes form one internal sample chamber. Equilibration occurs when the chemical constituents that enter through both membranes diffuse vertically and mix within the sampler, their concentrations become uniform throughout, and the concentrations match that in the water outside the sampler in the well. This sampler should be deployed in a well for at least 3 weeks to equilibrate for most constituents. When a DM sampler is removed from a well, the water in the nylon screen portion will leak out and only the water in the LDPE portion will be retained. Because of this, a DM sampler with the above dimensions will collect approximately 625 mL of water.

Figure 11. *A*, An EON Products, Inc. Dual Membrane (DM) sampler® and *B*, a vertical string of DM samplers being retrieved from a well. Photographs by Bradley P. Varhol, EON Products, Inc. and Rebecca Travis, U.S. Geological Survey.

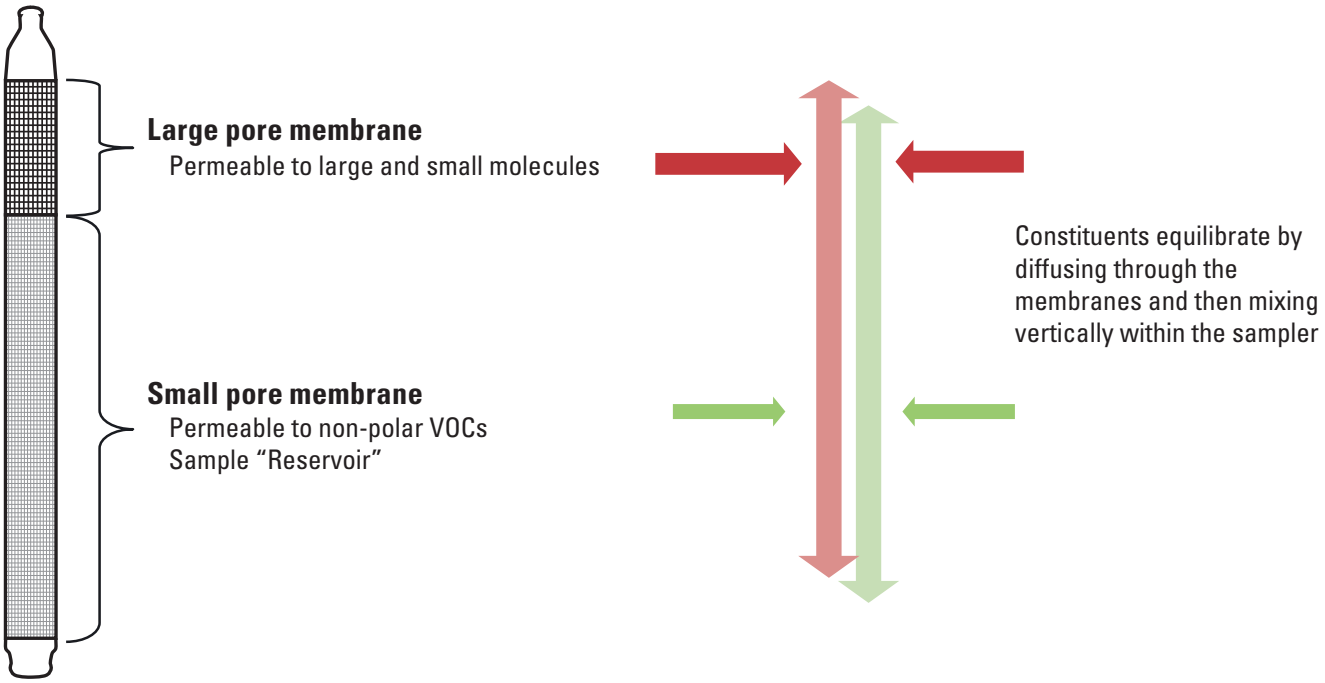

Figure 12. An EON Products, Inc. Dual Membrane sampler® with large pore and small pore membrane configurations. Modified from diagram by Bradley P. Varhol, EON Products, Inc. [VOCs, volatile organic compounds]

4.5.2 Advantages and Limitations

The advantages of the DM samplers are that they can be used to collect samples for a range of major cations and anions, trace metals, VOCs, and some PFASs; they are constructed of non-biodegradable materials, so they can remain in a well from one sampling event to the next; and they are disposable, so no decontamination is needed. The limitations of the DM samplers include, longer deployment times (at least 3 weeks) for equilibration of some constituents both into and within the sampler, and that filtration of samples through a 0.45-µm filter is required if dissolved concentrations are needed. The relatively small nylon membrane surface area compared to the larger internal volume of the DM sampler may lengthen equilibration times. Other limitations are that the samplers must be filled in the field or kept submerged in deionized water between the time of filling and deployment, the samplers need to be filled with oxygen-free deionized water if redox-sensitive constituents are to be collected, and the sample volume is restricted by the size of the sampler to 625 mL.

4.6 QED Snap Sampler®

The QED Environmental Systems, Inc. Snap Sampler® is an equilibrium-thief-type passive sampler. Snap Samplers were first introduced in 2004, initially to collect unaltered VOC samples from wells without purging (Britt and others, 2010). The sampler has specialized containers that can be triggered to close and seal at depth in a well. During equilibration, the samplers are left open (on both ends) to allow for advective or diffusive compound exchange with the surrounding environment (in this case well water). Once recovered, the closed containers are capped and sent directly to the laboratory for analysis, so no volatilization losses can occur during sample transfer at the surface (Britt, and others, 2010).

Snap Samplers can be used to collect samples for most constituents of interest including VOCs, 1,4-dioxane, cations, anions, trace metals, explosives, and methane, among others (Britt and others, 2010; Parker and others, 2011a; Parker and others, 2011b). Water samples collected with Snap Samplers are shipped to the laboratory for direct analysis of organic compound and inorganic constituent concentrations.

4.6.1 Description and Operation

The Snap Sampler consists of a polytetrafluoroethene or stainless-steel module that holds a 40-mL glass VOC vial-sized bottle that is open on both ends (fig. 13*A*). A 125-mL polyethylene bottle and 350-mL bottle are also available for collecting larger sample volumes (fig. 13*B*). The device keeps the spring-loaded caps open while the device is deployed in the well. After equilibration has occurred, a trigger line is pulled manually or by using a pneumatic device to allow the spring-loaded caps to snap shut and seal off the sample (fig. 14). The pneumatic trigger allows for deep deployment of the samplers (>2,000 ft). Upon retrieval from the well, caps are added to both ends of the sealed bottle, which is then sent to the laboratory for analysis. There is no sample transfer, so there is no exposure to air, no volatilization, and no loss of sample volume. As many as six Snap Samplers can be attached in series to collect a large-volume composite sample or to collect samples at six different depths.

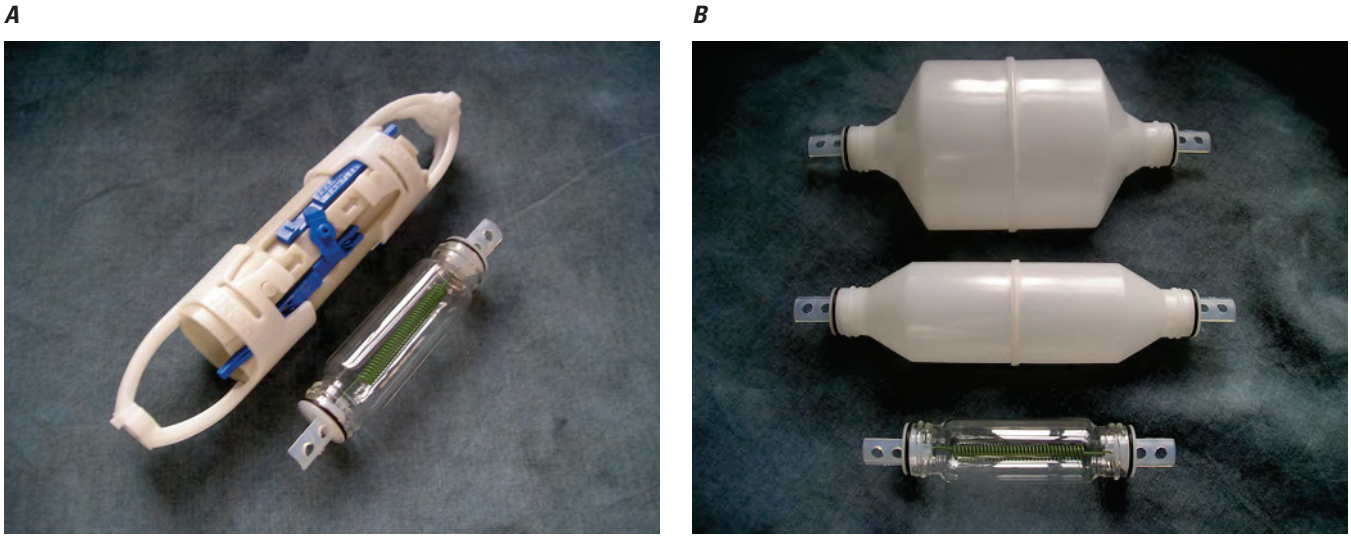

Figure 13. The QED Environmental Systems, Inc. Snap Sampler® with *A*, a volatile organic compound bottle (40-millileter vial), and *B*, variously sized volatile organic compound and inorganic constituent bottles. Photographs by Sanford Britt, QED Environmental Systems, Inc.

Figure 14. Various views of the QED Environmental Systems, Inc. Snap Sampler® operation in a well. Photographs by Sanford Britt, QED Environmental Systems, Inc.

When the Snap Sampler is left in the well for 1–2 weeks, permeation/diffusion through the open ends causes the chemical concentrations in the well water to equilibrate with those in the water inside the sampler. When triggered to close, the sample inside is sealed at the temperature and pressure present at the sampling depth.

4.6.2 Advantages and Limitations

The main advantage of the Snap Sampler is that it is the only passive sampler that can collect true "total" or "unfiltered" samples because it contains no membrane or sorptive media that might selectively filter out or sorb some chemicals. It can be used to collect samples for analysis of a wide variety of organic compounds and inorganic constituents, and it can be used to collect redox- and pressure-sensitive chemical constituents that may oxidize or degas upon retrieval at land surface. The primary limitations of the Snap Sampler are limited sample volumes of the individual bottles (40 mL, 125 mL, or 350 mL), the samplers are relatively expensive to buy compared to some other passive samplers (but may be leased at a lower cost), and operation and sampling procedures may require some training (available from the manufacturer). The sampler modules (the bottle holder part) are usually dedicated to a well, and the bottles may either be re-useable or disposable. Given that the sampler module is usually dedicated, there may be some long-term cost savings for monitoring wells that are sampled on a recurring basis. If dissolved concentrations are needed, the samples collected by the Snap sampler must be filtered through a 0.45-µm filter.

4.7 AGI Sample Module®

The AGI (Amplified Geochemical Imaging, LLC) Sample Module®, formerly known as the GORE-SORBER® Module, is an accumulation-type passive sampler. The AGI Sample Module was developed in the 2000s to sample for organic compounds in soil gas, tree borings, and groundwater (Einfeld and Koglin, 2001; ITRC, 2006, 2007). The device relies on diffusion and sorption to accumulate analytes onto resins in the sampler. The samplers are recovered from a well after a pre-determined deployment period and sent directly to the AGI Laboratory in Newark, Delaware, for analysis. Samples collected with these samplers are measured after extraction/desorption at the laboratory and produce a mass flux or a total mass of organic compounds sorbed over the time of deployment. Concentrations of organic compounds can be approximated with an algorithm developed by the manufacturer or can be compared to field samples collected using another sampling method during deployment (ITRC, 2006, 2007).

These devices have been used to detect VOCs and SVOCs, including halogenated solvents, aliphatic and aromatic hydrocarbons, ethers, alcohols, ketones, polycyclic aromatic hydrocarbons (PAHs), nitroaromatic explosives and their breakdown products, pesticides, herbicides, and polychlorinated biphenyls (PCBs) (ITRC, 2006, 2007).

4.7.1 Description and Operation

Each AGI Sample Module is approximately ¼-in. in diameter and 13 in. in length and consists of a tube of GORE-TEX® membrane that contains a series of four small packets of sorbent material (figs. 15 and 16). The GORE-TEX® membrane is microporous, expanded PTFE and is relatively chemically inert. The hydrophobic nature of the membrane allows organic vapor migration to the inner sorbent material but prevents water and sediments from passing through. A typical sorber module is about 9.8 in. (25 cm) in length, 0.12 in. (3 mm) in diameter, and contains four packets of a granular adsorbent material that is selected on the basis of the specific compounds to be detected. For VOCs and SVOCs, hydrophobic carbonaceous and polymeric resins are used, although the sorber packets can be custom designed for specific organic compounds.

Figure 15. The AGI Sample Module®. Photograph from Mark Arnold, Amplified Geophysical Imaging, LLC.

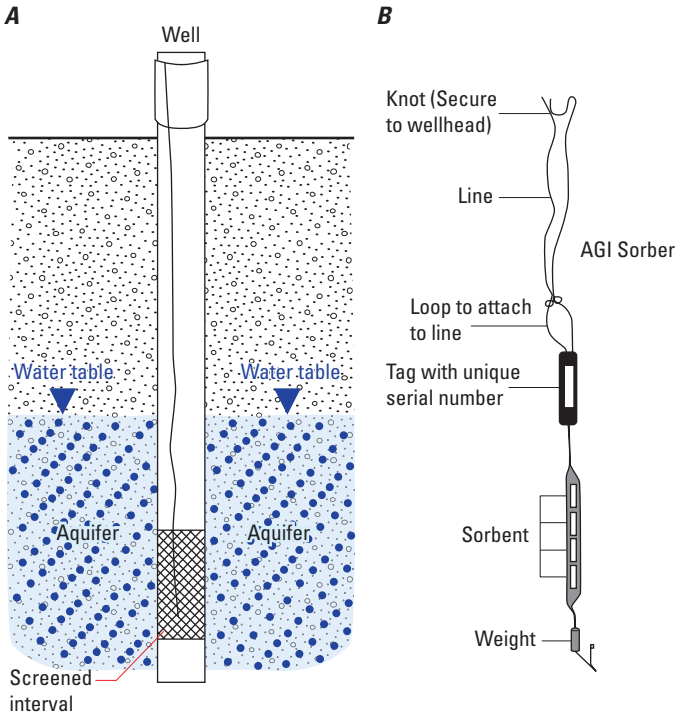

Figure 16. The installation of an AGI Sample Module® in a monitoring well. Modified from diagram by Mark Arnold, Amplified Geophysical Imaging, LLC.

Organic compounds dissolved in water, partition to the vapor phase according to Henry's Law and move through the PTFE membrane to the sorbent. For groundwater monitoring applications, the module is suspended in a monitoring well on a length of weighted line. The narrow diameter of the module allows deployment in piezometers and wells of ½-in.-inner diameter and larger.

Each AGI Sample Module is clean when it comes from the manufacturer and is contained in a sealed glass vial (fig. 15). Each module is labeled with a unique serial number. After the module is removed from the vial, it is placed at the desired depth in the screened or open interval (fig. 16), or several modules can be placed at multiple depths within the screened or open interval. After the exposure period (minutes to days, depending on the concentrations present), the module is retrieved and returned to the glass vial and shipping container. The glass vials containing the exposed modules, along

with trip blanks, are shipped overnight to AGI's dedicated laboratory. It has been determined that the modules do not have to be kept cold for shipment and will keep in the glass vials without refrigeration until they are analyzed, usually within 4–6 days (ITRC, 2007). The volume of water sampled during an AGI Sample Module deployment is a function of the sampling rate for a particular chemical and the sampling duration. The cost of an AGI Sample Module includes the trip blank, deployment supplies, laboratory analysis, and reporting. Costs per sample are dependent on the organic compounds being tested.

4.7.2 Advantages and Limitations

The main advantages of this passive sampler are that it can be used to collect samples for a wide range of VOCs and SVOCs; requires minimal handling, which reduces possible field sampling errors; is single use so no decontamination is needed; and can be used in monitoring wells and piezometers as small as ½-in. in diameter. In addition, these samplers have simple shipping requirements (no ice or coolers needed) and lower shipping costs, and the modules contain duplicate samples. Depending on the site and the constituents of interest being sampled, short deployment times may require only one trip to the field to collect a sample.

The limitations of the AGI Sample Module include that it cannot be used to sample for inorganic constituents and gives only flux results (mass per time) not concentration results, so a companion study is needed to correlate flux results with organic compound concentrations in groundwater, or an algorithm must be used to approximate concentrations. In addition, these samplers come from only one supplier, so the cost is set and relatively high, and the samples can be analyzed by only the supplier's laboratory.

4.8 Semi-Permeable Membrane Device (SPMD) Samplers

The SPMD sampler is an accumulation-type passive sampler. The SPMD samplers were developed in the mid-1990s by personnel at the USGS Columbia Environmental Research Laboratory primarily for sampling hydrophobic semi-volatile organic compounds and pesticides in surface water (Petty and others, 1995; Ellis and others, 1995; Lebo and others, 1995; Lebo and others, 1996; Gustavson and Harkin, 2000). Since that time, the sampler has been adapted to collect samples for organic compounds in groundwater in wells (Alvarez, 2010). The structure of the SPMD sampler simulates the surface and fatty tissues of a fish. Samples collected with an SPMD sampler are analyzed after extraction at the laboratory and produce a mass flux or a total mass of organics sorbed over the time of deployment in a well. Concentrations of chemicals can be approximated with an algorithm or can be compared to field samples collected during sampling using another method (Alvarez, 2010).

4.8.1 Description and Operation

The SPMD sampler consists of a length of lay-flat LDPE tubing containing triolein. Triolein is a triglyceride and is highly sorptive of semi-volatile organic compounds and pesticides. The triolein-containing membrane can be made to different lengths to vary the surface area for adsorption and is supported inside a stainless-steel protective housing, which is made to fit down 4-in. wells (fig. 17*A*). The LDPE membrane and the triolein approximate the scales and the fatty tissues of a fish. The sampler is suspended in the open interval of a well where groundwater passing through comes in contact with it. Dissolved organic compounds flowing past the sampler experience a strong concentration gradient to move into the sampler, then partition into and accumulate in the triolein (fig. 17*B*). After recovery, the sampler is taken to the laboratory where the triolein is removed, extracted with hexane, and analyzed. The result is a mass flux or the mass of organic compound sorbed over the time the sampler was deployed.

4.8.2 Advantages and Limitations

The advantage of the SPMD sampler is that it can be used to collect samples for a range of hydrophobic SVOCs (PAHs, PCBs) and pesticides. The primary limitation of the SPMD sampler is that it cannot sample for inorganic constituents, VOCs, or hydrophilic organic compounds. Also, a sample extraction step is required prior to analysis and this procedure is typically only available at one or two laboratories. In addition, SPMDs measure only chemical fluxes in wells and require an algorithm to estimate concentrations or a companion study to correlate flux results to organic compound concentrations in well water.

4.9 Other Equilibrium-Membrane-Type Samplers

A discussion of other equilibrium-membrane-type samplers is provided in Vrana and others (2005). In addition, and of note here, Gardner and Solomon (2009) developed a passive headspace sampler for sampling of noble gases. Gas-permeable silicon tubing is connected to conventional metal tubing by a gas-exchange port that can be shut off in situ by pressurization. This allows sealing of gas samples at depth. The concentration of the gas within the sampler can be calculated using Fick's second law of diffusion. Testing of the ability of the sampler to collect noble gases, such as argon, found that concentrations of argon from the sampler provided a good comparison (within 3 percent) with results from conventional sampling (Gardner and Solomon, 2009).

A diffusion sampler to collect samples for dissolved hydrogen in groundwater has been developed to determine redox conditions (Vroblesky and others, 2007b). This diffusion sampler is constructed with nitrogen-filled high-density polyethylene 50-mL syringes that can be installed in a well indefinitely. Over time, dissolved hydrogen in the groundwater

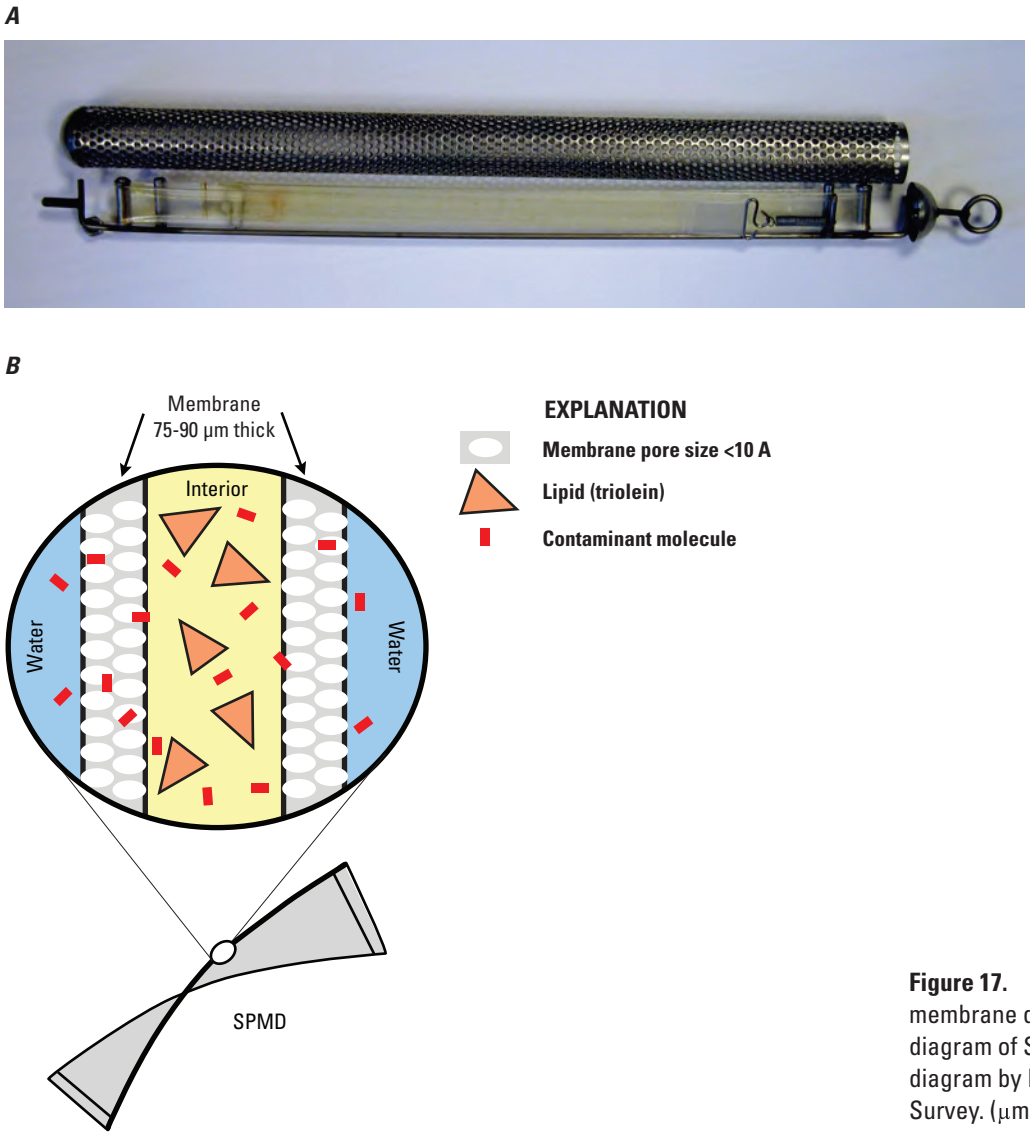

Figure 17. *A*, A downhole semi-permeable membrane device (SPMD) sampler and *B*, a diagram of SPMD operation. Photograph and diagram by David A. Alvarez, U.S. Geological Survey. (µm, micron)

equilibrates through the syringe walls into the nitrogen. Once the sampler is retrieved from the well, the gas sample can be directly injected into a gas chromatograph equipped with a hydrogen detector for analysis (Vroblesky and others, 2007b).

