

Equilibration times, compound selectivity, and stability of diffusion samplers for collection of ground-water VOC concentrations

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Abstract

Vapor-filled polyethylene diffusion samplers (typically used to locate discharge zones of volatile organic compound contaminated ground water beneath streams and lakes) and water-filled polyethylene diffusion bag samplers (typically used to obtain volatile organic compound concentrations in ground-water at wells) were tested to determine compound selectivity, equilibration times, and sample stability. The aqueous concentrations of several volatile organic compounds obtained from within water-filled diffusion samplers closely matched concentrations in ambient water outside the samplers. An exception was methyl-*tert*-butyl ether, which was detectable, but not reliably quantifiable using the diffusion samplers. The samplers equilibrated to a variety of volatile organic compounds within 24 h for vapor-filled passive diffusion vial samplers and within 48 h for water-filled passive diffusion bag samplers. Under field conditions, however, a longer equilibration time may be required to account for environmental disturbances caused by sampler deployment. An equilibrium period for both vapor- and water-filled diffusion samplers of approximately 2 weeks probably is adequate for most investigations in sandy formations. Longer times may be required for diffusion-sampler equilibration in poorly permeable sediment. The vapor-filled samplers should be capped and water from the diffusion bag samplers should be transferred to sampling vials immediately upon recovery to avoid volatilization losses of the gasses. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion samplers; Groundwater; VOCs

1. Introduction

It often is desirable to minimize well purging prior to collecting a water sample because removing three to five casing volumes of water prior to sampling may not always be necessary and may produce undesirable ef-

fects (Kearl et al., 1992; Powell and Puls, 1993; Barcelona et al., 1994). Moreover, disposal of purged water is subject to regulatory constraints. A variety of approaches are available to obtain ground-water samples with minimal disturbance of the borehole water column. These include inflatable packers (Oliveros et al., 1988; Kaminsky and Wylie, 1995), low-stress purging (Barcelona et al., 1994; Shanklin et al., 1995), multiport sock samplers (Schirmer et al., 1995; Jones et al., 1999), the DMLS passive sampler (Kaplan et al.,

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1991), and multi-level dialysis cells (Ronen et al., 1987). A variety of dialysis samplers also have been used widely to obtain pore-water concentrations, primarily of inorganic species (Hesslein, 1976; Mayer, 1976; Bottomly and Bayley, 1984; Carignan, 1984). Other devices include ping-pong balls and latex tubing, which have been used as diffusion samplers to measure helium in the subsurface (Dyck and Da Silva, 1981; Gascoyne and Sheppard, 1993).

This paper focuses on two types of low-density polyethylene (LDPE) diffusion samplers. One sampler consists of an air filled glass vial enclosed in two layers of polyethylene and is referred to in this paper as a passive vapor-diffusion (PVD) sampler (Fig. 1). The other sampler consists of a water-filled polyethylene bag sealed at both ends and is referred to in this paper as a passive diffusion bag (PDB) sampler (Fig. 2). The PVD samplers have been shown to be effective for delineating VOC-contaminated ground-water discharge zones beneath surface-water bodies (Vroblesky and Robertson, 1996; Vroblesky et al., 1996, 1999; Savoie et al., 2000). The PDB samplers have been shown to be an inexpensive alternative method for sampling VOCs in wells (Vroblesky and Hyde, 1997; Gefell et al., 1999; Parsons Engineering Science, Inc., 1999; McClellan AFB Environmental Directorate, 2000). The rationale behind the use of PDB samplers is based on investigations suggesting that the water in the screened portion of the well bore sometimes can be representative of aquifer water prior to purging (Robin and Gillham, 1987; Kearl et al., 1992; Powell and Puls, 1993). A modified version of the PDB sampler also has been used to obtain aqueous concentrations of VOCs in