4.10 Other Accumulation-Type Samplers

The diffusive gradient in thin-film (DGT) sampler is an accumulation-type passive sampler, so the sampler produces a flux measurement that is based on the mass of inorganic constituents sorbed over the period of time it is deployed in a well. It does not measure concentrations in the groundwater. The sampler accumulates analytes on a thin-film resin layer. Analysis of the sample requires elution of the analytes off the resins to measure the mass of the inorganic constituents of interest. The sampler has been shown to be effective in sampling of uranium (U) and U isotopes of ^{235}U and ^{238}U (Turner, 2013) as well as lead, copper, zinc, cadmium, nickel, iron, and manganese (Zhang and others, 1995; Dunn and others, 2003).

The ceramic dosimeter is another accumulation-type passive sampler. The sample produces a flux measurement that is based on the mass of organic compounds sorbed over the period of time the sampler is deployed in a well (Martin and others, 2003; Boppa and others, 2005). It does not measure concentrations in the groundwater. A comparison of results for benzene and naphthalene fluxes from the ceramic dosimeter with results for fluxes that are based on conventional water sampling of wells shows good agreement for relatively short-term (days) to long-term (months) deployments. The time-integrated flux measurements from the ceramic dosimeters were within representative ranges of results of fluxes calculated from conventional water sampling.

5.0 Considerations Prior to Use of Passive Diffusion Samplers

This section provides information on sampling objectives and the performance of passive samplers relative to physical and chemical conditions in the well and subsurface environments. Because passive samplers are affected by hydrologic and chemical conditions, substantial discussion is devoted to describing the dynamics between those conditions.

5.1 Data-Quality Objectives

Prior to the start of a passive sampling effort, data-quality objectives (DQOs) need to be clearly identified. Data-quality objectives frequently are defined by (1) project sampling goals, (2) target analytes, (3) hydrologic conditions, and (4) regulatory guidelines. These factors help formulate the type of water-quality data needed and how accurate and precise the data need to be to achieve the project goals.

If prior information is unavailable on groundwater quality or the type of contaminants present, then purge sampling is better as an initial reconnaissance tool than passive sampling because purge sampling can collect samples for a broader range of chemical constituents. For evaluating contaminant problems or general water chemistry in residential areas, purge sampling may more closely approximate the volume of the aquifer that is interrogated when pumping household supply wells. However, if the main sampling goal is to monitor the concentration of a known indicator class of contaminants over the long term in observation wells, passive sampling may be the better option because it will reflect the concentrations present in the water flowing into the well under ambient conditions and likely will be less expensive than purging methods. An added benefit of passive sampling is that it will affect the flow field around the well less than purge sampling and consequently may better reflect solute transport behavior in the formation.

A primary consideration when deciding whether to use passive samplers and the type of passive sampler to use is to ensure that the sampler is able to collect the constituents of interest. For example, if sampling is for just inorganic constituents, then PDB samplers would not be a good choice because they sample only for VOCs. In this case, RCDM, RPP, or NS passive samplers that can collect inorganic constituents and organic compounds may be more appropriate.

If one of the DQOs is to collect samples under unstressed (non-pumping) conditions, then one of the passive sampler types would be an ideal choice. In contrast, if the objective is to collect samples under different levels of stressed conditions in an aquifer, then use of a variable speed pump would be an effective sampling option.

The DQOs for the project may require the collection of samples by certain prescribed methods to produce results that are approved and accepted by a regulatory or water agency. Many times, purging a well with a pump to obtain samples may be written into guidelines. In other cases, the agency may have guidance on the accepted use of passive samplers in wells or may allow their use if comparisons between passive sampling results and purging results are favorable.

5.2 Hydraulic and Chemical Equilibration

Two types of equilibration, hydraulic and chemical, must take place in a well before any passive sampler can collect a representative sample. Hydraulic and chemical equilibrium in this case refers to achieving a hydraulic-flow pattern and a chemical distribution within the screened or open interval of a well that is stable over a predetermined time. When a passive sampler is lowered into a well, it physically mixes the water column in the well to a small extent and temporarily perturbs borehole flow and the pattern of groundwater flowing into and out of the screened or open interval: a partial analogy to this process is the lowering of a downhole flow meter tool that perturbs the flow in the well, as described by Bayless and others (2011). The ambient flow of groundwater from the formation into the well and past the sampler will take a finite amount of time to re-establish itself. Once in the screened or open interval of a well, passive samplers must either equilibrate chemically with the concentrations of constituents in the groundwater or sorb a mass of constituents from the water flowing past the sampler. These equilibration and sorption processes will both take a finite amount of time to occur. Only after hydraulic and chemical equilibration/sorption occur can a representative sample be collected.

5.3 Hydraulic and Hydrologic Well Considerations

Passive sampling relies on the ambient flow of groundwater into the screened or open interval of a well to bring water in contact with the samplers. Therefore, knowledge of the geologic formation adjacent to the screened or open interval of the well, the age of the well, the water level in the well, and the construction of the well is important in deciding the performance of passive samplers in a well. These factors are discussed in more detail in Sections 5.3.1–5.3.5.

5.3.1 Geologic Formation

The exchange of ambient groundwater in the aquifer formation with the water in the screened or open interval of a well will differ among geologic formations. In permeable sand-and-gravel formations, ambient flow through the screened interval occurs principally from the most permeable strata along the screened interval (Marsh and Lloyd, 1980; Kearl and others, 1994). In fractured rock formations, ambient flow occurs primarily from discrete fractures at different depths in the bedrock. On a relative scale, wells in porous

media likely will encounter more uniform diffuse flow across the entire open interval than wells set in fractured rock where flow is channeled only through discrete fractures. Regardless of the type of flow regime, proper placement of passive samplers in a well is important in any formation where hydrogeologic units promote stratified horizontal flow into a well and where minimal mixing occurs in the well.

If a well is completed in a permeable formation, it probably is in good hydraulic communication with the formation, and the water in the well probably is representative of water in the formation adjacent to the well opening. In such a well, a passive sampler will collect a sample that likely represents the groundwater chemistry in the formation for the deployment period. This can be confirmed by comparing concentrations in samples collected with passive samplers and purging methods in the same well. Harte (2002) found close agreement of tetrachloroethene concentrations measured in wells in very permeable sand-and-gravel glacial deposits using PDB passive samplers and purging.

If the well is screened in a less permeable or a hydraulically tight formation, the concentrations of constituents measured using a passive sampler may represent the concentrations in the well over the past few days but not the concentrations present in the formation. The reason for this is the slow flushing times of wells in low-permeability formations, where mixing or chemical reactions may be taking place in the well, such as volatilization losses of VOCs in the water column of the well (McAlary and Barber, 1987), which are not occurring in the formation. Mixing or chemical reactions may cause a passive sampler in such a well to collect samples with concentrations different from those in the formation.

To further illustrate the concept that the permeability of a formation and the relative rates of flow and transport can control the chemical concentrations recovered by a passive sampler, a schematic diagram of the relation between chemical concentrations from the well, formation, and sampler is shown in figure 18. Fundamentally there are two transport characteristics to consider when sampling with passive samplers. They are the rate of transport of constituents from the formation to the well and the rate of exchange between the well water and the sampler. The first characteristic is controlled by near-well transport in the formation (permeability and hydraulic gradients) and transport into and out of the well (well connectivity). The second characteristic is controlled by the passive sampler membrane and concentration gradient of the constituents of interest across the membrane. For extremely high-permeability formations (for example, karst environments) with high transport rates, equilibrium-membrane-type passive samplers will equilibrate over time but may not be able to monitor short-term changes in concentrations in water flowing rapidly past the sampler (fig. 18*A*). For example, the passive sampler could equilibrate to some time-weighted average concentration, but this average may not be representative of the chemical concentration in the formation at any moment in time. However, for some slower transport rates, it would be a closer representation (fig. 18*B*). Alternatively, in low-permeability formations, the transport from the formation to the well may be so slow that the chemical concentration in the well water is not representative of the concentration in the formation because chemical changes can occur once the water enters the well (fig. 18*C*). As a rule of thumb, in all but very low-permeability formations, 7–14 days has been found to be sufficient for the flow regime to re-equilibrate between the formation and the well.

5.3.2 Age of the Well

Well age or the time since the well was installed can have an important effect on whether to use passive sampling. Because contact time of the sample water with the well material is longer for passive sampling than for purge sampling, well-material degradation or reactivity of the water with the well material has the potential to affect passive samples more than the short-contact time for purge samples. In addition, if flow through the well screen or filter pack is diminished because of clogging by physical or biological processes, then the ambient water in the well is less likely to freely exchange with formation water. In this case, because a purge sample can force inflow through the screen, purge sampling may produce a more representative sample than the passive sampler. In general, wells constructed with inert materials that are not easily corroded or degraded and wells with screened or open intervals that are not clogged are preferred wells for passive sampling.

Another age-related factor that may affect passive sampling is related to well installation. The disturbance of the flow field in the groundwater system during the well installation process is important and affects the ability to collect representative samples from the well for a period of time after well installation. Ideally, at least 1–3 months should elapse before trying to sample a newly installed well using purging methods. Passive sampling will require a greater time period after installation than purge sampling to allow for hydraulic and chemical equilibration. Although some methods of well drilling disrupt the groundwater chemistry and ambient flow in the aquifer more than others, as a rule of thumb, passive samplers are not to be used to collect a sample in a well before the well is a minimum of 6 months old.

5.3.3 Monitoring History

New wells that have no monitoring history are not ideally suited for the use of passive samplers. Unless the new well is installed at a site that is well characterized for a specific constituent, the practitioner has little idea about which constituents to look for and, consequently, which passive sampler to choose. As discussed in Section 5.3.2, there is also the problem of flow into the well not equilibrating hydraulically or chemically for a long period of time after well installation.

Wells that are used for long-term monitoring with a known historical record are ideally suited for the use of passive samplers. Long-term monitoring wells have well-known

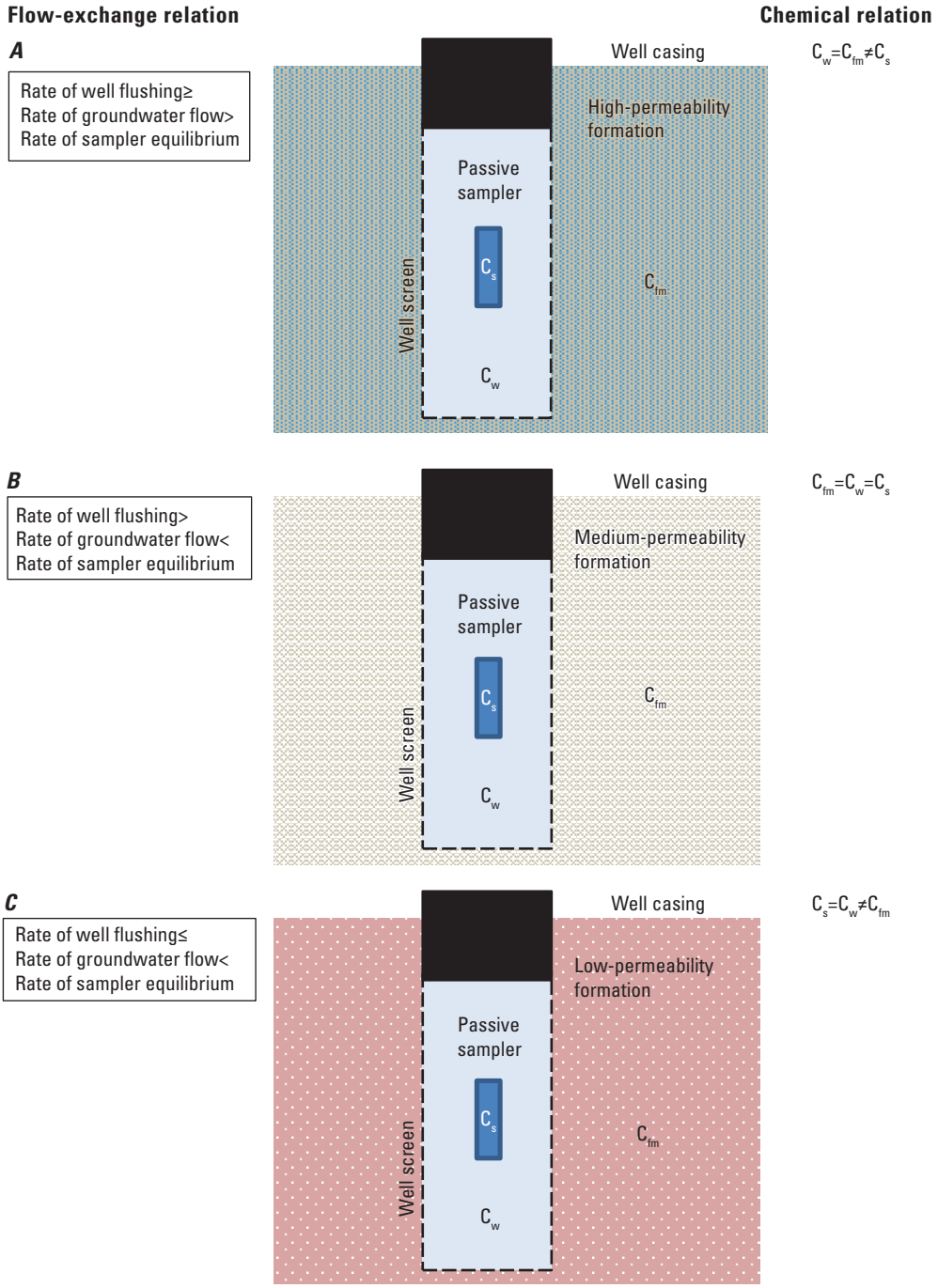

Figure 18. Hypothesized relation of passive sampler constituent concentration responses to rates of well flushing and groundwater flow and transport assuming constant sampler equilibrium rates for *A*, high-permeability, *B*, medium-permeability, and *C*, low-permeability formations. [Cs, constituent concentration in the sampler; Cfm, constituent concentration in groundwater in the formation; Cw, constituent concentration in the well bore; >, greater than; <, less than; ≥, greater than or equal to; ≤, less than or equal to]

hydraulic and chemical histories. This makes choosing a passive sampler that will collect the constituents of interest possible. Previous knowledge of the transmissivity of the well and the well construction helps with making decisions concerning the sampler depth and deployment/exposure time.

5.3.4 Water Levels

Knowledge of the water-level fluctuations in a well is important to prevent potential exposure of passive samplers to the atmosphere. Passive samplers ideally would be suspended in the well so that they remain submerged below the water level for their entire deployment period. If the water level in a well drops substantially over the deployment period and exposes the passive sampler to the atmosphere, chemical concentrations in an equilibrium-membrane-type passive sampler may not reach complete equilibrium with the chemical concentrations in the well water, and an accumulation-type passive sampler risks sorbing a reduced chemical mass from the well water, consequently yielding a low estimate for the mass flux.

Continuous submergence is usually not a problem for fully saturated screened or open intervals where the water levels in the well casing are well above the top of the screened or open interval. Continuous submergence is more problematic in partially saturated screened or open intervals or in wells with very little water above their openings. In the latter case, water-level declines may result in exposure of the passive sampler to the atmosphere. This is especially a problem when sampling for redox-sensitive constituents in formations with anaerobic water because contact with oxygenated water in the sampler could cause a chemical reaction that would affect concentrations in the sampler. For example, iron hydroxides could precipitate within the sampler and lower the dissolved iron concentrations. For sampling in aerobic waters, the exposure of the sampler is less stringent for redox-sensitive constituents because there is less of a chance that oxidation will affect the concentrations.

VOCs are a class of organic compounds that may also be sensitive to sampler exposure to the atmosphere. If sampling is for VOCs and the water level drops exposing the passive sampler to air in the well, loss of VOCs from degassing is possible. However, if the water level rises and the sampler is re-submerged for the last several days of its required equilibration time immediately prior to recovery, the collected VOC concentrations should be valid.

5.3.5 Well Construction

The construction of a well may have some effect on the use of passive samplers. If the well screen is properly sized for the aquifer sediments, open, and unclogged, the well hydraulic communication with the formation should be good, and the use of passive samplers should not be a problem. If, however, the screen is clogged with fine sediments or mineral deposits and not open to the formation, the well may not provide adequate exchange with groundwater for passive samplers to work properly.

The length of a well opening can be a factor affecting the use of passive samplers because of the potential for vertical flow and mixing within the well. Well openings greater than 10 ft have an increased probability of intersecting zones of differing permeability and hydraulic head and, therefore, an increased probability of vertical flow within the well opening. If vertical flow is prevalent in the well, the water chemistry of the well primarily reflects that of the units with the highest hydraulic head flowing into the screened or open interval. In contrast, where horizontal flow predominates, such as through short screens or longer screens intercepting little vertical variation in permeability and hydraulic head, the water chemistry of the well tends to reflect that of the formation approximately coincident with the sampler depth (Harte and Flanagan, 2011).

A filter pack around a screened interval can affect ambient flow in the well by redistributing inflow and outflow. Consequently, filter packs facilitate mixing of groundwater, which can alter water chemistry and potentially camouflage any stratification of groundwater chemistry found in the formation. Filter packs that extend beyond the well opening can intercept units with unique flow and chemistry characteristics that could then be redistributed into the well opening by way of the filter pack. Harte and others (2001) found that a filter pack that extended above a well screen contributed to tetrachloroethylene (PCE) concentrations that were 50 percent greater near the upper part of a 10-ft-long well screen than in the remainder of the well screen because the filter pack intercepted a permeable unit that transported PCE from above the screened interval into the well screen.

The diameter of a well will determine which passive samplers will fit down the well. All passive samplers discussed in this report are constructed to fit down a 4-in.-diameter well or greater. Versions of many of these samplers also have been constructed to fit down 2-in.-diameter wells or less. AGI Sample Modules will fit down wells as small as ½-in. in diameter.

5.4 Water-Quality Sampling Considerations

Water-quality considerations need to be taken into account before deciding whether to use a passive sampler and, if so, which sampler to use in the well. Issues like the materials used for sampler construction, the chemical constituents to be monitored, the size of the sampler, the deployment depth in the well, and the sampler deployment time in the well, among other things, will affect these decisions. These factors are discussed in Sections 5.4.1–5.4.8.

5.4.1 Analyte Suitability Considerations

The most important factor in choosing which passive sampler to use is that it must be able to sample for the constituents of interest. As pointed out in Section 4, each

passive sampler has a set of constituents for which the sampler has successfully been used to sample and some that it has not been able to sample. If, for instance, the site has VOC contamination, PDB samplers would be a good choice because they are inexpensive, reduce field sampling time, and have a proven track record of successful sampling for most VOCs. However, if there is a need to monitor for evidence of natural attenuation of the VOCs at the site, samples for ferrous and ferric iron, sulfate and sulfide, and carbon dioxide also will need to be collected. To sample for these additional inorganic constituents, a RPP sampler could be added in close proximity to the PDB sampler. Alternatively, a larger RCDM sampler could be used that would collect VOCs and inorganic constituents in one sampler. Additional discussion on the suitability of samplers for sampling specific constituents is presented in Section 6.

5.4.2 Sampler-Size Considerations

Many of the equilibrium-membrane-type passive samplers are small in diameter so they can fit down 2-in.- and 4-in.-diameter wells. As a result, most of these samplers collect small volumes of water. Before using a passive sampler in a well, one must be certain that enough water volume can be collected from the sampler to analyze for the constituents of interest. Once the sampler is constructed, the volume of water contained in any equilibrium-membrane type of passive sampler is fixed, so it is important to carefully determine at the outset of sampling the water volumes needed for analysis.

Volume limitations can be overcome by contacting the laboratory that will be analyzing the samples to discuss the minimum volumes necessary for the analyses. Frequently, laboratories ask for sample volumes that are several times larger than required simply to ensure that they have enough water for multiple analyses, dilutions, or reruns. Improvements in analytical technology have decreased the volumes required for many analyses. As an example, many anions are now analyzed by ion chromatography that requires only 5 mL of sample, whereas the laboratory may ask for a full 250-mL bottle for these analyses. Once the minimum volume has been agreed upon with the laboratory, this volume should be increased by 10–20 percent to account for volume used to rinse bottles or losses during sample handling in the field.

Some samplers can be made longer to increase their volume (PDB, RCDM), but some cannot because of pore-size limitations or design (RPP, NS, Snap). For example, the RPP sampler can leak the fluid sample if it is longer than 6 in. Also, as the length of a passive sampler increases, the sampler becomes more difficult to protect from harm during installation and recovery, and handling during sample collection becomes harder. The ITRC (2004) states that a single passive sampler should not represent more than a 5-ft interval in a well, so no passive sampler should be longer than 5 ft.

5.4.3 Sampler-Depth Considerations

The depth at which a passive sampler needs to be deployed must be known prior to going to the field so as to select the appropriate length of the suspension line required to deploy the sampler. Knowledge of the length and depth of the screened or open interval in a well is required. Screened and open intervals of 5 ft or less can be sampled by a single sampler suspended at their center point because vertical chemical stratification over this short distance is likely small. (The exception to this case is wells closer to hydraulic boundaries.) It is prudent, when initially using passive samplers in wells with screened or open intervals longer than 5 ft, to begin by deploying a string of passive samplers over the length of the open interval to decide whether the water is mixed or stratified, as discussed in Section 5.5. On the basis of the results of the initial vertical profiling and the DQOs of the project, the passive sampler typically is deployed at the depth where the highest concentration and (or) mass flux of the constituent of interest is found to be entering the well.

Passive samplers have no depth limit for their operation. As long as the samplers can be deployed and recovered from the selected depth in the well, they will work. RCDM samplers have been used in wells to depths of 410 ft but should be useable at greater depths (Imbrigiotta and others, 2007). DM samplers have been used at depths >1,000 ft in wells in New Mexico (Rebecca Travis, U.S. Geological Survey, written commun., 2018). Samplers that, by their design, are prone to leakage with time, such as the RPP sampler, are best not used in wells with depths to water greater than 200 ft.

5.4.4 Equilibration Time and Exposure Time

A variety of factors affect the equilibration time for equilibrium-type passive samplers and the exposure time for accumulation-type passive samplers. For equilibrium-thief-type passive samplers, the primary consideration is re-establishing hydraulic equilibrium after installation of the sampler. Once hydraulic equilibrium is achieved, chemical equilibrium via diffusion must then occur prior to sampling.

For equilibrium-membrane-type passive samplers, the rate of chemical equilibration of a constituent of interest between the sampler and the well water is dynamic and is a function of several factors: (1) the rate of ambient flow and transport past the sampler, (2) the physical characteristics of the membrane, (3) the affinity of the constituent of interest for the membrane material or materials of sampler construction, (4) the temperature of the groundwater, and (5) the diffusion coefficient of the constituent of interest. For most wells screened in sand-and-gravel deposits, fast flow through the screened interval allows for a quick and more complete exchange between equilibrium-type samplers and the groundwater.

The physical characteristics of a membrane refer to its thickness, area, pore size, and effective pore size. Thin membranes will equilibrate faster than thick membranes. For

example, equilibration through a 2-µm-thick LDPE membrane takes place faster than through a 4-µm-thick LPDE membrane. In general, membranes with large pores will equilibrate faster than membranes with small pores. The effective pore size depends not only on the size of the openings in the membrane, but also the tortuosity or length of the path a molecule must travel to diffuse through the membrane.

The chemical affinity and permeability of a variety of membrane materials have been determined in the laboratory for a large number of organic compounds and inorganic constituents (Vroblesky and Campbell, 2001; Vroblesky and others, 2003; Martin and others, 2003; Divine and McCray, 2004; Imbrigiotta and others, 2007; Britt and others, 2010). If a chemical constituent is strongly sorbed to a membrane material, equilibration will take longer to occur than if the chemical is not strongly sorbed because the strongly sorbed constituent passes through the membrane more slowly.

Groundwater temperature can affect the length of the deployment of a passive sampler. Molecules of a chemical constituent dissolved in warm shallow groundwater will diffuse faster and presumably equilibrate faster than the same chemical in cold groundwater at the same location.

The diffusion coefficient (D) of a chemical in water is an important factor in equilibration time because it is an important characteristic in Fick's first law (eq. 2). VOCs like trichloroethene (TCE) have a relatively high D (1.5×10^{-5} cm^2/s) compared to the D for inorganic constituents like uranium or selenium (2×10^{-8} cm^2/s). Equilibrium time as expressed by the $C_s(t)$ term in equation 3 is shorter for higher values of D.

As a general rule of thumb, the deployment time for many equilibrium passive samplers is on the order of 1–3 weeks with 2 weeks being the most commonly used deployment time. However, in some cases for compounds with low diffusion coefficients, the deployment time could be much longer than 2 weeks. Deployment times can differ at a given site for given constituents, depending on the conditions present in the aquifer. For example, if a well in a high permeability formation is sampled for chlorinated VOCs, a RCDM passive sampler probably will hydraulically and chemically equilibrate in a matter of a few days to a week (Imbrigiotta and others, 2007). On the other hand, if a well in a low-permeability formation is sampled for these same organic compounds, the RCDM sampler will probably take longer to hydraulically equilibrate, and the necessary deployment time will probably be closer to 2 weeks. The manufacturer of an equilibrium-type passive sampler always should be consulted when estimating deployment times for a sampler for various constituents.

For accumulation-type passive samplers, the exposure time needs to be determined on the basis of the constituents of interest and the concentrations present at the field site. The constituents of interest must be able to readily adsorb to the sorbent material of the sampler for effective sampling. For accumulation samplers, exposure time in the well should be shorter than the time it takes to completely saturate all the sorption sites on the sorbent material in the sampler, yet long enough to sorb sufficient mass to be able to detect the chemicals of interest at the lowest concentration of interest. Frequently, the exposure time is determined during the first sampling event by deploying multiple samplers in a well and removing them at different times (Martin and others, 2003) to determine when saturation occurs. For accumulation samplers, it is important to have some idea of the range of concentrations of the constituents of interest that are present in the well before deploying the samplers. The range of exposure times for accumulation-type samplers extends from minutes where constituent concentrations are high to several days or weeks where constituent concentrations are low.

5.4.5 Sampler Hydration Considerations

Some equilibrium-membrane-type passive samplers need to be kept hydrated after construction so the membrane will not dry out or to keep the sample chamber filled. Samplers such as the RCDM, RPP, NS, and DM samplers should be constructed and (or) filled within a few days of deployment, and all need to be kept immersed in deionized water between filling and deployment. If allowed to dry out, the membrane's diffusive properties can change, or the sample chambers can lose fluid from within the sampler.

5.4.6 Redox Considerations

The redox conditions of groundwater in the formation need to be considered prior to deployment of passive samplers when sampling for redox-sensitive constituents. For example, equilibrium-membrane-type passive samplers used to collect redox-sensitive constituents in anaerobic groundwater should be filled with water sparged with nitrogen or another relatively inert gas to remove the oxygen. Further, the sampler should not be exposed to atmospheric conditions prior to deployment because atmospheric oxygen will diffuse through the membrane into the sampler. De-oxygenated samplers can be transported to the field in a cooler full of sparged deionized water. If the samplers are used in an aerobic aquifer, then sparging the sampler-fill water is not necessary.

The reason that de-oxygenated water is needed to sample redox-sensitive constituents in anaerobic systems is that oxygen within the sampler can potentially react with chemicals diffusing into the sampler. For example, an equilibrium-membrane-type passive sampler filled with aerobic deionized water installed in a well with anaerobic groundwater and a high dissolved iron concentration can be problematic because, as dissolved iron diffuses across the membrane and contacts the oxygenated water inside the sampler, iron hydroxides can be precipitated out. This can result in lower dissolved iron concentrations being measured inside the sampler than in a pumped sample from the same depth in the well.

Sorption of a redox-sensitive constituent to the membrane of an equilibrium sampler can also be a problem, but with the reverse effect. For example, if high concentrations of iron are sorbed to the membrane itself, the inward concentration

gradient may be increased between the membrane and the water inside the sampler. This may result in a higher concentration of dissolved iron being measured inside the sampler than that measured in a pumped sample from the same depth in the well (Imbrigiotta and others, 2007).

5.4.7 Biological Considerations

Some semi-permeable membranes can be perforated or clogged over time by bacteria present in groundwater systems. This can take the form of bacterial or fungal growth clogging or fouling the membrane or, in some cases, perforating the membrane, which can cause the sampler to fail. Previous researchers have noted that some RCDM membranes have become discolored or bio-fouled during extended equilibration periods ranging from 2 to 3 weeks in shallow wells with warm groundwater temperatures (about 21 degrees Celsius [°C]) (Vroblesky and others, 2002b; Vroblesky and Pravacek, 2002; Vroblesky and others, 2003). Imbrigiotta and others (2007) compared biodegradation of four identical RCDM samplers in an anaerobic groundwater system in a 75-ft-deep well with an average groundwater temperature of about 15 °C at the Naval Air Warfare Center, West Trenton, N.J. These samplers discolored only slightly and lasted 4–6 weeks before developing perforations. Iwakun and others (2008) found that RCDM samplers survived intact for 6 months at a site in Canada where the average groundwater temperature was 4 °C ± 1 °C. Because the RCDM samplers require only a 2-week deployment to equilibrate for most constituents of interest, biodegradation of the membrane was not considered to be a major limitation for these samplers.

5.4.8 Temperature and Density Effects

Small density differences in water of 0.005 percent (approximately 50 milligrams per liter [mg/L] in total dissolved solids) and small temperature gradients (0.2 °C per meter) can induce mixing and the formation of thermal convective cells (Martin-Hayden, 2000). Thermal convection can induce vertical flow rates in a well to exceed 200 mL/min (Martin-Hayden, 2000). Thermal convection can inhibit the ability to determine depth-dependent concentrations. Instead, the concentrations derived would represent a mixed average concentration across depths contributing inflow within the convection interval.

Thermal convection also can inhibit a sampler's ability to collect representative redox-sensitive constituents of interest. In the winter in wells with a shallow depth to water, the shallower water can become colder than the deeper water in the well. The cold shallow water can sorb oxygen, initiate convection, and transport this DO to the deeper parts of the well. Thermal convection during the winter months was found to rapidly transport (within days) DO throughout much or all of the water column in wells with shallow depths to water (less than 30 ft) in South Carolina (Vroblesky and others, 2006, 2007a). Therefore, well water under ambient conditions is not representative of groundwater in an anaerobic formation under the influence of thermal convection and DO transport. Given the potential effect of thermal convection, passive sampling for redox-sensitive constituents should not be done without mitigating thermal convection and DO transport. One approach to mitigating thermal convection is to use a simple, inexpensive baffle system (Vroblesky and others, 2006, 2007a). Although the simple baffle system is unlikely to prevent strong advective (head-driven) vertical flow in a well because of pressure differences forcing flow around the baffle, it is generally effective in mitigating thermal convection. Other more complex baffle systems, such as packers, could be used to mitigate both thermal convection and advective flow.

5.5 Vertical Profiling

Vertical profiling in a well can be of two types, hydraulic-flow profiling and chemical profiling. Hydraulic-flow profiling refers to the determination of the depths where water is entering or leaving the open interval of a well and where there are zones within the open interval with no water movement. Hydraulic-flow profiling is useful for designing subsequent chemical-profiling surveys. Chemical profiling refers to the determination of the vertical distribution of chemical constituents within the open interval of a well under ambient (or pumped) conditions. Specific techniques used to conduct both types of profiling are discussed in the Sections 5.5.1–5.5.2.

5.5.1 Hydraulic-Flow Vertical Profiling

Hydraulic-flow vertical profiling to determine where groundwater is entering the well usually is done using either a straddle-packer pump setup or a borehole flow meter. The straddle packer with a pump in between the packers is used to seal off a zone in the well, measure the distribution of hydraulic head in the different zones, pump the zone, and watch the change in water level with time as it recovers. These data cannot only be used to determine whether water is entering the zone based on head measurements, but also can be used to calculate transmissivities of the packed-off zones. These zones can be portions of a long screen in unconsolidated aquifers in the absence of a sand pack or portions of an open bedrock borehole around discrete fractures. By moving up or down the open interval and repeating these tests, transmissivities at different depths can be determined, and the vertical change in transmissivities and the depths of groundwater inflow and outflow over the length of the open interval of a well can be evaluated (Shapiro, 2007).

Hydraulic-flow vertical profiling with borehole flow meters can be done with several different types of meters. For small flows (vertical flow rates of 0.01–0.5 gal/min) a heat-pulse flow meter has been used. The heat-pulse flow meter tracks an initiated pulse of heat by measuring a temperature increase above or below the sensor and determines the vertical

direction of groundwater flow. The rate of the heat-pulse transport can be measured and used to identify the vertical distribution of inflow and outflow in the well under ambient and pumped conditions. Also, the vertical variation in transmissivities with depth of layers intersecting the open interval of a well can be calculated under pumped conditions. Locations of vertical flow between layers or fractures in the well, or stagnant zones where there is negligible inflow or outflow, also can be determined.

Many of the borehole-flow meters measure only vertical flow where horizontal flow between successive vertical flow measurements is inferred. Horizontal flow, specifically cross flow where inflow into the well equals outflow from the well at the same or similar depth, cannot be determined with these meters (Harte and others, 2014). In this case, other borehole flow meters will need to be used, including point-dilution meters (Masciopinto and Palmiotta, 2014). Annable and others (2005) developed a passive-flux meter that estimates horizontal flow through an open interval by measuring the rate of loss of a dye off a sorbent over a deployment period to calculate a flux through the open interval of a well.

Knowledge of inflow and outflow patterns in a well helps to guide deployment of passive samplers. The depth of deployment of a passive sampler is crucial to collecting a representative sample from the well and should not be arbitrarily chosen in a well where mixing is minimal. The passive sampler typically needs to be placed at a depth where the highest mass flux of the constituent of interest passes through the open interval of a well (ITRC, 2004). This means the vertical variation in groundwater chemical concentrations also needs to be determined.

5.5.2 Chemical-Vertical Profiling

Chemical-vertical profiling can be accomplished with passive samplers by deploying a series of equally spaced samplers over the entire length of a screened or open interval of a well. This is easily done because of the relatively small interrogation volume of the samplers (Harte and others, 2001; Vroblesky and Peterson, 2004; Divine and others, 2005). Analysis of samples collected with this series of passive samplers will give the vertical variation in concentrations of a constituent of interest. The vertical variation in concentrations can be used to assist in identifying which zones or fractures have inflowing groundwater containing the constituent of interest. Vertical chemical profiling also can help to corroborate flow patterns in open boreholes from various types of hydraulically active fractures if fracture water chemistry has been determined with discrete sampling. During vertical profiling with passive samplers, the use of baffles can be incorporated onto the suspension line to help segregate or isolate flow in the well.

Samplers can be spaced as close or as far apart as desired over the open interval of a well, constrained by the length of the sampler (Appendix A, Case Study A1). A minimum spacing distance equal to the length of the passive sampler is recommended to improve detection of distinguishable differences in vertical water chemistry while balancing the costs of analyses. For example, a 1-ft-long sampler would have a minimum spacing distance of 1 ft between the bottom of the upper sampler and the top of the lower sampler. Obviously, using more samplers in vertical profiling means more analyses, so the cost of the analyses is often the controlling factor in the number of samplers deployed in vertical profiling. In general, one passive sampler should represent no more than 5 ft of the open interval of a well (ITRC, 2004).

Sampler deployment for vertical profiling can be designed on the basis of results from borehole geophysical logging (Appendix A, Case Study A2). Stratigraphy (geologic layering) and formational contacts are important considerations in vertical profiling. These data can be ascertained from lithologic logs and borehole geophysical logs, such as natural-gamma ray logs, which help map lithologic and mineralogic characteristics of a formation. Other borehole logs that are useful in deployment of samplers include electromagnetic (EM) induction conductivity, fluid conductivity, and temperature. The EM induction logs measure apparent conductivity induced from an EM signal. The EM induction log responds to electrical conductivity of the solids and groundwater. Fluid conductivity and temperature can be used to identify ambient flow circulation in the well. An example of vertical deployment that is based on stratigraphy and depths of inferred hydrogeologic contacts for an alluvial aquifer in New Mexico is shown in figure 19. A description of the study area and formations is presented in Appendix A, Case Study A2.

5.5.3 Profiling for Determining Deployment Depth

In wells with open intervals longer than 5 ft, the depth of deployment for a passive sampler ideally is not arbitrarily chosen but is based on the information collected from hydraulic-flow profiling and chemical profiling. Some depths may have high constituent concentrations but not much groundwater flowing into the well. Other depths may have low constituent concentrations but most of the water coming into the well. In most cases, passive samplers should be positioned at the depth of highest mass flux of the constituent of interest. That is, the depth at which the product of the groundwater inflow rate and the constituent concentration gives the highest mass per unit time. Deployment at this depth allows for the collection of a sample of groundwater that has the highest transport potential of the constituent of interest in the well.

5.5.4 Relation Between Borehole Flow and Water Chemistry

Ambient flow can occur horizontally and vertically in a well. The direction of ambient flow is an important influence on samples obtained from a passive sampler. Horizontal flow through the screened or open interval is dependent on the hydraulic properties of the formation and the horizontal

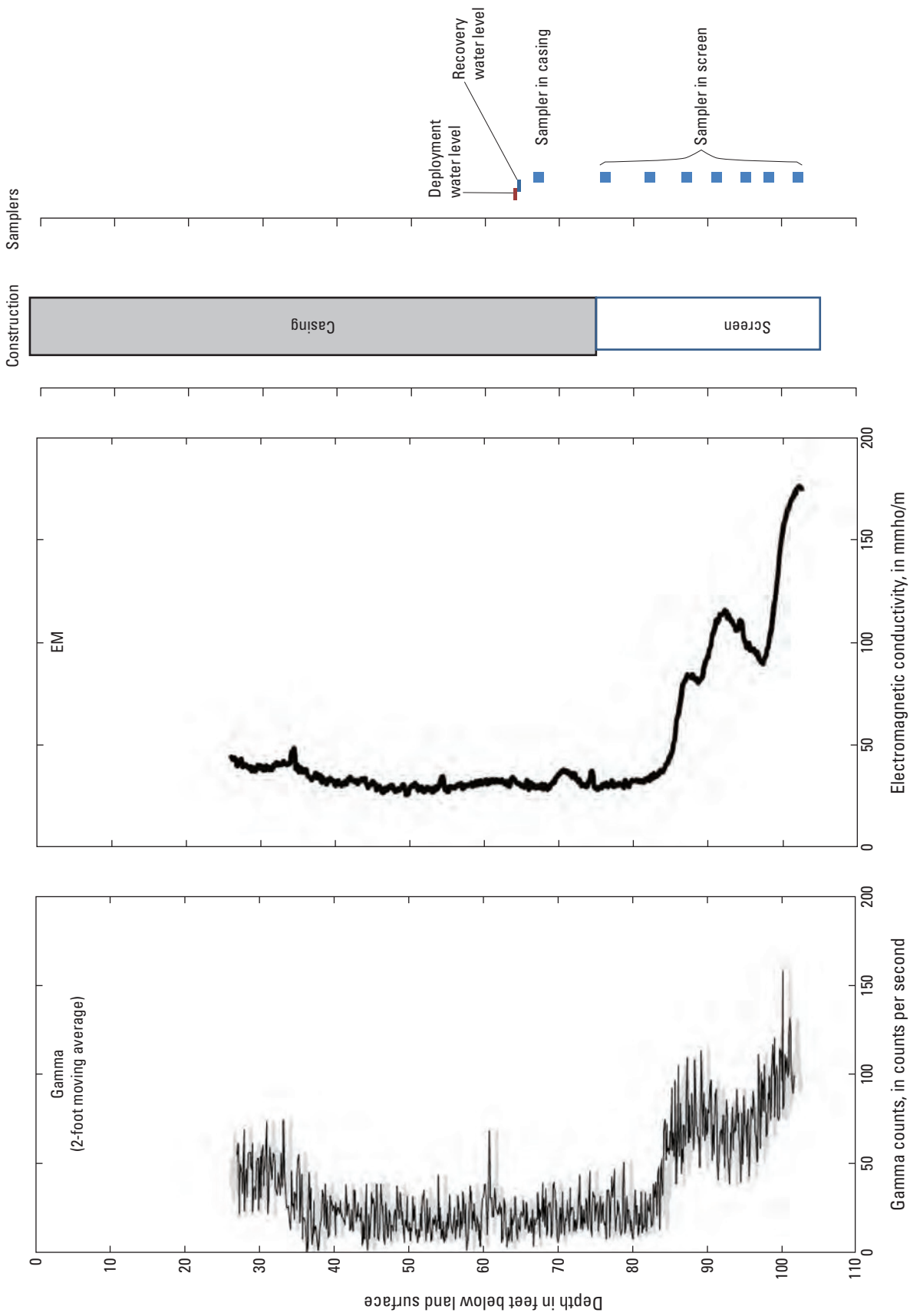

Figure 19. Example of vertical profiling with passive samplers, based on borehole geophysical logs, water levels, and well construction in an alluvial aquifer in New Mexico. [mmho/m, millimhos per meter; ft, feet; EM, electromagnetic]

hydraulic gradients between the formation and the head in the well. A well dominated by stratified horizontal flow (fig. 6*A*) likely will have greater variability in vertical water chemistry than a well dominated by vertical flow from a single zone. Vertical flow in the well is dependent on the vertical-head gradients in the formation and differences in the permeability across the opening (fig. 6*B*).

In-well mixing can obscure the ability of a sampler to identify vertical water chemistry in the formation (Church and Granato, 1996). The presence of sand packs in screened wells also can obscure the chemistry in the formation by redirecting ambient flow. Research on ambient flow indicates there is a tendency toward chemical homogenization in the screened interval of a well such that most wells experience strong redistribution effects of groundwater chemistry (Britt and others, 2014). However, some wells may maintain stratification or perhaps re-stratify differently from the surrounding formation (Britt and others, 2014). In some cases, the ambient flow in the well can be modified with use of baffles or packers that segregate flow vertically from in-well mixing (Vroblesky and others, 2007a).

Harte and others (2014) identified several different flow types of hydraulically active fractures in crystalline rock on the basis of borehole dilution logging. Flow types included inflowing fractures, outflowing fractures, and several different types of cross-flowing fractures. Deployment of passive samplers at hydraulically active fractures in this study helped identify chemical influent and confirmed inflowing groundwater at a fracture. In this case, three samplers were arranged vertically, in an upper, middle, and lower configuration, adjacent to three fractures to allow for delineation of chemical influent and vertical transport of influent in the borehole (fig. 20).

Borehole-flow patterns in fractured rock can be complex and lead to well-mixed borehole fluid from differing chemical zones in the formation. Several examples of borehole flow are illustrated in figure 20. In some cases, the passive sampler positioned adjacent to a fracture may not measure the water chemistry of the adjacent fracture on the basis of flow patterns and the type of flow in the fracture (whether inflowing, outflowing, or cross flowing). Figure 20*A* shows an example of upward flow where the outflowing fracture (F1) receives water from all three fractures; the closest adjacent passive sampler (P1) to fracture (F1) is primarily sampling water from fractures F3 and F2 with some contribution from the inflowing side of F1. Figure 20*B* shows an example of a convergent flow to an outflowing fracture (F2) that is not contributing water chemistry to the adjacent passive sampler (P2). In other cases, the passive sampler collects a mixture of water chemistries from several fractures (fig. 20*C*; samplers P1 and P2). Lastly, the passive sampler may be relatively unaffected by any particular water chemistry from a fracture and instead may reflect the chemistry of stagnant borehole water (fig. 20*D*; sampler P3).

Before using a passive sampler in a well, it is important to know whether there are stagnant zones where water is not flowing into the open interval. In fractured-rock wells where fracture frequency may be sparse, particularly in some deep wells (greater than 500 ft deep), flow may be focused in the shallow depth of the open interval. In such a case, the passive sampler should be suspended at a shallow depth to collect a sample from water in the formation. It is important to remember that passive samplers collect only samples that are representative of the water passing by them.

Passive samplers also have been deployed to measure primarily hydraulically inactive flow zones of a rock block. Harte and others (2015) and Harte and Brandon (2020) developed a screening methodology to utilize findings from chemical-vertical profiling with PDB samplers to identify the active and inactive flow zones of an open borehole in fractured rock at a cis-1,2-dichloroethene (cisDCE) contamination site. The screening methodology coupled borehole flow conditions and changes in vertical concentrations to identify flow- or diffusion-dominated processes in an open borehole set in fractured rock (table 2).

6.0 Decision Tools

Prior to groundwater sampling, an assessment needs to be done to determine whether passive sampling is a viable alternative to other sampling methods. Decision tools are provided in the following sections to aid in determining (1) whether a passive sampler could be used at a particular well, (2) which passive samplers can be used to collect water for certain classes of chemical constituents, and (3) what are the minimum water volumes that can be collected to provide enough volume for the required analyses. The decision tools include several tables that can be used as general guides for addressing each topic. Obviously, each well, site, and analysis will have its own unique characteristics that will need to be considered.

6.1 Passive Sampler Use

Table 3 provides 10 questions that field personnel need to ask when deciding whether or not to use passive samplers in wells. The table has been modified from a similar one in the ITRC (2004) technical regulatory guide.

6.2 Passive Sampler Capabilities

It is important when considering the use of passive samplers to make sure that the selected sampler is capable of collecting a representative concentration of the chemical constituents in question. Table 4 presents groups of constituents that have been successfully sampled and analyzed in laboratory equilibration tests or in field tests and the type of passive sampler used to collect the sample. As more testing is done, this list likely will change and be expanded.