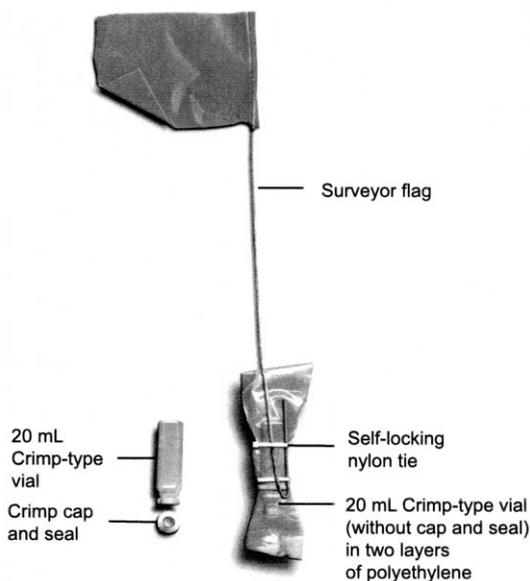


Fig. 1. Typical air-filled passive vapor diffusion (PVD) sampler.

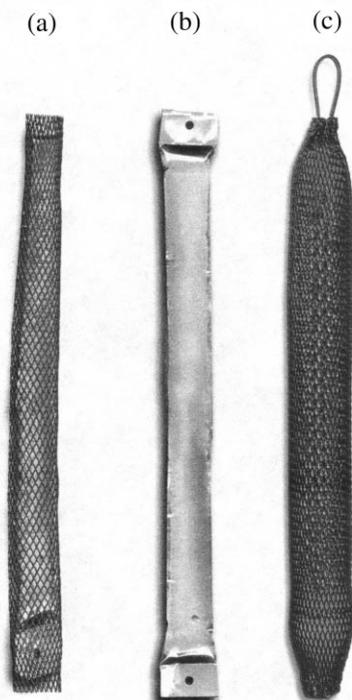


Fig. 2. Typical water-filled passive diffusion bags (PDB) used in wells, including (a) diffusion bag with polyethylene mesh, (b) diffusion bag without mesh, and (c) bag and mesh attached to bailer bottom.

ground water at the ground-water/surface-water interface (Vroblesky et al., 1999; Savoie et al., 2000).

Because of the increased interest in the use of polyethylene-based diffusion samplers for collecting ground-water samples, questions have arisen regarding the equilibration times and the compound selectivity of the polyethylene membrane. The purpose of this paper is to present laboratory and field data on issues involving the use of PVD and PDB samplers. These issues include the time required for sampler equilibration, the types of volatile compounds that readily diffuse through the membrane, and the amount of time that the samplers can be stored prior to sealing or transferring the water to sample vials.

2. Methods

Both field and laboratory methods were used in this investigation to examine PVD samplers, and laboratory methods were used to examine PDB samplers. Abbreviations for several of the tested compounds are shown in Table 1.

The PVD sampler consisted of a 20-ml serum vial

Table 1
Abbreviations of compounds used in this investigation

BDCM	Bromodichloromethane
BF	Bromoform
BM	Bromomethane
CT	Carbon tetrachloride
CB	Chlorobenzene
2-CVA	2-Chlorovinyl ether
CF	Chloroform
CM	Chloromethane
DBCM	Dibromochloromethane
EDB	1,2-Dibromoethane
DBM	Dibromomethane
1,2-DCB	1,2-Dichlorobenzene
1,3-DCB	1,3-Dichlorobenzene
1,4-DCB	1,4-Dichlorobenzene
DCDFM	Dichlorodifluoromethane
1,1-DCA	1,1-Dichloroethane
1,2-DCA	1,2-Dichloroethane
1,1-DCE	1,1-Dichloroethene
<i>c</i> DCE	<i>cis</i> -1,2-Dichloroethene
<i>t</i> DCE	<i>trans</i> -1,2-Dichloroethene
1,2-DCPA	1,2-Dichloropropane
<i>c</i> DCPE	<i>cis</i> -1,3-Dichloropropene
<i>t</i> DCPE	<i>trans</i> -1,3-Dichloropropene
EB	Ethyl benzene
MC	Methylene chloride
MI	Methyl iodide
MTBE	Methyl- <i>tert</i> -butyl ether
Napht	Naphthalene
PCA	1,1,2,2-Tetrachloroethane
PCE	Tetrachloroethene
1,1,1-TCA	1,1,1-Trichloroethane
1,1,2-TCA	1,1,2-Trichloroethane
TCE	Trichloroethene
TCFM	Trichlorofluoromethene
1,2,3-TCPA	1,2,3-Trichloropropane
VC	Vinyl chloride