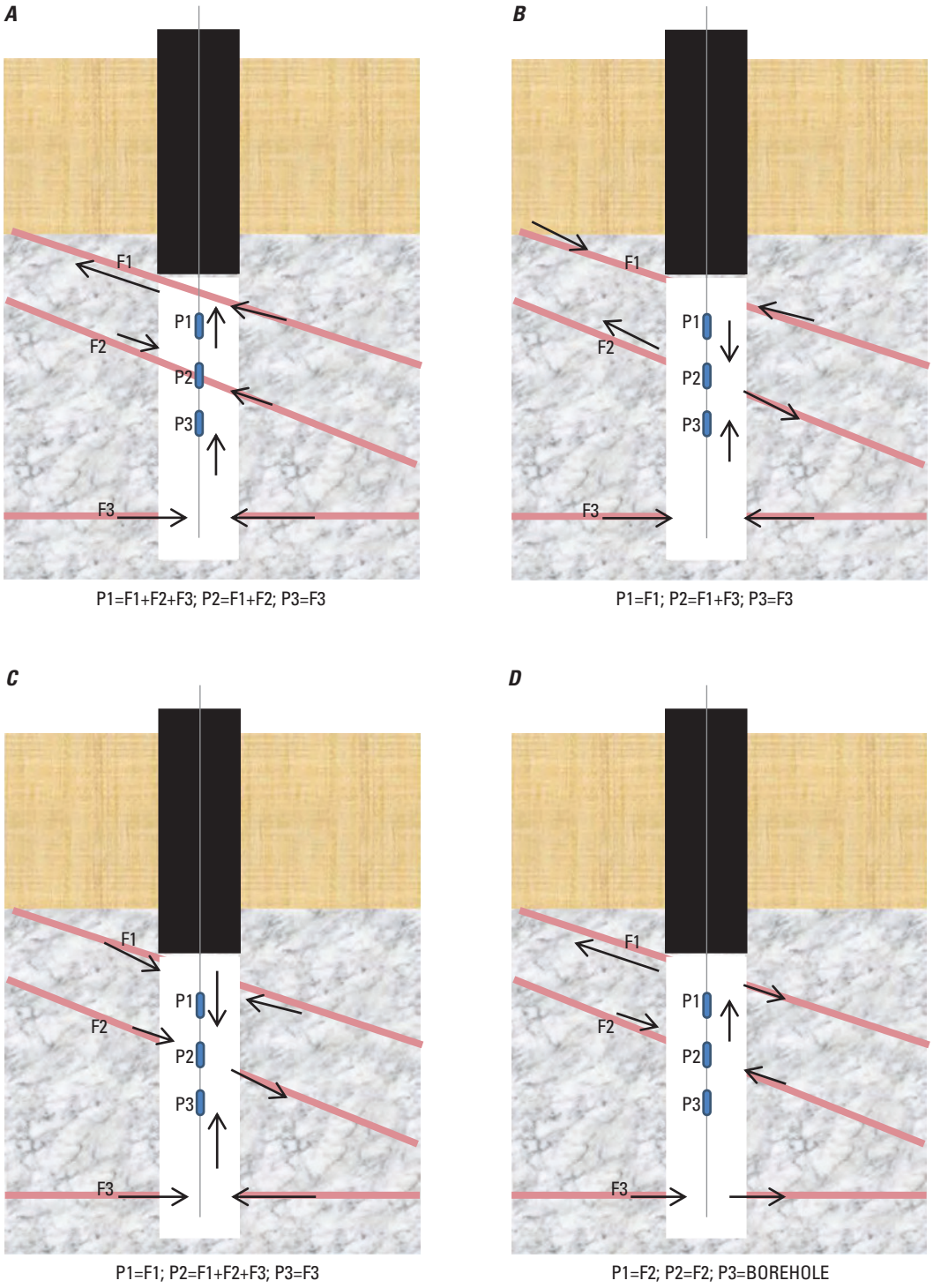

Figure 20. Ambient borehole flow patterns and relation to vertical water chemistry as measured by passive samplers: *A*, upward flow, *B*, convergent outflow, *C*, mixed cross flow, and *D*, mixed stratified flow. [P, passive sampler; F, inflowing or outflowing groundwater location of fracture; arrow, indicates direction of flow]

Table 2. Classifications of intervals in open borehole fractured-rock wells, based on distinguishing hydraulic and chemical characteristics of zones. From Harte and Brandon (2020).

Hydraulic zones	Chemical zones		
	Static, negligible change in concentration along interval of well	Increase in concentration along interval of well	Decrease in concentration along interval of well
Inflow (Active)	Active-Static chemical zone	Active-Influx chemical zone	Active-Dilution chemical zone
Outflow (Active)	Active-Nonparticipating chemical zone	Active-Mixed chemical zone (likely some small inflow present)	Active-Nonparticipating chemical zone
Non-flow (Inactive)	Inactive-Chemical diffusion zone	Inactive-Potential unidentified hydraulically active zone or back diffusion chemical zone	Inactive-Potential unidentified hydraulically active zone or adsorption chemical zone

Table 3. Decision analysis summary of appropriateness of passive sampler use. Modified from ITRC (2004).

[A negative answer to any of the following questions will require further action or investigation before passive samplers can be deployed. If all answers are affirmative, passive samplers are likely to be a viable option for the site. ft, foot; cm/s, centimeter per second; >, greater than; <, less than]

No.	Question	YES	NO
1	Is sampling being done for long-term groundwater monitoring?		
2	Has the groundwater chemistry at the site been fully characterized?		
3	Can the passive sampler being considered collect samples for all constituents of interest?		
4	Can the passive diffusion sampler being considered collect the sample volume necessary to analyze the constituents of interest given the well construction?		
5	Have hydraulic and chemical vertical profiling been done in the wells to be sampled?		
6	Are the monitoring wells to be sampled in an area where there is sufficient groundwater velocity (>0.5 ft/day)? Low groundwater velocity can result from either a low hydraulic conductivity ($<10^{-5}$cm/s) or a low hydraulic gradient (<0.001).		
7	Are the monitor wells currently free of dedicated pumps or other sampling equipment?		
8	Has a cost evaluation shown the passive sampler being considered offers a cost savings compared to current sampling techniques?		
9	Have you discussed the potential use of the passive sampler with site regulators?		
10	Are the site regulators familiar with the passive sampler technology, and will they allow the data to be used for the same purposes as those obtained by purge sampling?		

Table 4. Chemical constituents and corresponding sampling capability of passive samplers.

[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; HCO_3, bicarbonate; Cl, chloride; SO_4, sulfate; F, fluoride; Br, bromide; NO_3, nitrate, NO_2, nitrite; NH_4, ammonium; PO_4, 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; organo$P0_4$, organo-phosphate; PAH, polycyclic aromatic hydrocarbons; BN, base-neutral organics; PCB, polychlorinated biphenyls; ClO_4, perchlorate; PFOS, perfluorooctane sulfonic acid; PFOA, perfluorooctanoic acid; PFNA, perfluorononanoic acid, NT, not tested]

Passive diffusion samplers	Polyethylene diffusion bag sampler (PDB)	Regenerated cellulose dialysis membrane sampler (RCDM)	Rigid porous polyethylene sampler (RPP)	Nylon screen sampler (NS)	Downhole thief sampler (Snap)	Sorbent sample module (AGI)	Semi-permeable membrane device sampler (SPMD)	Dual membrane sampler (DM)
Chemical constituents and characteristics								
Field physiochemical characteristics (Temp, pH, SC, DO, ORP)	Some	Some	Some	Some	Some	None	None	Some
Major cations and anions (Ca, Mg, Na, K, HCO_3, Cl, SO_4, F, Br)	None	All	All	All	All	None	None	All
Nutrients (NO_3, NO_2, NH_4, PO_4)	None	All	All	All	All	None	None	All
Trace elements (Fe, Mn, Al, Ag, Zn and others)	None	Most	Most	Most	All	None	None	Most
Perchlorate (ClO_4)	None	All	All	All	All	None	None	All
Organic carbon (dissolved or total)	None	All	All	All	All	None	None	All
Dissolved hydrocarbon gases (Methane, ethane, ethene)	All	All	All	All	All	None	None	All
Volatile organic compounds (Chlorinated solvents, BTEX)	Most	Most	Most	Most	All	All	None	Most
Semi-volatile organics (1,4-Dioxane, BN, Phenols, PAH, PCB, dioxins, furans)	Some	Some	Some	NT	All	Some	Most	NT
Pesticides (organoCl, organoPO_4)	None	NT	NT	NT	All	Some	Most	NT
Explosive compounds (RDX, HMX, TNT)	None	Most	Most	NT	All	Most	NT	NT
Poly- and perfluoroalkyl substances (PFASs)	None	Some	NT	NT	NT	NT	NT	Some

6.3 Minimum Required Analytical Volumes

Because the volume of water that passive samplers typically collect is limited, it is a good idea to check with the laboratory to determine whether the laboratory can conduct all the analyses of interest with the volume that the selected sampler can collect. The volume of water typically requested by laboratories for each analysis is often larger than the volume actually needed for analysis in order to anticipate spills, reruns, or analytical difficulties. Table 5 shows the volume of water the USGS National Water Quality Laboratory (NWQL) typically requests for selected constituents and analytical methods, and the minimum volume the laboratory can use and still complete these analyses. Summing the minimum volumes will give the actual amount needed by the laboratory for all the analyses. Again, prior to the collection of any samples, it is advisable to check with the laboratory to be sure of the minimum acceptable water volume required by the laboratory for sample analyses. ITRC (2004) has a similar table for minimum volumes needed for U.S. Environmental Protection Agency analytical methods.

Table 5. Minimum volumes required for selected analytes from the U.S. Geological Survey National Water Quality Laboratory.

[Schedules and laboratory codes from internal USGS websites accessed online November 19, 2018; mL, milliliter; RU, raw untreated; FU, filtered untreated; FA, filtered acidified; FCC, filtered chilled; TDS, total dissolved solids; GCV, 40-mL glass vials; GCC, baked glass container; PCBs, polychlorinated biphenyls; NWQL, National Water Quality Laboratory; DOC, dissolved organic carbon; VOCs, volatile organic compounds; SVOCs, semi-volatile organic compounds; HNO_3, nitric acid; NH_4, ammonium; NO_2, nitrite; NO_3, nitrate; H_2SO_4, sulfuric acid; HCl, hydrochloric acid; °C, degrees Celsius]

Analyses	Filtration requirement/ preservation	Lab code (LC) or Schedule (SH)	Volume requested by NWQL (mL)	Minimum volume required by NWQL (mL)	Comments
Field physiochemical characteristics: Specific conductance and pH	Raw, untreated, chilled (RU)	LC69 + LC68	250	100	Recommend collected in field (50 mL each)
Alkalinity	Filtered, untreated, chilled (FU)	LC2109	250	100	
Major cations and anions and silica: Bromide, Calcium, Chloride, Fluoride, Iron, Magnesium, Manganese, pH, Potassium, Total dissolved solids, Silica, Sodium, Specific conductance, Sulfate	Filtered, acidified w/HNO_3 (FA)	SH1	250	50	Must measure specific conductance and pH in the field
Trace elements: Aluminum, Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Lithium, Manganese, Molybdenum, Nickel, pH, Selenium, Silver, Specific conductance, Strontium, Thallium, Uranium, Vanadium, Zinc	Filtered, acidified w/HNO_3 (FA)	SH2710	250	50	Must measure specific conductance and pH in the field
Nutrients: Nitrogen, ammonia; Nitrogen, nitrite; Nitrogen, nitrite + nitrate; phosphorous, phosphate, ortho; Total nitrogen (NH_3+NO_2+NO_3+organic)	Filtered, chilled (FCC)	SH2755	125	80	
Residue on evaporation (180 °C) (TDS)	Filtered, chilled (FU)	LC27	250	100	Must measure specific conductance in field
Dissolved organic carbon (DOC)	Filtered, acidified w/H_2SO_4 (DOC)	LC2612	125	125	
Volatile organic compounds (VOC)	Raw, acidified w/HCl (GCV)	SH1307 or SH1380	3 × 40	3 × 40	
Semi-volatile organic compounds: Base/neutral/acids (SVOC)	Raw, untreated, chilled (GCC)	SH1383	1,000	500	
Organonitrogen pesticides	Raw, untreated, chilled (GCC)	SH1379	125	100	
Halogenated organic compounds: PCBs, pesticides	Raw, untreated, chilled	SH8099	500	250	

7.0 Sampler Deployment, Retrieval, and Sample Collection

This section identifies critical information needed for passive samplers to collect water chemistry samples from wells. To aid in passive sampler deployment and retrieval, a field form (Appendix B) has been developed by the authors as part of this report to help facilitate the use of passive samplers in collecting groundwater samples. The field form is referenced throughout this section when applicable.

7.1 Well Dimensions and Water Level

Before going to the field to deploy the passive sampler, the casing and screened or open interval diameter, the total depth of the well, and the depth and length of the open or screened interval need to be obtained. This information typically can be found in the well construction log. The data need to be entered as reported well information on the field form (Appendix B). It is important to know the diameters of the well casing and screened or open interval because some wells telescope to smaller diameters with depth, thus having smaller diameter open intervals or screens than the casing. Some passive samplers can fit down 2-in.-diameter wells or screens, but others will require a minimum 4-in.-diameter well or screen.

The current depth to water needs to be measured prior to installation of a passive sampler to ensure that the desired target depth of the sampler is completely below the water level in the well and is located within the screened or open interval. The total well depth also can be checked at this time if confirmation is needed (Appendix B, sounding depth).

7.2 Installation of the Sampler

Prior to installation of a single passive sampler, the suspension line must be measured out, so the length will allow the sampler to be suspended at the chosen deployment depth in the screened or open interval. Sampler lengths, depths, and reference position used (top or midpoint) must be noted on the field form such as the one shown in Appendix B. The passive sampler is attached to the suspension line at the appropriate depth using cable ties or stainless-steel clips. A stainless-steel weight is attached to the end of the suspension line or the bottom of the passive sampler. The sampler is then lowered slowly into the well. Once submerged in the water column, the sampler should sink easily to the desired depth if it includes sufficient weight to overcome its buoyancy. If the suspension line is made of polypropylene and the passive sampler is deployed in a well greater than 100 ft deep, some line stretch may occur and needs to be taken into account when determining the actual depth of deployment. If the suspension line is made of Teflon-coated cable or stainless steel, it is unlikely to stretch even during deep deployments.

During deployment, the sampler should be lowered **slowly and carefully** until the desired depth on the line is at the measuring point (MP) or other reference point, such as land surface. The phrase slowly and carefully is emphasized to minimize mixing of the water column in the well and to prevent abrasion of the sampler against the inside of the casing or open hole. The suspension line must be secured at the top of the casing, so the position of the sampler will not change during the period of equilibration. An example of securing a suspension line to the top of the well is shown in figure 21. The suspension line is attached to a bolt that is secured through the casing and bolted with nuts on both sides of the casing wall. When the attachment is covered by a locked well cap, the line and bolt are tamper resistant. In addition, a caution sign can be placed on a well, such as that shown in Appendix C, to indicate samplers are installed in the well.

The installation of most passive samplers is easily accomplished by one person, but obviously can be done faster by two people. However, two people are recommended for vertical profiling of wells with the deployment of multiple passive samplers.

The amount of weight to attach to the line for a passive diffusion sampler is based on the need to overcome the buoyant force, as described in Archimedes' principle. Essentially, the upward buoyant force that is exerted on a passive sampler and its deployment line is equal to the weight of the fluid that the sampler displaces and acts in the upward direction at the center of mass of the displaced fluid. Since most passive samplers are filled completely with water, the buoyancy that must be overcome is from the weight of the materials of sampler construction and the deployment line. The greater the number of passive samplers attached to a line, the greater the material weight that will need to be overcome, and thus, the greater the amount of weight that will be needed on the end of the line. The deeper that the passive samplers are deployed, the greater the weight of the deployment line and the more weight that will be needed on the end of the line. Assuming minimal material is used in the construction of passive samplers, which is particularly true for PDB samplers, buoyancy can be roughly calculated by the volume (cubic feet [ft^3]) of water displaced by the suspension line, if water-filled samplers are used, multiplied by the density of water (62.4 pounds (lb) per ft^3). For a 3/8-in.-diameter by 100-ft-long polypropylene suspension line, the amount of weight needed would be 0.03 lb per ft of line or 3 lbs total.

7.3 Deployment Period

For equilibrium-membrane-type passive samplers, the deployment period, that is the time the passive sampler is left in a well, is dependent primarily on two factors: (1) the length of time it takes the flow regime passing through the well to re-stabilize after introduction of the sampler (time 1) and (2) the length of time it takes a passive sampler to chemically equilibrate with the water in the well (time 2). The minimum

Figure 21. Tamper-resistant attachment of a weighted passive sampler suspension line to an interior bolt. Photograph by Thomas E. Imbrigiotta, U.S. Geological Survey.

deployment period should be the longer of time 1 or 2. A more conservative approach is to make the deployment period the sum of time 1 and 2. In high-permeability formations, the flow re-stabilization may occur quickly, on the order of hours. In low-permeability formations, the flow stabilization may be quite slow, on the order of weeks. Prior to deployment, all passive samplers should be tested in the laboratory to determine how long it takes for a variety of chemicals to reach chemical equilibrium in test solutions containing known concentrations. Results of such tests are available in reports and papers published on the development of these samplers. Some passive samplers chemically equilibrate with some constituents in a day or two, whereas other constituents take weeks to equilibrate. As a general rule of thumb, unless you are dealing with a very low permeability formation or the constituent being sampled takes a very long time to chemically equilibrate because of a low diffusion coefficient ($D < 1 \times 10^{-8}$ cm^2/s), 2 weeks is the most frequently used deployment time for most passive samplers.

7.4 Sampler Retrieval

After the appropriate deployment time, the passive samplers are retrieved. Visual inspection of the well should be done to identify whether tampering has occurred during deployment. Water levels should be measured prior to sampler retrieval and recorded on the field form (Appendix B). The start time of retrieval is recorded on the field form as the time when the suspension line begins its ascent to the surface. Once the sampler is at the surface, visual observations of the condition of the sampler should be made prior to transfer of the sample into the sample bottle (if required). Examples of possible changes to be noted are loss of volume, color change, the presence of biological growth, and any perforations in the membrane. After retrieval of the last passive sampler, the end time of retrieval is noted on the field form.

7.5 Sample Collection

Sample collection should occur as soon as possible after retrieval of the passive sampler from the well. In most cases, the sample collection should occur within 10 min after the sampler is at land surface to avoid exposure of the sample to oxygen, lower pressures, and possible loss of volatile compounds. The time of sample transfer from the passive sampler to the laboratory bottle should be noted on the field form (Appendix B).

Collection of water samples from passive samplers is most easily done by two field persons. For most samplers, one person holds and pours out the passive sampler while the other person holds and caps the sample container(s). All of these actions also can be done by one field person with a supported hook or clamp to act as a third hand. Sample collection likely will take longer with only one person. It is more of a challenge to retrieve and collect samples quickly if multiple samplers are used to vertically profile a well. Two persons are a benefit

in this case, where one person is sampling while the other is retrieving samplers from the well. If multiple bottles are filled from each sampler or it takes longer than 10 min to collect a sample, the remaining passive samplers still attached to the line can be carefully lowered down the well into the water column to prevent exposure to the air and to prevent drying of any membranes.

For most of the passive samplers, sample collection is described in more detail in Section 4 and is briefly summarized here. For PDB samplers, the samplers are pierced with a straw or the corner of the bag is clipped off, and the sample stream is directed or poured into sample containers. For RCDM samplers, the sampler is inverted, the bottom valve is rinsed with deionized water to remove any particulates that may have fallen in from the well casing, and the sample is emptied through the valve directly into sample containers. For RPP samplers, the capped end of the sampler is removed, and the water sample is poured out directly into sample containers. For the NS samplers, the screened top of the NS sampler is removed, and the contents of the bottle are poured directly into the sample containers. In some cases, the same bottle can be used, and a solid cap is exchanged for the screened cap. For the DM samplers, the sampler is pierced with a straw, and the stream is directed into sample containers. For the Snap sampler, samples are collected by triggering the spring-loaded sample containers to close at depth in the well, bringing them to the surface, and then screwing caps onto both ends of the sample containers. For the AGI sample modules, the samplers are placed back in the glass container they were shipped in. For the SPMD samplers, the polyethylene membrane containing triolein is detached from the sampler body, rolled up, placed in an air-tight metal container, and chilled on ice for shipment to the laboratory.

7.6 Disposal and Decontamination

If the passive sampler is sized correctly for the number and type of sample bottles being filled, essentially no water or only a minimal amount of water should be left over at the end of sample collection. With the exception of the Snap sampler, which has sample containers that may be cleaned and reused, and the SPMD sampler, which has a support structure that is cleaned and reused, passive samplers are made of disposable materials and can be discarded once the samples are collected. The suspension lines can be saved and dedicated to the same well for use in subsequent samplings. The stainless-steel weights should be saved, cleaned using standard equipment cleaning protocols, and baked to remove volatile contaminants, so they can be reused in subsequent samplings.

8.0 Data Reporting Procedures

The discrete nature of passive sampling lends itself to data collection, coding, and entry into databases that are different from the data collection, coding, and entry for standard purge sampling. For databases such as the USGS National Water Information System (NWIS), placement, time, and type of sample must be clearly identified to avoid confusion. The same station identifier needs to be used for all passive samples from the same well. Either single or multiple samplers used in vertical profiling need to be designated by a depth location in the well. The collection time differs between purge and passive sampling. Purging produces an instantaneous sample, whereas the passive sample needs to have a collection period equivalent to the last few days or weeks of the deployment period. Designation of sample type, whether filtered or total, should be based on the membrane pore size and whether it is coarser or finer than a 0.45-mm filter. A comparison of pertinent NWIS identifiers and parameter codes used for purge samples and passive samples are listed in table 6.

9.0 Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) with passive sampling includes a few procedures that differ from those for purge sampling. Many of the passive samplers require that a water source is tested for the presence of constituents of interest. Other differences and details are outlined in this section.

9.1 Recommended QA/QC Samples

As with all groundwater sampling, QA/QC samples must be collected when using passive samplers. QA/QC samples help determine whether there is contamination in the water used to fill the samplers, contamination from the construction materials of the sampler, or cross-contamination in the cooler during shipment to the laboratory. QA/QC samples also can be used to explain the variability of the results from the water samples that the samplers produce.

9.1.1 Deionized Water Source Blank

Passive samplers that require filling with water in the laboratory or field (some PDB, RCDM, NS, and DM samplers) typically are filled with high-quality deionized water from a laboratory treatment system, such as ASTM Type 1 water (ASTM, 2014), or NWQL inorganic blank water or NWQL organic blank water. A sample of the blank water should be collected and analyzed for the constituents of interest for the project prior to its use in filling any passive samplers. Some commercially available passive samplers, such as PDB and RPP samplers, come pre-filled and enclosed in a sleeve of blank water. In this case, the manufacturer usually attaches a certificate stating the concentrations of chemicals in the water inside the sampler.