enclosed in a heat-sealed, low-density polyethylene (LDPE) lay-flat tube (Fig. 1). The tube was 4 mm in thickness and 2 inches in width when flat, or approximately 1.5 inches in diameter when filled. The vial was arranged such that a single layer of polyethylene was held tightly in place over the vial opening. The LDPE tubing was secured to the vial by a plastic self-locking tie. The assembly then was placed inside a second LDPE tube and heat sealed, trapping a minimum of air. Samplers used in the field were attached by means of plastic self-locking ties to a surveyor flag to mark the sampling site and to facilitate sampler recovery.

Upon recovery of the PVD samplers, the outer LDPE bag was cut open, leaving the inner LPDE bag intact. A vial cap with a Teflon¹-coated stopper then was crimped

onto the vial and inner bag. Gas samples were obtained from the PVD samplers by inserting a syringe needle tip through the Teflon-coated stopper beneath the vial cap and using a gas-tight syringe to extract 100 μ l of vapor. Analysis of the gas was performed by photo-ionization detection using a Photovac 10SPlus gas chromatograph.

The PDB samplers tested under laboratory conditions consisted of a single layer of the 4-mm LDPE lay-flat tubing heat-sealed at both ends and containing approximately 50–70 ml of deionized water. The equilibration times determined from the laboratory tests are valid for PDB samplers used in the field (Fig. 2), which typically contain approximately 300 ml of water, because the sampler diameters are the same for each application.

PDB samplers were recovered by cutting the samplers open and pipetting the contents of the samplers into 40-ml volatile organic analysis (VOA) vials. The water in the vials was acidified with hydrochloric acid and capped leaving no headspace. All sample vials were stored on ice until analyzed for VOCs by a commercial laboratory using US Environmental Protection Agency (EPA) Method 8260b (US Environmental Protection Agency, 1999).

2.1. Equilibration time

To determine the equilibration times of PVD samplers, the samplers were added in groups of three to 480-ml test jars containing water spiked with various VOCs and maintained at approximately 21°C. The mixture added to the jars for PVD samplers contained benzene, *cis*-1,2-dichloroethene (*c*DCE), tetrachloroethene (PCE), trichloroethene (TCE), toluene, and 1,2-dibromoethane (EDB). The PVD samplers were recovered at various times over the course of approximately 60 h. Each of the three recovered vials was analyzed to produce an average and standard deviation of concentration for the time point. Water samples from selected test jars were analyzed for VOC concentrations.

To determine the equilibration time of PVD samplers under field conditions, samplers were buried beneath streambed sediments by using a hand auger or a shovel at four sites in South Carolina where VOC-contaminated ground-water discharges to surface water. Site 1 was in highly permeable Coastal Plain sands at the Savannah River Site, Aiken, South Carolina. The remaining three sites were in silty to sandy parts of the Piedmont. Site 2 was down gradient from an area where approximately 3000 drums of various wastes had been discovered and removed. Site 3 was down gradient from a dry-cleaning company where chlorinated solvents had discharged to ground water, and Site 4 was down gradient from an apparel manufacturer where

¹The use of tradenames does not imply endorsement by the US Geological Survey.

PCE used for fabric cleaning leaked to the aquifer. At each site, several PVD samplers were buried in streambed sediment in an area of approximately 6 square foot. At various time intervals, two or three PVD samplers were removed and capped from each site. Recovery of PVD samplers continued for a few days. The samplers were analyzed in duplicate or triplicate by using photoionization gas chromatography.