Table 6. Identifiers and parameter codes for data associated with purge and passive samples for input into the U.S. Geological Survey National Water Information System database.

[STAID, station identifier; MEDIM, sample medium; STYPE, sample type; H, composite (through time), environmental sample; WG, groundwater; —, no data]

Identifier	Purge, bulk sample			Passive, discrete sample		
	Description	Parameter code	Sub parameter code	Description	Parameter code	Sub parameter code
Sample site identifier	One unique site identifier	STAID	—	One unique site identifier	STAID	—
Date of sample	Begin date	DATES	—	Begin and end date span the deployment period	DATES	—
Time of sample	Begin time (one sample per time)	TIMES	—	Begin and end times with time offset for each depth/deployed sampler	TIMES	—
Deployment period	Instantaneous with no duration	—	—	Begin and end date span the deployment period	—	—
Medium	Groundwater	MEDIM	WG	Groundwater	MEDIM	WG
Type of sample	Grab	STYPE	9	Composite	STYPE	H
Total or dissolved	Based on filter pore size	—	—	Based on sampler membrane pore size	—	—
Sample interval (feet)	Well screen	00003	—	Specified by position and depth of sampler (feet below land surface)	72015 (top of sampler) or 72016 (bottom of sampler)	—
Depth of well (feet)	Depth including sump	72008	—	Same as purge	72008	—
Depth of water level (feet below land surface)	Multiple readings for static and purge	72019	—	Multiple readings for start and end deployment date	72019	—
Purpose of site visit	Primary	50280	2001	Primary	50280	2001
Sample purpose	Routine	71999	10	Routine	71999	10
Sampling method	Peristaltic pump	82398	4080	Other	82398	8010
Sampling method	Submersible pump	82398	4040	Passive diffusion	82398	140
Sampling type	Purge, bulk sample	—	—	Passive diffusion	84164	3090

9.1.2 Equipment Blank and Field Blank

An equipment blank is collected to determine whether the sampler construction materials are contributing any of the constituents of interest to the sample. An equipment blank should be collected from an extra sampler (typically the first sampler constructed) that is identical to all the others that are purchased or constructed for deployment. Once all samplers are deployed, this extra sampler can be handled in two different ways. First, it can be sampled immediately, and the sample sent to the laboratory for analysis of the constituents of interest. This is the preferred option because it reduces the possibility of additional exposure to contamination beyond the time of installation and best reflects initial conditions of deployment for all the samplers (option 1). Second, the extra sampler can be suspended in the same deionized water used to fill the sampler in a covered clean container in the laboratory or at the field site for the same length of time that the passive samplers are deployed in the wells in the field (option 2). After the deployment period is complete, the passive sampler stored in the deionized water container is sampled for an equipment blank, which is analyzed using the same identical method as the samples from the passive samplers recovered from the wells. For either option, the equipment blank will determine whether the constituents of interest are desorbing from the materials of the passive sampler itself. For option 2, it is assumed that the covered deionized water containers are clean at the start, do not contain materials that leach the constituents being sampled, and are not located in an area of the laboratory or field site during the deployment period that is contaminated with the constituents being collected by the passive samplers.

For most passive samplers, field blanks are essentially identical to equipment blanks because most of the passive samplers discussed in this report are single-use samplers. However, some passive samplers have containers and housings that are reused between sampling events, such as the Snap sampler and the SPMD sampler. Potential leaching of constituents from these reused, cleaned containers and housings warrants the collection of separate field blanks for these two types of passive samplers. Field blanks consist of the collection of a sample of deionized water poured over or through the reused, cleaned containers or housings, similar to field blanks collected for cleaned submersible pumps or bailers.

9.1.3 Trip Blanks

A trip blank should be prepared in the laboratory, particularly if VOCs are being analyzed in the samples. A trip blank consists of vials filled with deionized water in the laboratory, preserved, brought to the field in the cooler used to store the other sample vials, and then sent to the laboratory for analysis along with the VOC samples collected from the passive samplers. A trip blank for VOCs helps to determine whether these compounds may have been introduced by cross contamination with other samples in the cooler during shipment to the laboratory.

9.1.4 Replicates

Replicate samples are QA/QC samples collected to determine the variability in the passive sampler's ability to collect reproducible chemical concentrations. Passive sampler replicates should be collected from identical samplers suspended either side-by-side at the same depth in the well or vertically adjacent in the well. Replicate samples should be collected at a rate of at least 1 for every 10 samples to determine the reproducibility of the passive sampling device.

9.2 Acceptability of Passive Sampling Blanks and Replicate Variability

Deionized water source blanks should not contain concentrations of the chemical constituents exceeding detection levels. If the constituents of interest are found at greater than detection level concentrations, a cleaner source of deionized water should be found and utilized. Alternately, if the levels of the constituents of interest are much greater in the groundwater than in the deionized water, then the current source of water can still be used, and the concentrations can be adjusted by subtracting the small amount found in the blank.

Equipment blanks should not contain detectable levels of the chemical constituents being sampled at greater than their detection level concentrations. If the equipment blank results fail this test and it is determined that the deionized water is not a contributor, then the constituents may be desorbing from the materials of the passive sampler. In this case, different sampler construction materials should be found that contain no leachable concentrations of the chemical constituents of interest.

Replicate variability from passive samplers is likely to be greater than replicate variability from purge sampling because two different samplers are typically used during passive sampling. Variability may be increased if the samplers are stacked vertically in the well and there are differences in the vertical water chemistry between the formation and the well. In general, for example, results from replicate samples collected using the same type of passive samplers should agree within an RPD of ±25 percent for VOC concentrations greater than or equal to 10 micrograms per liter (µg/L) and an RPD of ±50 percent for VOC concentrations less than 10 µg/L. If VOC concentrations are not within these ranges, the protocol for recovery and sampling of the passive samplers should be reviewed to determine what may be causing the difference. As a general rule of thumb, replicate variability from passive samplers should not exceed the variability in results from a vertical profile of passive samplers in the same well.

10.0 Data Evaluation

If a well has been monitored previously using only purge sampling methods, some comparison of results from passive sampling methods may be needed to identify any differences. This comparison typically is done in one of two ways. First, the current concentrations of constituents of interest obtained from the passive sampler can be compared to historical concentrations obtained using previous purging methods. If the concentrations of the constituents of interest are similar between the current passive sampling results and the previously used purging results, then it can be reasonably concluded that the passive samplers are providing comparable results. If, however, the current passive sampling results do not compare favorably to the historical purging results, then some additional direct comparison of new sample results needs to be undertaken. The comparison to the historical results should incorporate time corrections and perceived temporal trends in the long-term water-quality record, if available. Further, constitution of a favorable comparison is case dependent on sampling objectives. Section 10.2 discusses considerations in comparative analysis between sampling methods.

The second type of evaluation is a side-by-side comparison of results from the passive sampler and the previously used purging method during the same sampling event. This type of comparison usually is carried out by deploying the passive sampler in a well at a specific depth and allowing it to equilibrate for the appropriate length of time. The sampler is then retrieved from the well and samples are collected. Then the pump is lowered into the well to the same depth as the deployed passive sampler and a purging procedure is used to flush the well, monitor field physical and chemical characteristics, and collect a sample. Results have shown that the process

of retrieving passive samplers and lowering a pump, if done carefully, can maintain some degree of chemical stratification present in the well (Divine and others, 2005); however, logic would dictate that deviation from following an extremely careful approach has the potential to mix concentrations.

The results of the passive sampler and purge sampling method allow a direct comparison of the two sampling methods at the same depth, representing a time-weighted sample from the passive sampler and an instantaneous sample from the purge method. The rate and volume of pumping used for the purge sample should be carefully considered for the comparison. The majority of the data evaluations have been done using a low-flow purge method; however, micropurging (a small volume extracted) and volumetric purging have also been compared (Harte and others, 2018; Appendix A, Case Study A2).

If the concentrations of the constituent of interest generally compare favorably (see Section 10.2), then it is likely the formation is in good hydraulic communication with the water in the screened or open interval, and the use of passive samplers likely will be acceptable. If the concentrations from the side-by-side comparison are in poor agreement, there are a variety of possible reasons why this might occur, and further investigation may be needed to determine which of the two sampling methods is the preferred approach for achieving the data-quality objectives. Potential reasons for disagreement between the purge and passive sample results are discussed in Section 10.2.

10.1 Data Comparison

The most common way to compare constituent concentration results between the purging method and passive sampler methods is to tabulate the results and calculate a RPD between the recovered concentrations for the constituents of interest at that particular well. In general, the results should agree within an RPD of ±25 percent for VOC and trace metal concentrations greater than or equal to 10 µg/L and an RPD of ±50 percent for VOC and trace metal concentrations less than 10 µg/L. The results for major cations and anions should agree within an RPD of ±15 percent because these concentrations should be higher (in the milligrams per liter range).

For each constituent of interest, one of the more effective ways to compare concentration results between purging methods and passive samplers is to plot the data on a 1:1 correspondence graph. Concentrations obtained with the passive sampler should be plotted on the x-axis and the concentrations obtained from the same well using the purging method should be plotted on the y-axis. If the two sampling methods collect the same concentrations, the points will plot on or close to the 1:1 correspondence line (figs. 22–24). The three examples in figures 22–24 are for RCDM samplers in relation to low-flow purging for a VOC (cisDCE), a trace metal (manganese), and an anion (chloride), respectively. In general, there is good agreement in the three examples. If the points plotted far off the line, this would indicate that one sampling method was collecting higher concentrations than the other. The causes for any significant differences would need to be investigated.

Another way to compare passive sampler and purging method results for a study is to plot the results on maps or cross sections to evaluate spatial tendencies. If the results agree approximately in some areas but not in others, the comparative results may provide insight into possible explanations for differences.

Previous discussion in this section focused on comparisons of results from a single passive sample to those from a single purge sample from the same well. When multiple samplers are deployed for chemical-vertical profiling of a well, then considerations on how to compare results need to take into account the volume of water purged and the pump rate. For small purge volumes (either micropurge or low-flow methods), the pump can be placed at the same depth as one of the passive samplers, and samples can be compared similarly to the comparisons demonstrated in figures 22–24. For larger purge volumes (volumetric sample method), the results from the entire profile of passive samplers can be statistically summarized as a mean or another statistical indicator and then compared to the purge sample results. An example of the latter is found in Divine and others (2005).

10.2 Potential Reasons for Differences between Purge and Passive Sampling Results

There are several reasons that passive sampler results may differ from purge sampling results for the same well. The primary reason results may differ is due to the physical mechanism of each sampling method used to collect samples and the differences between ambient flow and pumping-induced flow in the well. Specifically, these physical differences can be grouped into three categories: (1) temporal, (2) flow regime, and (3) volume of sample integrated during sampling.

Passive samplers typically produce samples that represent the chemical concentrations in the water that the samples have been in contact with over the last 3–4 days prior to sampling, especially if the chemicals have relatively high diffusion coefficients. Purge sampling methods induce flow into a well and produce an instantaneous sample. Therefore, the two methods collect samples that may differ temporally.

Passive samplers collect samples under an ambient flow regime. The degree of mixing in the well under ambient flow usually is substantially less than during purging. The difference in flow regime affects sampling tendencies. Passive sampling has a tendency to collect a volume-weighted sample, whereas purge sampling collects a flow-weighted sample (Divine and others, 2005). Samples from passive samplers reflect the chemistry of inflowing groundwater controlled by the distribution of hydraulic head and permeability along the open interval of the well under ambient conditions, whereas purge samples reflect the chemistry of the more permeable units along the open interval of the well under pumping conditions.

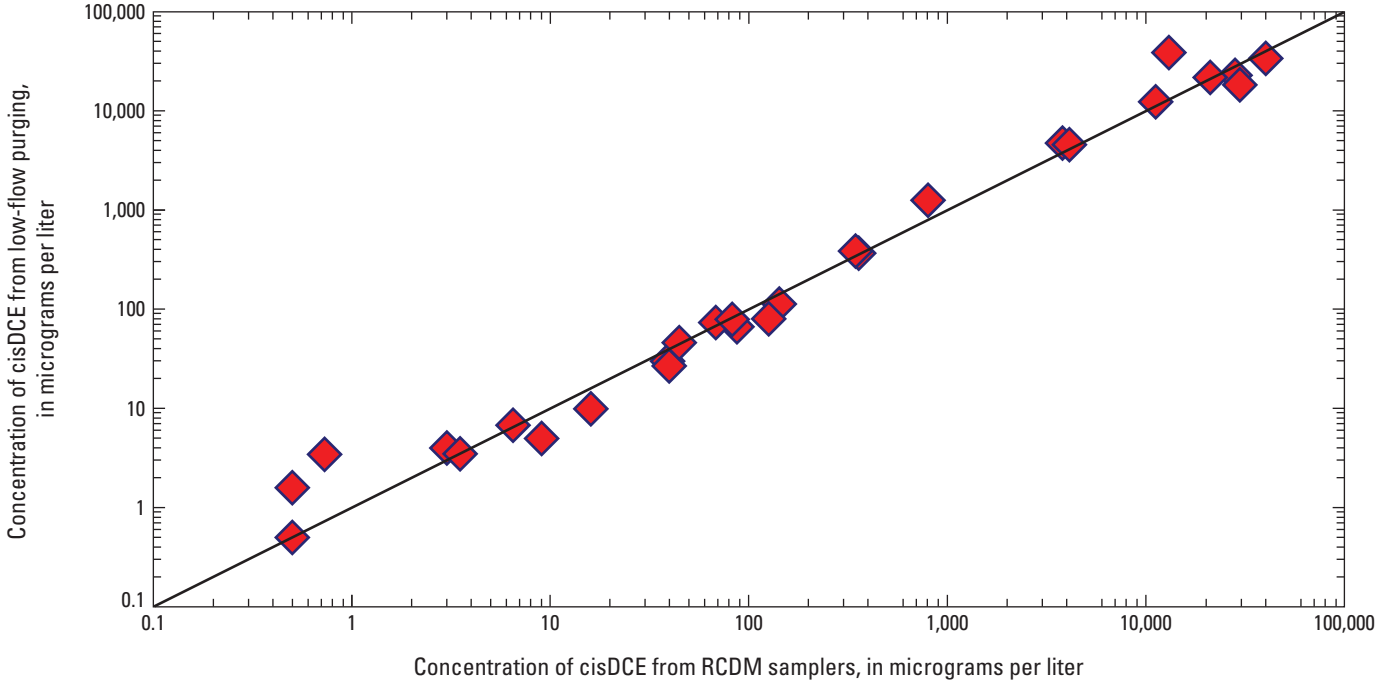

Figure 22. Concentrations of cis-1,2-dichloroethene (cisDCE) from regenerated cellulose dialysis membrane (RCDM) samplers in relation to concentrations of cisDCE from low-flow purging, with a 1:1 linear relation line. Data from Imbrigiotta and others (2002, 2007).

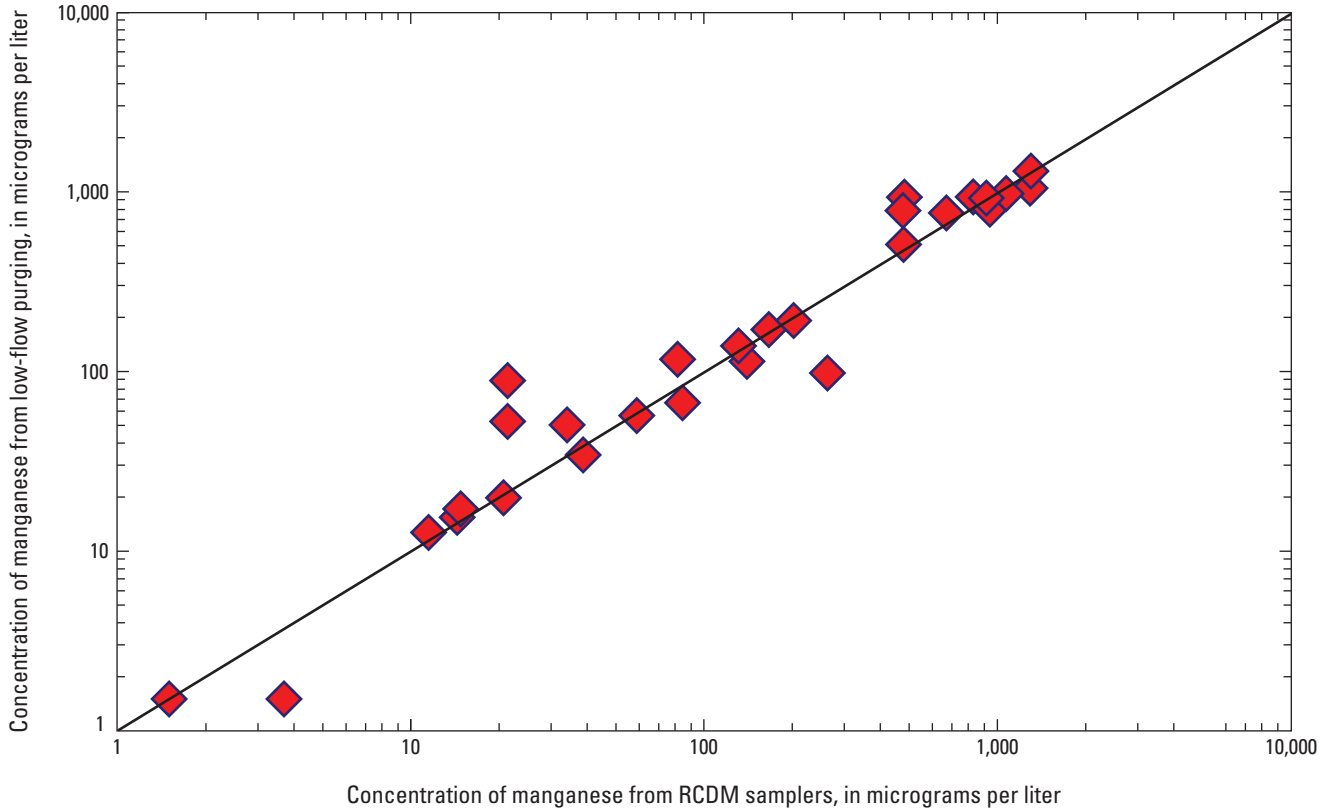

Figure 23. Concentrations of manganese from regenerated cellulose dialysis membrane (RCDM) samplers in relation to concentrations of manganese from low-flow purging, with a 1:1 linear relation line. Data from Imbrigiotta and others (2007).

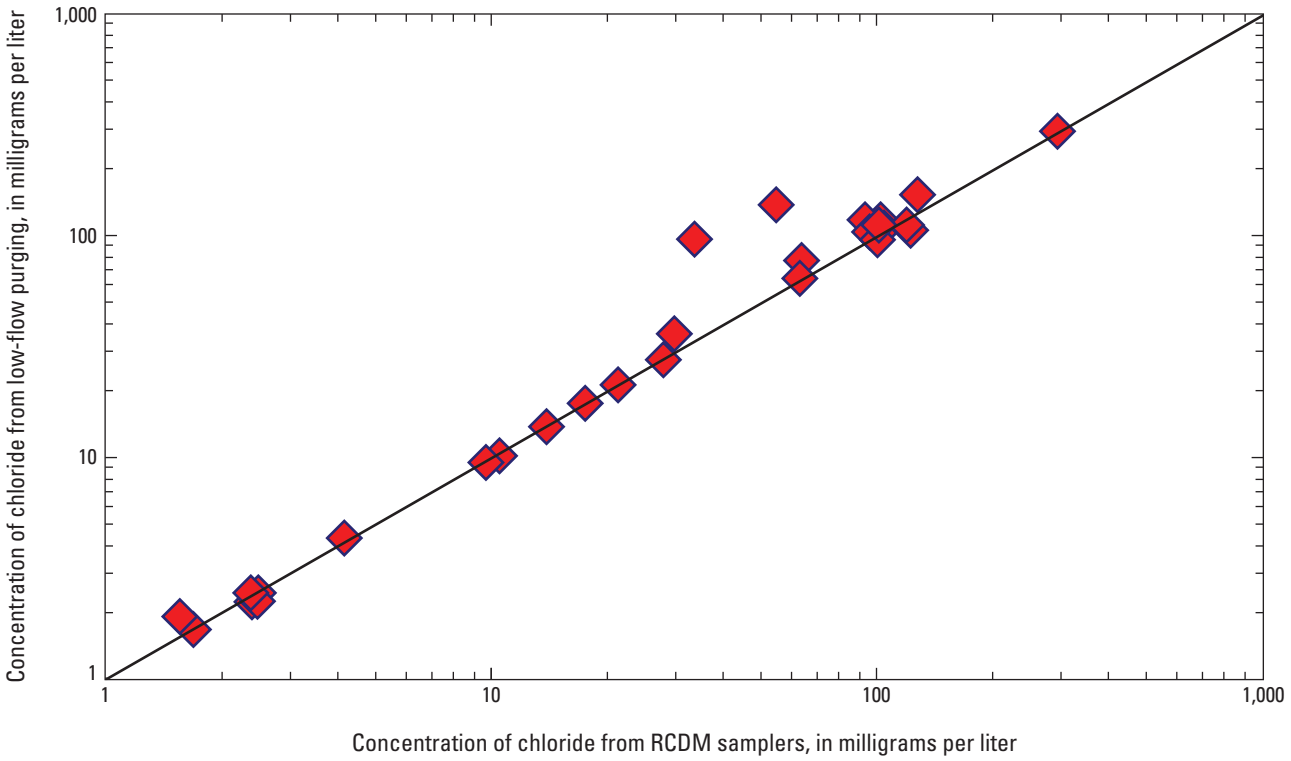

Figure 24. Concentrations of chloride from regenerated cellulose dialysis membrane (RCDM) samplers in relation to concentrations of chloride from low-flow purging methods, with a 1:1 linear relation line. Data from Imbrigiotta and others (2007).

The volume of sample and compositional mix of water interrogated during purging is independent of the depth of the pump intake if a steady-state flow field exists and sufficient time is allowed for in-well transport (Harte, 2017). The effects of in-well transport during pumping can be evaluated following methods described by Harte and others (2019). In contrast, the volume of the sample and compositional mix of water interrogated during passive sampling can be depth-dependent in the well. A difference in volume of samples interrogated using the two different sampling methods is important when vertical chemical stratification and hydraulic heterogeneities are present over the length of the screened or open interval. For example, if the well is in good hydraulic communication with transmissive zones intersecting the screened or open interval, most of the water pumped during purging will originate from those zones (Divine and others, 2005). If the passive sampler is not positioned at the same depth or affected by vertical flow that originates from those same zones, then the chemistry in water from the passive sampler will likely be different from the chemistry in the purge sample. Therefore, for wells undergoing stratified flow and where there is a tendency for the water to not be well mixed under ambient conditions, depth dependency of the sampler is important.

Pressure changes from pumping can induce degassing of constituents of interest with high Henry's Law coefficients (Roy and Ryan, 2010). Degassing of the water sample also may occur with passive sampling from exchange at land surface between the sampler and the final sample collection bottle. Some passive samplers can collect gas samples and minimize degassing by allowing the sampler to be sealed downhole in the well. Water from passive sampling may be more susceptible to volatilization under ambient conditions in the water column than water samples obtained from purging. A way to assess the effect of volatilization with passive sampling is to deploy multiple samplers in the well casing above the top of the well opening to identify the direction of chemical gradients (Harte and Brandon, 2020). If there is little vertical change in constituent concentrations in samples from the samplers in the well casing and samples from the open interval, then volatilization is unlikely. Thermal convection may cause inversions in the well water column and induce mixing between water in the casing and water in the screened interval (Vroblesky and others, 2006, 2007a). This process could affect passive and purge methods differently and camouflage volatilization losses in the water column.

There is a greater potential for water from the casing (especially if large volumes are present in the well) to mix with water from the open interval using purge sampling methods than using passive sampling methods because of the inducement of converging flow. Casing water can have

chemistry different from that of groundwater in the formation under anaerobic conditions because of exposure to the atmosphere at the top of the water column. In such a case, the mixed purge water may be more oxic than the open interval water in which the passive sampler is suspended during its deployment period.

The ability of the membrane used in the passive sampler to collect a representative sample of well water is an obvious factor in potential differences in results. If a passive sampler cannot collect samples for the constituents of interest, then the results will differ from those of purge sampling. An example of this would be the inappropriate use of a PDB sampler to sample for major cations and anions. Another possible reason that passive sampler results may differ from purge sampling results is that the passive sampler may have sustained damage during its deployment or retrieval that changed the diffusive properties of the membrane, which may alter the diffusion process across the membrane. For example, a perforated membrane damaged during installation may allow the collection of chemical constituents by the sampler that have not diffused through the membrane or equilibrated between the well and the sampler.

Passive samplers and purge sampling methods can yield different results if improper transfer techniques are used to fill sample containers. Passive samplers need to be sampled immediately after removal from the well. They should not be allowed to sit exposed to the atmosphere allowing loss of volatile compounds and the introduction of atmospheric oxygen, which can change the concentrations of redox species in the samples.

10.3 Potential Reasons for Differences Between Passive Sampler Replicate Samples

Differences in results between replicate samples from passive samplers may be due to several factors. Samplers may not be constructed identically from the same materials or assembled in the same way. Samplers used for replicates may not be suspended at the same depth in a well that has a strong vertical chemistry difference. Differences may occur in post-retrieval handling of the passive sampler and in transferring the sample to the sample container; for example, one replicate sampler might be recovered from a well and the sample transferred immediately, whereas the other sampler sits exposed to the atmosphere.

10.4 Regulatory Acceptance for Switching from Purge Sampling to Passive Sampling

In most cases, State regulators will require some sort of "side-by-side" evaluation before allowing passive samplers to replace purge sampling methods. The number of comparison samples should be large enough (10–20) to produce a dataset that will allow confidence in the results. Prior to the comparison of sample results, the acceptable statistical range of results must be agreed upon with the regulator. As an example, State regulators at the New Jersey Department of Environmental Protection have approved the use of RCDM samplers in 50 wells in the long-term monitoring plan of the former Naval Air Warfare Center facility in West Trenton, N.J. The U.S. Navy contractor saves a considerable amount of time in the field by not having to pump the 50 wells to collect samples. The contractor does not have to decontaminate pumps in between these wells and does not need to collect, transport, and treat any contaminated IDW from these wells. Use of RCDM samplers is therefore saving the U.S. Navy a substantial amount of money annually in field sampling costs. More information is given about this example in Appendix A, Case Studies A3 and A4.

10.5 Cost Comparison Between Purge and Passive Sampling

Passive samplers have been shown to have many advantages in sampling groundwater wells. Sampling time in the field using a passive sampler is decreased by 67–83 percent (3–6 times less) compared to sampling time in the field using low-flow purging methods (Imbrigiotta and others, 2007; Parsons, 2005). Overall, collection of samples using a passive sampler is 50–75 percent less expensive (2–4 times less expensive) than using low-flow purging (Imbrigiotta and others, 2007; Parsons, 2005). Even higher savings would be anticipated using passive sampling rather than traditional 3-volume purge sampling methods.

Passive samplers eliminate purge-water production and therefore IDW disposal costs. Many passive samplers exclude particulates from groundwater samples owing to the small pore size of their semi-permeable membranes, so in many cases no field filtration is required for samples collected with these devices. Most passive samplers are disposable, so there is no need for field decontamination. All of these attributes save money and time.

Passive samplers have been used most frequently in long-term monitoring program wells because they substantially decrease sampling costs compared to purge sampling techniques. Cost savings are cumulative for periodic, long-term monitoring wells, and most of the savings come from a decrease in personnel time required to collect samples using passive samplers relative to the time spent to purge a well. Cost savings from sampling long-term monitoring wells can be substantial because these kinds of wells usually are designed to be sampled on a repeating basis over a period of 20–30 years.

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Appendixes A–C

Appendix A. Case Studies

Case Study A1

Title and location: Vertical profiling of a tetrachloroethene plume near a dense non-aqueous phase liquid source location (OK Tool facility), Savage Superfund Site, Milford, New Hampshire

Background: The Savage Superfund site in Milford, New Hampshire, consists of a large (several miles long) tetrachloroethene (PCE) plume that originated adjacent to a losing river reach of the Souhegan River (Harte and others, 2001). The source of the plume is a former manufacturing facility (OK Tool facility; fig. 1.1 inset) that disposed of solvents in a pit near the facility. Fully penetrating (50-foot [ft] -long screen) wells were installed next to the pit to facilitate remediation of the dense non-aqueous phase liquid (DNAPL). The wells were left in place after surfactant-enhanced recovery pilot tests were performed.

Study and sampling objectives: Vertically profile the fully penetrating wells over time to assess vertical changes in dissolved PCE and potential attenuation of the DNAPL source.

Geology: Glacial deposits of stratified drift overlying a basal till within the Souhegan River valley.

Description of well network: Short-screened (5- to 10-ft screens) and long-screened (40- to 50-ft screens) wells finished in the overlying glacial drift.

Sampling approach: Sampler type: (1) Passive diffusion bag (PDB); (2) Deployment in the well: Multiple samplers, uniformly spaced in the fully penetrating well screen; (3) Deployment duration: 2–3 weeks.

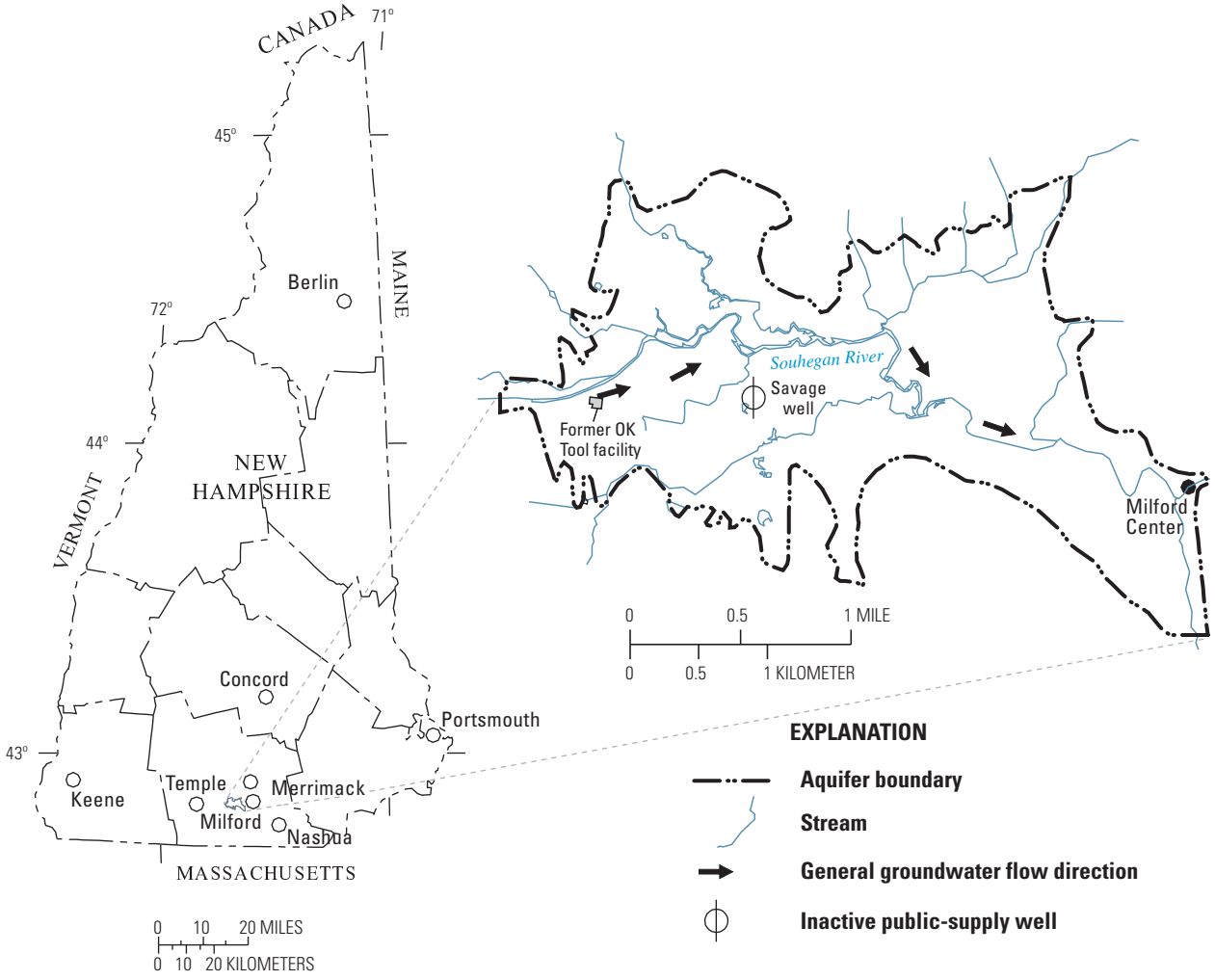

Figure 1.1. Location of the former OK Tool facility at the Savage Superfund site, Milford, New Hampshire.

Performance assessment: Concurrent low-flow samples at coincident depths were collected from a subset of wells, as reported in Harte and others (2001) and Harte (2002). Comparison of results from the two sampling methods (low flow and passive) showed good linear relation with a regression equation in the form of

PDB sample concentration = 0.9378 (low-flow sample concentration) + 102.8 with a coefficient of determination (R^2) of 0.966. (1)

Findings: Vertical profiling with PDB samplers (17 samplers) spaced uniformly in a fully penetrating, long-screened well adjacent to a known DNAPL source detected decreases of one order of magnitude of PCE concentrations from 2002 to 2007 (fig. 1.2). For profiles in 2002 (January and March) and 2007, the highest PCE concentrations occurred at depth (below an altitude of 225 ft above the National Geodetic Vertical Datum of 1929 (NGVD 29)) near the contact between the stratified drift and underlying basal till, indicating some pooling of the DNAPL at that contact. The largest decreases between 2002 and 2007 also occurred at that depth. The change in profile concentrations likely reflects decreases in mass of the adjacent DNAPL pool from a variety of processes. Concentrations of PCE were slightly higher in 2007 than 2002 above an altitude of 225 ft above NGVD 29.

Utility of passive sampling: Vertical profiling with PDBs provided semi-discrete depth sampling in a long-screened well adjacent to a DNAPL pool, which allowed for documentation of apparent decreases in DNAPL mass.

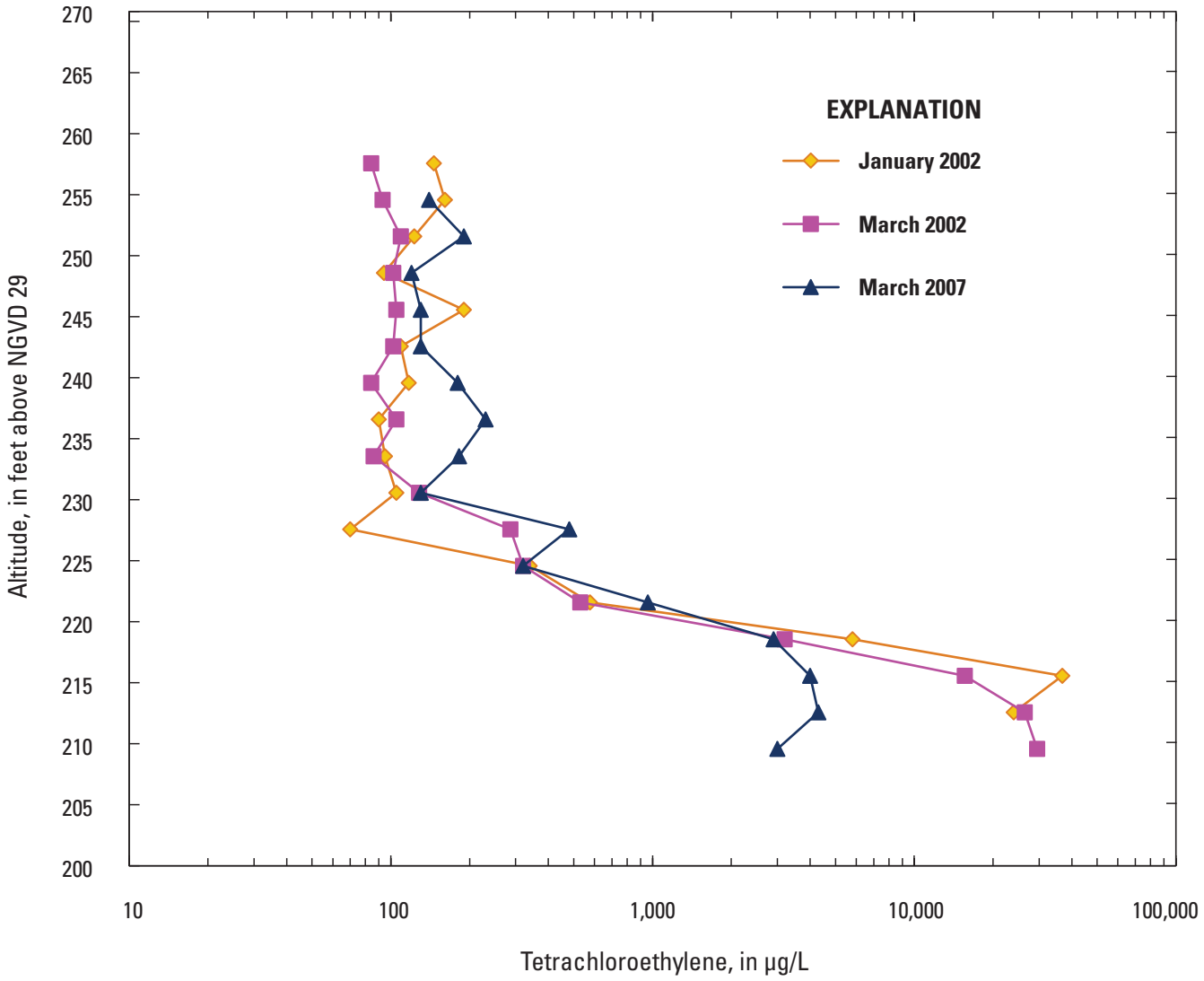

Figure 1.2. Vertical chemical profile of tetrachloroethene concentrations from a long-screened (50-foot) well using uniformly spaced passive diffusion bag samplers, at the former OK Tool facility at the Savage Superfund site, Milford, New Hampshire, 2002–07. [µg/L, microgram per liter; altitude is referenced to National Geodetic Vertical Datum of 1929 (NGVD 29)]

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Case Study A2

Title and location: Vertical profiling for concentrations of uranium and selenium in groundwater of an alluvial aquifer, Homestake Superfund site, near Milan, New Mexico.

Background: The Homestake Mining Company Superfund site (Homestake Superfund site) is in the San Mateo Creek Basin of New Mexico, which is part of the Grants Mineral Belt where several geologic formations, such as the Morrison Formation, contain uranium (U) ore deposits. The site itself was a mill operation facility for processing of uranium ore from the local area. A large pile of residual U tailings sits atop the alluvial aquifer and is a local source of elevated U concentrations in excess of several hundred milligrams per liter (mg/L). An understanding of the difference in U concentrations between those in regional and local waters and those in water affected by leaching from the tailing pile is needed to assess sources of U. Selenium (Se) can be a co-contaminant with anthropogenic U from regional mines and mills in the upper San Mateo Creek Basin and is a good indicator of regional, anthropogenic-affected waters.

Study and sampling objectives: The main objective of this study was the determination of regional and local occurrence of U by assessing the variation of U and Se concentrations (Se co-occurrence with U in regional waters) in groundwater. Observation wells completed in the alluvial aquifer were vertically profiled using passive samplers to determine the vertical variation in U and Se concentrations in groundwater. Results were compared to borehole geophysical logs of natural gamma-ray (NGR) and spectral gamma-ray to assess heterogeneity of the aquifer (Harte and others, 2019).

Geology: Alluvial deposits of Quaternary age. Deposits are mostly composed of silts and fine sands with clay layers. Underlying the alluvium is a rock formation of the Chinle Group of Triassic age.

Description of well network: Five polyvinyl chloride (PVC) wells with screen lengths ranging from 20 to 40 feet (ft) and approximately 4 inches in diameter. One PVC well with a screen length of 80 ft.

Sampling approach: (1) Sampler type: All passive samplers were nylon screen (NS) type and had 125-micron screen openings. (2) Deployment in the well: Multiple samplers (7–12), variably spaced in wells and deployed on the basis of borehole logs and inferred hydrogeologic contacts (fig. 2.2). (3) Deployment duration: 4–5 weeks.

Performance assessment: Concurrent micropurge samples (7) were collected at selected coincident depths with passive samplers from all wells (6) after retrieval of the passive samplers. The micropurge sampling is a minimal purge technique where samples are collected after pumping a volume of water equal to 1.5–2 times the volume of water contained in the pump and hose line. The pump intake was set at the same depth as a passive sampler. Approximately 1.5–2 liters of water were pumped prior to sampling. Neither the micropurge nor passive samples were filtered (total sample). Micropurge sampling allowed for collection of a semi-discrete instantaneous sample comparison of the results to those from the passive sampler. Comparison of results from the two sampling methods (micropurge and passive) showed a linear relation for U ($R^2 = 0.99$) and Se ($R^2 = 0.98$). However, the U and Se concentration from the NS samplers were found to be consistently low by a factor of 3.55 for U and 3.46 for Se between the passive samplers and micropurge samples (Harte and others, 2018). Because of the excellent linear relation and consistent differences, results from the passive samplers were adjusted by these factors. Further, rates of concentration uptake of the NS samplers were evaluated by equation 3 and found to agree with these factors.

Purge samples also were collected by volumetric methods where the pump was set near the base of the casing and the top of the screen (if saturated), and samples were collected after three well volumes were purged. Comparisons also were made between passive sample results and volumetric sample results using two different approaches. Results from individual passive samplers from the closest depths to the pump intake of the volumetric sample were compared, and the results from the profile of passive samplers (the arithmetic mean of all samplers) were compared to the results from the volumetric sample.

Findings: Table 2.1 summarizes U concentration results from the three different sampling methods at the seven wells. In the six wells sampled with both volumetric purge and micropurge methods, similar concentrations were found with both sampling techniques in all cases, indicating that well water within the screened interval of the well is representative of the formation. Therefore, volumetric sampling, which requires large amounts of purging, is not needed to collect a representative sample. The passive sampler concentrations were adjusted to the purge sampler concentrations according to methods described by Harte and others (2018). The variability in concentrations from the passive sampling profile can be identified by the relative magnitude of the standard deviation of U concentrations from the passive samplers (table 2.1).

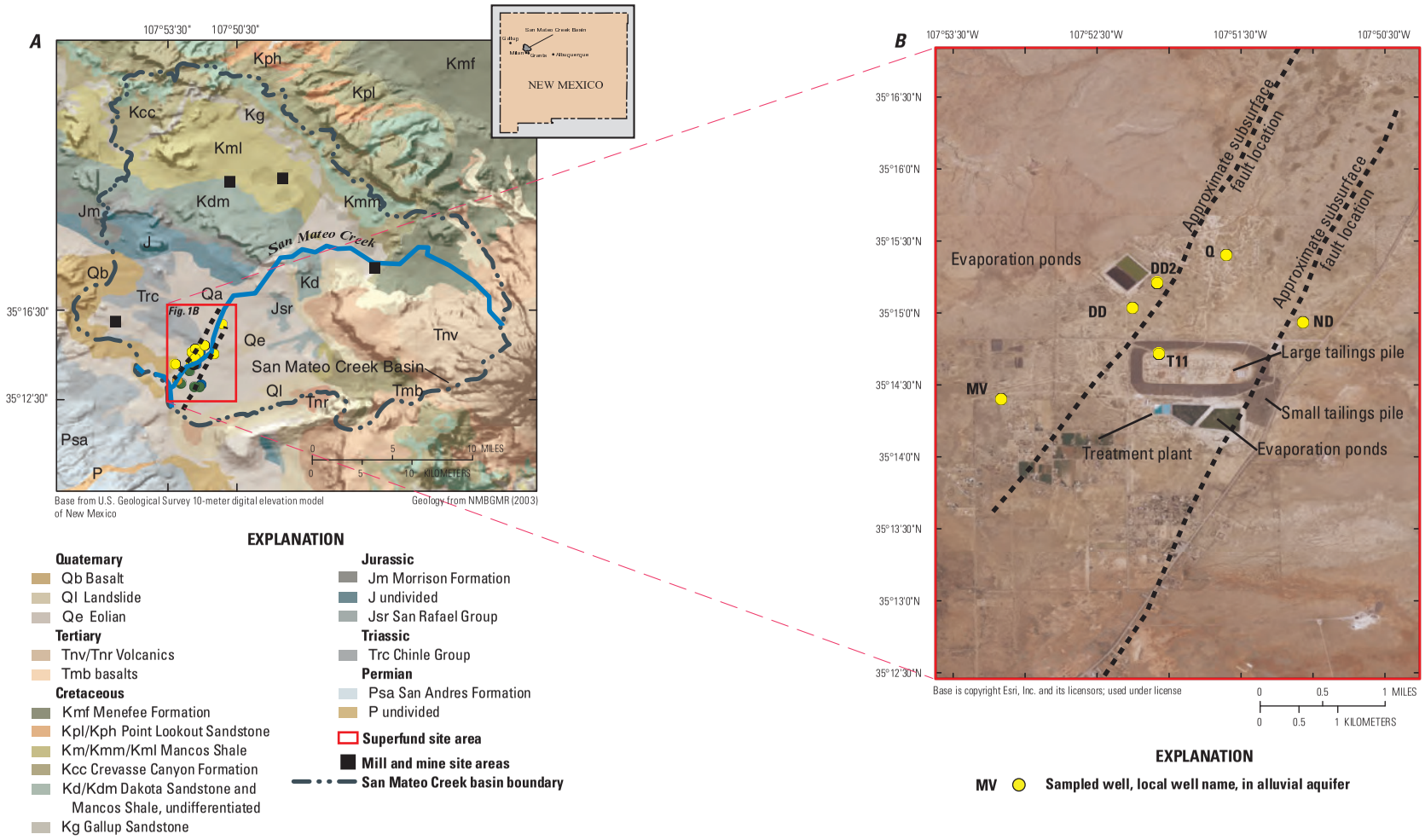

Figure 2.1. Location of *A*, Homestake Superfund site, San Mateo Creek Basin, and *B*, passive sampling wells, near Milan, New Mexico.

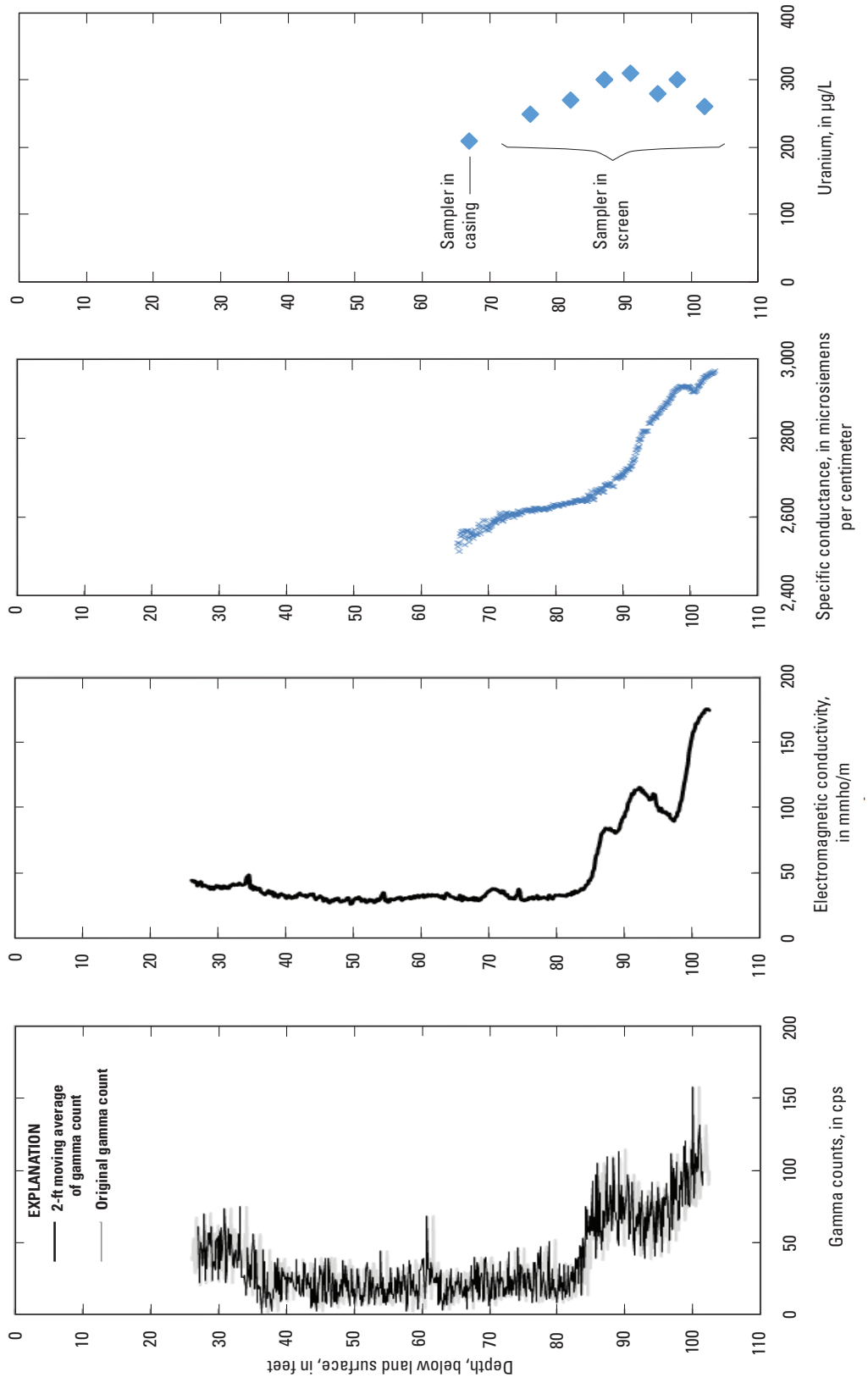

Figure 2.2. Borehole geophysical logs from well MV and uranium concentrations from passive samplers, Homestake Superfund site, near Milan, New Mexico.
[cps, counts per second; mmho/m, millimhos per meter; µg/L, micrograms per liter; ft, foot]

Table 2.1. Summary of uranium concentrations obtained using different sampling methods, including passive sampling, Homestake Superfund site, near Milan, New Mexico.

[Uranium concentrations are in micrograms per liter (µg/L); none, no sample; —, use previous value from same well; **, concentrations adjusted by Harte and others (2018)]

Type of sample	Parameter	Sample description	Units	Well name						
				ND	MV	Q	DD	DD2	DD2	T11
**Volumetric	Total uranium	Sample collected after evacuation of three well volumes	µg/L	25	297	66	103	250	—	10,677
**Micropurge	Total uranium	Sample collected after evacuation of pump and hose volume	µg/L	31	353	61	90	263	257	10,353
**Passive	Total uranium	Passive sample located within casing (casing sample)	µg/L	None	238	46	None	44	—	None
	Mean total uranium	Mean concentration from profile of passive samples excluding sample from casing zone	µg/L	24	322	54	65	180	—	16,508
	Standard deviation of total uranium	Exclude passive sample from casing zone	µg/L	6.4	23.4	3.7	23.8	50.5	—	7,502

The adjusted concentration of U for passive sampling shows small variations at two of the wells profiled (wells ND and Q; table 2.1) and larger variations at four of the wells (wells MV, DD, DD2, T11; table 2.1), as identified by the relative magnitude of the standard deviation of U concentrations from the passive samplers. Well T11 had the highest mean U concentration and largest standard deviation from the profile of passive samplers and is at the large tailings pile (fig. 2.1). Well ND had the lowest mean U concentration but not the lowest standard deviation from the profile of passive samplers and is upgradient from the tailings pile (base map). Well Q is upgradient from the tailings pile (base map) but downgradient from regional mills and mines in the upper part of the San Mateo Creek Basin. Well Q had the smallest standard deviation, which indicates that water in the well and potentially the formation is well mixed with little vertical variation in U concentrations. Wells DD, DD2, and MV are proximal to the tailings pile (fig. 2.1). Despite being in close proximity to well DD, well DD2 had a larger variation in U concentrations than well DD. Wells ND and Q are screened in predominantly silt and sands, whereas wells DD and DD2 are screened in interbedded clays, and silts and sands. Wells T11 and MV are screened in sands. Well MV had a vertical variation in U concentration similar to that of well DD, despite having a five-fold increase in mean U concentration. Well MV is downgradient from the tailings pile and likely receives U groundwater transport from the tailings.

Physical heterogeneity of the alluvium likely affects U concentration variability. The interbedded clays at wells DD and DD2 may contain reduced waters where U in the form of U(IV) may be sorbed onto sediments and in proximity to oxic waters that induce mobilization of U by converting U(IV) to mobile U(VI). Where there are primarily sands and silts (wells Q and ND), the aquifer is well mixed and shows less U variability.

Se concentration results from the three different sampling methods at the seven wells are summarized in table 2.2. In the six wells where both volumetric purge samples and micropurge samples were collected, similar concentrations were found with both sampling techniques for four of the six wells. The passive sampler concentrations were adjusted to the micropurge sample concentrations, according to methods described by Harte and others (2018). The variability in concentrations from the passive sampling profile can be identified by the relative magnitude of the standard deviation of Se concentrations from the passive samplers (table 2.2).

Selenium variability is similar to U variability at wells T11 and MV, which receive transport of anthropogenic U. This similarity indicates there is likely a local, anthropogenic source of Se. At two wells (ND and Q) that show little variation in U (table 2.1), Se shows greater variability (table 2.2). Well DD2 shows variability in U but little variability in Se (table 2.2). Selenium like U is affected by redox conditions, and Se (and U) is less mobile under reducing conditions. Well DD2 had low dissolved oxygen (DO) concentrations (<1 mg/L) and low Se concentrations. In contrast, well DD near well DD2 had high DO (>5 mg/L), and Se concentrations were higher at well DD than well DD2 (table 2.2). Well Q, despite showing little variability in U, had relatively high variability in Se. Well Q is downgradient from mines and mills in the upper San Mateo Basin and receives discharge of regional groundwater enriched in Se.

An example of a profile of U concentrations from the passive samplers in well MV is shown in figure 2.2. Two passive samplers straddling the inferred contact as determined from borehole logs were deployed to identify chemistry differences in aqueous uranium concentrations near a depth of 85 ft (fig. 2.2). Samplers were set at depths corresponding to low

Table 2.2. Summary of selenium concentrations obtained using different sampling methods, including passive sampling, Homestake Superfund site, near Milan, New Mexico.

[Selenium concentrations reported in micrograms per liter (µg/L); >0.5, less than detection level; none, no sample; —, use previous value from same well; µg/L, micrograms per liter; lsd, land surface datum; ft, foot; **, concentrations adjusted by Harte and others (2018); *, concentration of passive sampler potentially affected by low water column]

Type of sample	Parameter	Sample description	Units	Well name						
				ND	MV	Q	DD	DD2	DD2	T11
Volumetric	Total selenium	Sample collected after evacuation of three well volumes	µg/L	150	35	460	130	13	—	180
	Depth of sample below lsd		ft	64	71	68	54	50	—	140
Micropurge	Total selenium	Sample collected after evacuation of pump and hose volume	µg/L	51	29	380	170	2	8	350
	Depth of sample below lsd		ft	64	82	88	54	72	60	140
**Passive	Total selenium	Passive sample located within casing (casing sample)	µg/L	None	4.3	381	*25	>0.5	—	None
	Mean total selenium	Mean concentration from profile of passive samples excluding casing sample	µg/L	65	28.0	411.0	163.0	13.0	—	121
	Standard deviation of selenium	Exclude sample from casing	µg/L	23.7	8.2	20.8	23.7	3.3	—	75.1

NGR counts and low electromagnetic (EM) induction conductivity (two samplers), and high NGR counts and high EM conductivity (five samplers). Another sampler was placed in the casing (68-ft depth) to help understand the effect of stagnant water chemistry from the casing on passive sampler and purge method samples from the well. The results from the passive samplers show a slightly lower concentration of U, although not significantly different, from the samplers at depths corresponding to the relatively low NGR and low EM induction conductivity values, whereas higher concentrations of U are found from samplers at depths corresponding to relatively high NGR and EM induction conductivity (fig. 2.2). Because the fluid conductivity (specific conductance) log shows a large change along the screened opening, which indicates stratified and distinct well inflow from the two inferred units straddling the contact at the 85-ft depth, the relative similarity in U concentrations from the samplers above and below the inferred contact indicates that there are small differences in U concentrations in the two inferred units.

Utility of passive sampling: Vertical profiling with passive samplers provided insight into the vertical variation in U concentrations in the alluvial aquifer. Vertical variation in U (and Se) can be compared to hydrogeologic units to identify the presence of constituents. At sites with limited wells for sampling, vertical profiling allows for an expanded view of the effects of physical and chemical heterogeneity on U and Se occurrence.

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Harte, P.T., Blake, J., and Becher, K.D., 2018, Determination of representative uranium and selenium concentrations from groundwater, 2016, Homestake Mining Company Superfund Site, near Milan, New Mexico: U.S. Geological Survey Open-File Report 2018–1055, 40 p., https://doi.org/10.3133/ofr20181055.

Harte, P.T., Blake, J., Thomas, J., and Becher, K.D., 2019, Identifying natural and anthropogenic variability of U in groundwater at the well scale by use of borehole geophysical and passive chemical profiling, Homestake Superfund site, Milan, New Mexico: Journal of Environmental Earth Science, v. 78, p. 95, accessed June 5, 2019, at https://doi.org/10.1007/s12665-019-8049-y.

Case Study A3

Title and location: Comparison of organic compound and inorganic constituent concentrations recovered by regenerated cellulose dialysis membrane (RDCM) passive samplers, polyethylene diffusion bag (PDB) passive samplers, and low-flow purging at the former Naval Air Warfare Center site in West Trenton, New Jersey.

Background: The former Naval Air Warfare (NAWC) site was a naval jet engine testing facility from the mid-1950s to 1999 before the base was closed (fig. 3.1). Trichloroethene (TCE) was used as a refrigerant in a 25,000-gallon cooling system that allowed adjustment of engine test chamber temperatures. TCE was spilled or leaked from the system over the more than 40 years of operation and entered the underlying fractured bedrock. More than 100 wells were installed at the site to define the groundwater flow and contamination. Initially all wells were sampled for volatile organic compounds (VOCs) using a three-well-volume purge method. Because well diameters ranged from 4 to 8 inches and depths from 6 to 410 feet (ft), this resulted in large volumes of contaminated purge water (IDW) being produced during sampling that needed to be drummed and transported to the onsite treatment plant. In 1995, low-flow purging was used in many wells to decrease the purge volumes produced. In 2002, PDB samplers were used at the site to collect VOC samples and to reduce the purge volumes further. Concentrations of VOCs from PDB samplers were found to compare well with concentrations from the low-flow purging method in most wells. In 2003, an investigation into the potential for natural attenuation of TCE at the site required the collection of samples of VOCs and inorganic constituents (chloride, ferrous iron, nitrate, sulfate, sulfide, methane). Regenerated cellulose dialysis membrane (RCDM) samplers were developed and tested as a way to collect organic compounds and inorganic constituents using passive samplers and to reduce the volume of purge water that had to be treated.

Study and sampling objectives: A study of low-flow purging, PDB samplers, and RCDM samplers was conducted to determine whether the three sampling methods gave comparable results for organic compounds and inorganic constituents (Imbrigiotta and others, 2007).

Geology and hydrology: The NAWC site is in the Newark Basin in central New Jersey. The site is underlain by a thin (<10 ft) layer of unconsolidated overburden over a thick (>200 ft) sequence of weathered and unweathered fractured mudstones and siltstones of the Lockatong Formation. Most of the groundwater flow in the aquifer takes place in bedding plane fractures between alternating layers of varying permeability in the mudstones and siltstones.

Description of the well network: More than 100 shallow and deep wells were installed at this site. Most shallow wells are constructed of low-carbon steel or polyvinyl chloride (PVC) casing and are screened in the overburden. All bedrock wells onsite are constructed using steel or PVC casing through the overburden and are open to the formation in the bottom 10–25 ft of the borehole.

Sampling approach: Passive samplers, both RCDM and PDB, were installed at known depths in the open interval of a group of wells and allowed to equilibrate. After 2 weeks, the RCDM and PDB samplers were retrieved and sampled. A variable-rate stainless-steel submersible pump was then lowered to the same depth. The wells were low-flow purged, field physical and chemical characteristics were monitored to stability, and samples were collected.

Findings: Concentrations of TCE, cis-1,2-dichloroethene (cisDCE), and vinyl chloride (VC) were all recovered comparably by RCDM samplers versus low-flow purging, and RCDM samplers versus PDB samplers (figs. 3.2 *A–F*) (Imbrigiotta and others, 2007). The closer the data points are to the 1:1 correspondence line in figure 3.2, the closer the results for each sampling method agree. The results presented on the graphs indicate that VOC samples can be collected using any of the three sampling methods, and all methods should yield basically the same result.

In addition, concentrations of inorganic constituents useful in assessing natural attenuation potential, such as chloride, ferrous iron, sulfate, and alkalinity, also were recovered comparably by RCDM samplers and low-flow purging (figs. 3.3 *A–D*) (Imbrigiotta and others, 2007). PDB samplers were not included in this comparison because they are not permeable to inorganic constituents. Again, the closer the data points fall to the line, the closer the sampling methods agree.

The results for the VOC concentrations collected using the three different sampling techniques were compared using a non-parametric Kruskal-Wallis rank sum test. The results of the testing are given in table 3.1. VOCs with four or more comparable sampling results greater than the minimum detection limit collected with each of the three sampling methods were included in this analysis. For all chlorinated VOCs, no significant difference was found between samples collected using the RCDM sampler, PDB sampler, and low-flow purging (Imbrigiotta and others, 2007). Thus, even though the 1:1 correspondence plots seemed to indicate that some sampling techniques were better than others at recovering VOCs, these differences were not significant statistically. The results indicate that in most cases, RCDM samplers accurately collected chlorinated VOCs that varied widely in volatility, solubility, and Henry's Law constant.

Inorganic constituent and selected organic compound concentration data collected with the RCDM passive sampler and low-flow purging methods were compared using a non-parametric Wilcoxon signed rank test. The results of the testing are given in table 3.2. For all the inorganic constituents listed in table 3.2, no significant difference was found between samples collected using the RCDM sampler and low-flow purging (Imbrigiotta and others, 2007). Thus, even though the 1:1 correspondence points appeared to indicate one sampling technique or another was better at recovering some constituents, these differences turned out to be not significant statistically. These results indicated that in most cases, RCDM samplers were able to collect inorganic constituents and organic compounds as accurately as low-flow purging over a range of concentrations (Imbrigiotta and others, 2007).

Figure 3.1. Location of former Naval Air Warfare Center site, West Trenton, New Jersey, trichloroethene contamination areas, and passive sampler wells.
[TCE, trichloroethene; mg/L, micrograms per liter; <, less than; >, greater than; ≥, greater than or equal to]

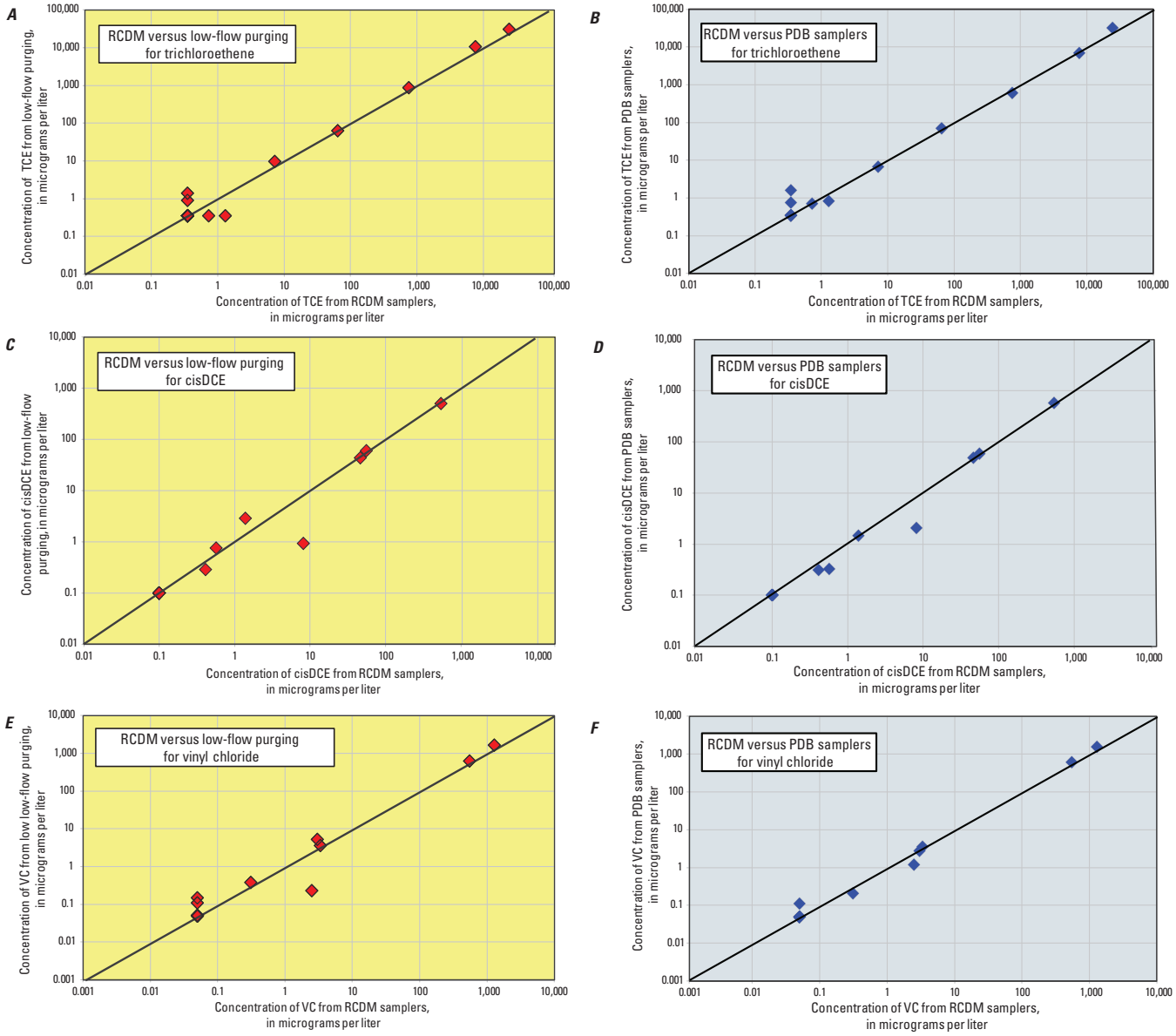


Figure 3.2. 1:1 Correspondence plots of concentrations of *A*, trichloroethene (TCE) collected with regenerated cellulose dialysis membrane (RCDM) samplers versus low-flow purging, *B*, TCE collected with RCDM samplers versus polyethylene diffusion bag (PDB) samplers, *C*, cis-1-2-dichlorothene (cisDCE) collected with RCDM samplers versus low-flow purging, *D*, cisDCE collected with RCDM samplers versus PDB samplers, *E*, vinyl chloride (VC) collected with RCDM samplers versus low-flow purging, and *F*, VC collected with RCDM samplers versus PDB samplers. [Data from Imbrigiotta and others (2007).]

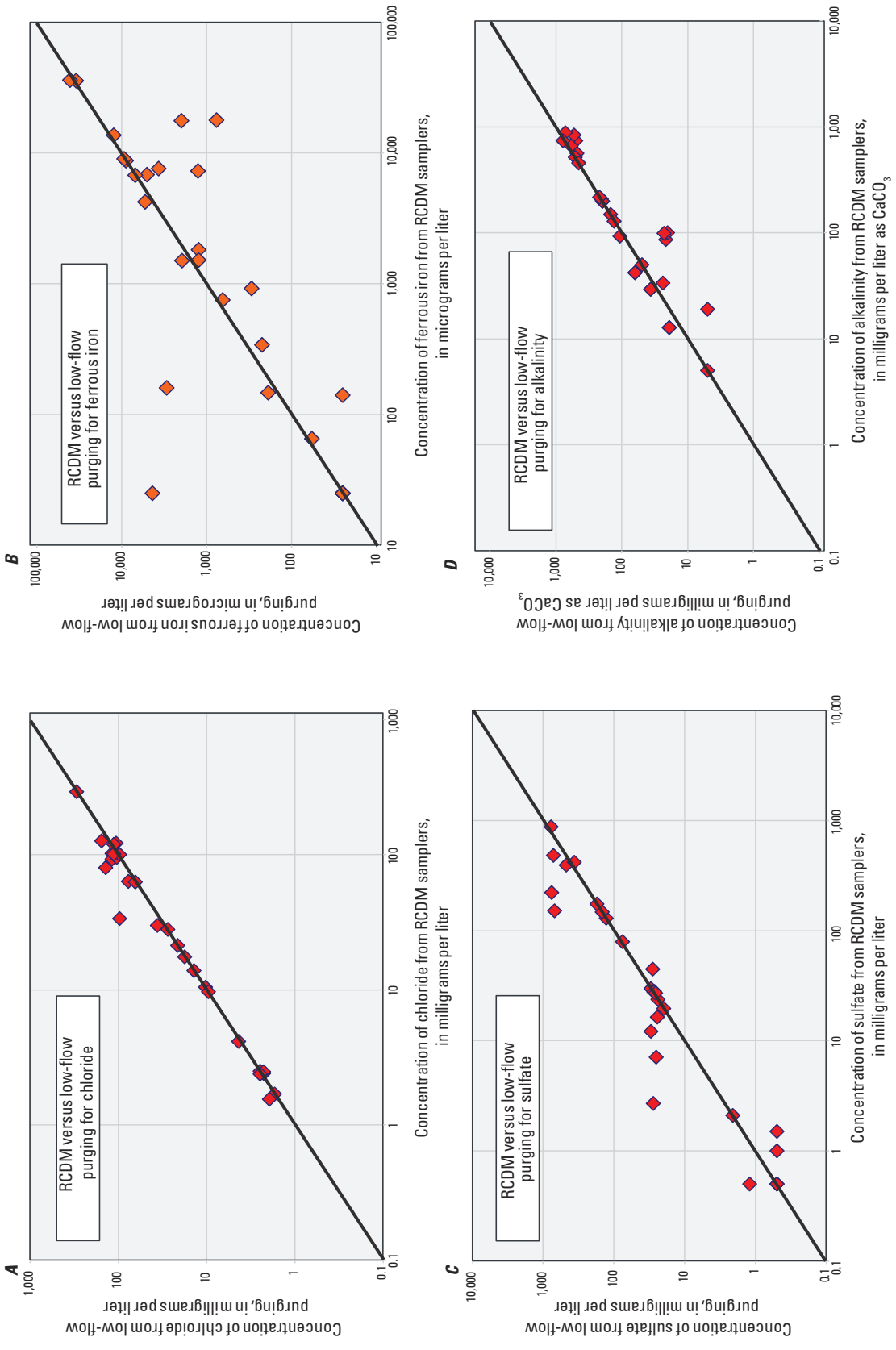


Figure 3.3. 1:1 Correspondence plots of concentrations of *A*, chloride collected with regenerated cellulose dialysis membrane (RCDM) samplers versus low-flow purging, *B*, ferrous iron collected with RCDM samplers versus low-flow purging, *C*, sulfate collected with RCDM samplers versus low-flow purging, and *D*, alkalinity collected with RCDM sampler versus low-flow purging. [Data from Imbrigiotta and others (2007).]

Table 3.1. Chlorinated volatile organic compounds for which concentrations recovered by the regenerated cellulose dialysis membrane sampler, polyethylene diffusion bag sampler, and low-flow purging were compared using the Kruskal-Wallis Test and no significant difference was found.

[RCDM, regenerated cellulose dialysis membrane; PDB, polyethylene diffusion bag; (at $p<0.05$), the presence or absence of differences are significant at the 95-percent confidence level for the number of comparisons; (12), number of comparisons for the constituent at concentrations greater than the minimum detection limit]

Volatile organic compounds for which no significant difference was found between concentrations in samples collected with the RCDM sampler, PDB sampler, and low-flow purging (at $p<0.05$)
trichloroethene (12)
cis-1,2-dichloroethene (10)
1,1-dichlorethene (10)
trans-1,2-dichloroethene (5)
vinyl chloride (9)
dichlorodifluoromethane (4)

Conclusions: RCDM diffusion samplers were effectively used to collect both organic and inorganic chemical constituents that are indicators of natural attenuation of VOCs in groundwater. A deployment time of 1–2 weeks was sufficient for equilibration of all chemical constituents monitored in the study. For chlorinated VOCs, RCDM samplers produced graphically and statistically identical results to results produced by PDB samplers and low-flow purging. For inorganic constituents, RCDM samplers produced graphically and statistically identical results to results produced by low-flow purging.

On the basis of this comparison study, the New Jersey Department of Environmental Protection agreed to allow the U.S. Navy and its contractors to use RCDM and PDB passive samplers to replace low-flow purging in 50 wells at the NAWC site. The use of passive samplers saves the Navy as much as 70 percent of the low-flow purging field sampling costs each time the wells are sampled.

Reference Cited

Imbrigiotta, T.E., Trotsky, J.S., and Place, M.C., 2007, Demonstration and validation of a regenerated cellulose dialysis membrane diffusion sampler for monitoring ground-water quality and remediation progress at DoD sites (ER-0313): ESTCP Final Technical Report for Project ER-0313, 136 p., accessed June 5, 2019, at http://www.estcp.org/Technology/upload/ER-0313-FR.pdf.

Table 3.2. Inorganic constituents and selected organic compounds for which concentrations recovered by the regenerated cellulose dialysis membrane sampler and low-flow purging were compared using the Wilcoxon Signed Rank Test and no significant difference was found.

[RCDM, regenerated cellulose dialysis membrane; (at $p<0.05$), the presence or absence of differences are significant at the 95-percent confidence level for the number of comparisons; (22), number of comparisons for the constituent greater than the minimum detection limit]

Constituents for which no significant difference was found between concentrations in samples collected with the RCDM sampler and low-flow purging (at $p<0.05$)		
Aluminum (22)	Chloride (28)	Selenium (8)
Arsenic (18)	Chromium (5)	Silica (28)
Barium (25)	Fluoride (16)	Sodium (28)
Bicarbonate/Alkalinity (27)	Iron (23)	Sulfate (25)
Bromide (8)	Lead (14)	Vanadium (7)
Cadmium (5)	Magnesium (28)	Zinc (18)
Calcium (28)	Manganese (27)	Nitrate (11)
Carbon dioxide (28)	Molybdenum (11)	Potassium (28)
Total dissolved solids (27)	Methane (21)	Ethene (9)
Dissolved organic carbon (27)		

Case Study A4

Title and location: Comparison of aromatic volatile organic compound concentrations recovered by regenerated cellulose dialysis membrane passive samplers, polyethylene diffusion bag passive samplers, and low-flow purging at the Naval Base Ventura County (NBVC) gas station site in Port Hueneme, California.

Background: The shallow sand-and-gravel aquifer underlying the NBVC was contaminated by leaking gasoline tanks from the primary base filling station over many years prior to discovery of the leak. The primary contaminants at this site were aromatic volatile organic compounds (VOCs) (benzene, toluene, ethylbenzene, xylene [BTEX] and methyl-tert-butyl ether [MTBE]) caused by the leakage of fuel into the aquifer. Long-term monitoring sampling costs for the well network were substantial for the U.S. Navy.

Study and sampling objectives: A study of low-flow purging, polyethylene diffusion bag (PDB) samplers, and regenerated cellulose dialysis membrane (RCDM) samplers was conducted to determine whether all samplers gave comparable results for aromatic organic compounds.

Geology and hydrology: The NBVC site is within 1 mile of the Pacific Ocean near Oxnard, California. The site is underlain by a shallow sand-and-gravel deposit. The groundwater flow in the aquifer moves from the northeast to the southwest towards the Pacific Ocean.

Description of the well network: Shallow wells were installed in the sand and gravel aquifer to investigate the contamination at this site. All shallow wells were constructed of polyvinyl chloride (PVC) casing and were screened 14–27 feet below land surface. Six wells were sampled for this study.

Sampling approach: Passive samplers, RCDM and PDB, were installed at known depths in the screened interval of the six wells and allowed to equilibrate. After 2 weeks, the RCDM and PDB samplers were retrieved and sampled. A variable-rate stainless-steel submersible pump was then lowered to the same depth, the wells were low-flow purged, field physical and chemical characteristics were monitored to stability, and samples were collected.

Findings: Concentrations of most BTEX compounds were recovered comparably by RCDM samplers versus low-flow purging and RCDM samplers versus PDB samplers (figs. 4.2 *A*–*F*) (Imbrigiotta and others, 2007). The closer the data points are to the 1:1 correspondence line in figure 4.2, the closer the agreement for the results of each sampling method. The results shown in the graphs indicate that aromatic VOC samples can be collected using any of the three sampling methods, and all methods should yield basically the same results (Imbrigiotta and others, 2007).

The results for the aromatic VOC concentrations in samples collected using the three different sampling techniques were compared using a non-parametric Kruskal-Wallis rank sum test. The results of the testing are given in table 4.1. Aromatic VOCs with five or more comparable sampling results greater than the minimum detection limit collected with each of the three sampling methods were included in this analysis. For all aromatic VOCs, no significant difference was found between samples collected using the RCDM sampler, PDB sampler, and low-flow purging (Imbrigiotta and others, 2007). Thus, even though the 1:1 correspondence plots appear to indicate that one sampling technique or the other was better at recovering some VOCs, most of these differences were not significant statistically. These results indicate that RCDM samplers accurately collected aromatic VOCs that varied widely in volatility, solubility, and Henry's Law constant (Imbrigiotta and others, 2007).

Conclusions: RCDM diffusion samplers were found to collect aromatic VOCs effectively from groundwater in wells. A deployment time of 1–2 weeks was sufficient for equilibration of all organic compounds monitored in the study. For aromatic VOCs, RCDM samplers produced graphically and statistically identical results to results produced by PDB samplers and low-flow purging. On the basis of this comparison, the Navy and its contractors were able to ask state of California regulators to use passive samplers to reduce long-term monitoring costs.

Reference Cited

Imbrigiotta, T.E., Trotsky, J.S., and Place, M.C., 2007, Demonstration and validation of a regenerated cellulose dialysis membrane diffusion sampler for monitoring ground-water quality and remediation progress at DoD sites (ER-0313): ESTCP Final Technical Report for Project ER-0313, 136 p., accessed June 5, 2019, at http://www.estcp.org/Technology/upload/ER-0313-FR.pdf.

Figure 4.1. Location of the Naval Base Ventura County gas station site, Port Hueneme, Oxnard, California, aromatic volatile organic compound contamination area, and wells in which passive samplers were deployed. [BTEX, benzene, ethylbenzene, toluene, and xylene; mg/L, micrograms per liter]

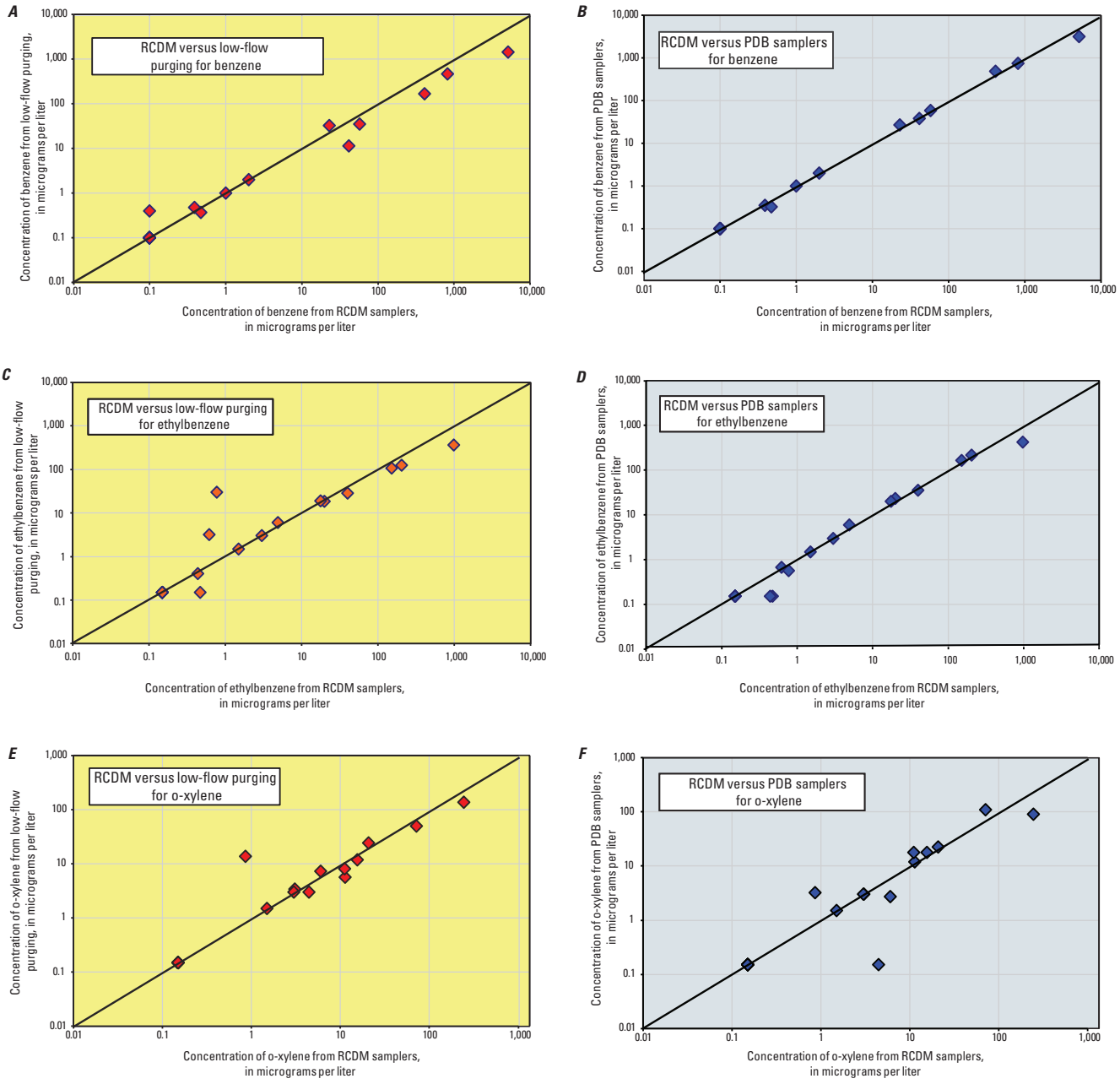


Figure 4.2. 1:1 Correspondence plots of concentrations of *A*, benzene collected with regenerated cellulose dialysis membrane (RCDM) samplers versus low-flow purging, *B*, benzene collected with RCDM samplers versus polyethylene diffusion bag (PDB) samplers, *C*, ethylbenzene collected with RCDM samplers versus low-flow purging, *D*, ethylbenzene collected with RCDM samplers versus PDB sampler, *E*, o-xylene collected with RCDM samplers versus low-flow purging, and *F*, o-xylene collected with RCDM sampler versus PDB samplers. [Data from Imbrigiotta and others (2007).]

Table 4.1. Aromatic volatile organic compounds for which concentrations obtained using the regenerated cellulose dialysis membrane sampler, the polyethylene diffusion bag sampler, and low-flow purging were compared using the Kruskal-Wallis Test and no significant difference was found.

[RCDM, regenerated cellulose dialysis membrane; PDB, polyethylene diffusion bag; (at $p<0.05$), the presence or absence of differences are significant at the 95-percent confidence level for the number of comparisons; (17), number of comparisons for the constituent at concentrations greater than the minimum detection limit]

Compounds for which no significant difference was found between concentrations in samples collected with the RCDM sampler, PDB sampler, and low-flow purging (at $p<0.05$)	
ethylbenzene (17)	benzene (13)
isopropylbenzene (17)	toluene (15)
n-propylbenzene (14)	m,p-xylene (17)
tert-butylbenzene (7)	o-xylene (15)
naphthalene (12)	styrene (6)
1,2,4-trimethylbenzene (17)	
1,3,5-trimethylbenzene (13)	
methyl tert-butyl ether (5)	

Appendix B. Field Form for Deployment and Retrieval of Passive Samplers

Passive Sampler Deployment Field Sheet-page 1

[Mar. 2020 version 12

Location _____ Date: _____

Local well name _____ USGS SID# _____

Weather conditions _____ Temperature (degrees C or F) _____

Measurement point (MP) _____ [eg. Top of Casing (TOC), Land Surface (LS), ETC.]

Is there an outer protective casing? Y or N (Circle) Stickup of outer casing (ft) _____ [from LS]

Well material (inner pipe) _____ [Eg. PVC, Steel] Stickup of inner casing (ft) _____ [from LS]

Well Diameter (inner pipe) _____ [Units; inches, feet, cm, m] _____

Units of Measurement below if not noted [Circle: M-meters; Ft-feet; other_____]

3 MP Distance Relative to Land Surface _____ (Circle Inner or Outer for MP)

4 Sounding Depth of Well from MP _____ [Source: Borehole Log, handheld reading, etc]

5 Depth to Water Level (DTW) from MP _____ [Two readings]

6 **Date/Time of water level** _____

7 **Corrected DTW (DTWLS)from Land surface (LS)** _____ (Line 5-3)

8 Reported Well Depth from LS _____

9 Reported Open Interval from LS **Top= ; Bottom=** _____

10 Reported water column length (Circle Datum LS or MP) _____ [Depth to water - depth of well]

11 Reported water casing length (Circle Datum LS or MP) _____ [Depth to water - depth to top of opening]

12 Reported water open interval length (Circle Datum LS or MP) **Top= ; Bottom=** [If line 12 > 0; same as line 9; otherwise, depth to top of opening - line 12]

13 Reported Well Depth from MP _____ [Same as line 8 if LS datum=MP]

14 Reported Open Interval from MP **Top= ; Bottom =** _____ [Same as line 9 if LS datum=MP]

15 Reported water column interval from MP **Top= ; Bottom =** _____ [Entire well]

16 Reported water casing interval from MP **Top= ; Bottom =** _____ [Casing only]

17 Reported water open interval from MP **Top= ; Bottom =** _____ [Open interval only]

18 Correction factor based on well sounding _____ [Sounding depth (line 4)-reported depth (line 13)]

19 Corrected Well Depth (MP) from sounding _____ [Adjusted by line 18]
(If sounding depth = reported depth from MP then no correction)

20 Corrected Open Interval (MP) from Sounding **Top = ; Bottom =** _____ [Adjusted by line 18]
(If sounding depth = reported depth from MP then no correction)

21 Corrected water well column interval (MP) **Top = ; Bottom =** _____ [Adjusted by line 18]

22 Corrected water well casing interval (MP) **Top = ; Bottom =** _____ [Adjusted by line 18]

23 Corrected water well open interval (MP) **Top = ; Bottom =** _____ [Adjusted by line 18]

24 Range of Passive Sampler Deployment from (MP) From: _____ To: _____

25 Number and depths of samplers from MP to midpoint of sampler: # _____ of samplers

Depths:

Other Notes on Deployment Depths:

Passive Sampler Deployment Field Sheet-page 2 Well_____

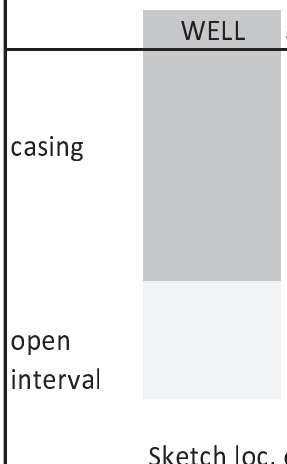
Type of sampler _____ [Circle types: PDB,NSPS,RPP,RCDM, ETC.]
Length of sampler _____ ; _____ ; _____ [Units]
Diameter of sampler _____ ; _____ ; _____ [Units]
Mouth/opening diameter for NS sampler _____ [Units]
Membrane material and size of pore _____ ; _____ [Pore Units]
Medium Type _____ [D.I. water, other]
Medium Blank Sample Date _____ Source of blank _____
Sampler housing _____ [eg. polyethene mil type, mesh type]
Deployment Start Time: _____ **Deployment End Time:** _____
Number of Samplers Deployed and Types _____
Suspension information _____ [eg. line, weight, material]
Line length _____ Add on length of weight _____ [Feet,meters,other]

Units of Measurement below if not noted [Circle: M-meters; Ft-feet; other_____]

Sampler spacing distance (sampler midpoint) _____ MP (top of inner pipe, bottom depth, other)

s#1	**First Deepest Sampler (ID), depth relative to MP (midpoint)**	Dups: y or n
s#2	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#3	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#4	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#5	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#6	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#7	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#8	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s#9	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s10	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s11	Next Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n
s12	Last Sampler (I.D.), depth relative to MP (midpoint-midpoint)	Dups: y or n

Duplication position relative to sampler: _____ (+ means deeper than sample)



Comments:

Notes/Attachments-Page 3 Deployment

Well I.D. _____

Additional notes:

Picture

Passive Sampler Recovery Field Sheet-page 1

Well ____________________

Location ________________________________ Date ____________

Local well name ____________________ USGS SID# ____________________

Weather conditions ____________________ Temperature (degrees C or F) ________

Measurement point (MP) ____________________ [eg. TOP OF PIPE, ETC.]

Well construction material ____________________ [EG. PVC, Steel]

Well Condition ________ [good or tampered] Well diameter ________ [Units]

Units of Measurement below if not noted [Circle: M-meters; Ft-feet; other_______]

MP Distance Relative to Land Surface ____________________

Pre DTW from MP ____________________

Date and Time of DTW ____________________

Bottle or sampler type ____________________ [Poly bottle size, RPPM etc]

Analytical consitiuent and method ____________________

Retrieval start time ____________________ (Circle, all that applies)

s#	**Top Sampler I.D./condition**	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Next Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n
s#	Bottom Sampler I.D./condition	/	[Good, poor, any leakage, Staining, Fe, Mn, etc.]	Dups: y or n

Retrieval end time ________ Post DTW from MP:

Notes on filling of bottles:

WELL Stickup

casing

Fm

open interval

Sketch loc. of samplers and I.D.

Comments:

Notes/Attachments-Page 2 Recovery

Well I.D. _____

Fill and Bottle notes: _____

s#	Top Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Next Sampler I.D./condition	/	Time:
s#	Bottom Sampler I.D./condition	/	Time:

Additional notes:

Picture

Comparison Tests Notes-Page 3 Recovery

Well I.D. ______________________

Additional Type of comparison____(Bailer, purge)

Date and time _____________________ DTW (FT) FROM MP ______________________

Depth of collection from MP (FT) ____________________ MP ____________________

Samples collected ____

Purge information:

Pump Type: Pump Placement (FT) from MP

san	Pump Time	/Ref time	Rate (m3/h	Rate (LPM)	SC	T	PH	DO	FG
					umhos/cm	deg-c		MG/L	fluro units

Comparison Tests Notes-Page 4 Recovery

Well I.D. ______________________

Additional Type of comparison____(Bailer, purge)

Date and time _____________________ DTW (FT) FROM MP ____________________

Depth of collection from MP (FT) ____________________ MP ____________________

Samples collected ____

Purge information:

Pump Type: Pump Placement (FT) from MP

san	Pump Time	/Ref time	Rate (m3/h	Rate (LPM)	SC	T	PH	DO	FG
					umhos/cm	deg-c		MG/L	fluro units

Appendix C. Well Label for Deployed Passive Samplers

CAUTION!

Do not disturb

Passive sampler installed in well

Please close cover carefully

Direct questions to:

Agency Name

Contact Name_____; ph_____

For more information about this report, contact:
Director, New England Water Science Center
U.S. Geological Survey
10 Bearfoot Road
Northborough, MA 01532
dc_nweng@usgs.gov
or visit our website at
https://www.usgs.gov/centers/new-england-water

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