Vertical hydraulic gradients were measured at the four sites to aid in understanding water movement through the streambed sediments. To measure vertical head gradients at each site, 1-inch-diameter steel pipes were driven into the streambed to depths of 1.5 and 3 foot. A bolt loosely seated into the downward end of the pipes prevented sediment from moving up into the pipe during emplacement. The bolt then was driven out of the pipe to allow water to enter. After a few hours of equilibration, the water levels in the pipes were measured relative to the stream stage outside the pipes, which provided an approximate measurement of the upward hydraulic gradient.

The experiment to determine PDB sampler equilibration time at 21°C for benzene, *c*DCE, PCE, TCE, toluene, EDB, methyl-*tert*-butyl ether (MTBE), naphthalene (Napht), and total xylenes was done by adding three PDB samplers to 480-ml test jars containing between 100 and 1200 µg/l of the target compounds. The diffusion samplers were recovered from the test jars at various times over a 145-h period. At each recovery time, water from the diffusion samplers was transferred to 40-ml VOC vials to provide a single sample for laboratory analysis. Water from the test jar was collected immediately prior to collecting the water from the diffusion-sampler. Both the water from the test jar and the diffusion sampler were sent to the same contract laboratory for analysis.

2.2. Compound selectivity

Additional testing was done to determine the selectivity of PDB samplers to 40 VOCs. In the first laboratory experiment, the PDB samplers were tested to determine their selectivity to a mixture of 37 VOCs (Table 2). Concentrations of the target compounds ranged from approximately 20 to 280 µg/l. The selectivity test consisted of placing three PDB samplers in each of several 3.8-l glass jars containing a mixture of the target compounds in water. Some of the diffusion samplers were allowed to equilibrate at 8°C and others at 21°C. The samplers were recovered at various time intervals ranging between 14 and 21 days. Water from the test jars and the diffusion samplers was collected and analyzed by EPA Method 8260b (US Environmental Protection Agency, 1999).

In a second test, the selectivity and equilibration of PDB samplers to higher VOC concentrations was ex-

Table 2
Volatile organic compounds for first selectivity test

Benzene	1,3-DCB	MI
BDCM	1,4-DCB	Napht
BF	DCDFM	PCA
BM	1,1-DCA	Toluene
CT	1,2-DCA	1,1,1-TCA
CB	1,1-DCE	1,1,2-TCA
CE	<i>c</i> DCE	TCE
CF	<i>t</i> DCE	TCFM
CM	1,2-DCPA	1,2,3-TCPA
DBCM	<i>c</i> DCPE	VC
1,2-DBA	<i>t</i> DCPE	Total xylenes
DBM	EB	
1,2-DCB	MC	

amined at 8°C. This test consisted of a slightly different suite of 30 compounds (Table 3). Three samplers each were placed in 1-l jars containing a mixed solution of the 30 VOCs at concentrations ranging from approximately 100 to 2200 µg/l. After equilibration times of 5, 7 and 14 days, a jar was opened, and the enclosed samplers were recovered. Water from both the diffusion sampler and the test jar were collected for analysis at each recovery time. A similar test was conducted using only MTBE, in which PDB samplers were recovered at various times over a period of 145 h.

2.3. Sample stability

Tests also were conducted to determine the stability of VOC concentrations within the samplers between the time of sampler recovery and sealing of the sampler vials. To test the stability of gases in PVD samplers, the samplers were allowed to equilibrate for 2 weeks in water having mixed VOCs. The samplers then were removed from the water and allowed to stand at 21°C for various time intervals over a period of hours prior to capping. The samplers then were analyzed by photo-ionization gas chromatography.

The sample-stability test for PDB samplers consisted of allowing the water-filled samplers to equilibrate for

Table 3
Volatile organic compounds for second selectivity test

Benzene	1,2-DCB	MC
BDCM	1,3-DCB	Napht
BF	1,4-DCB	PCA
CT	1,1-DCA	PCE
CB	1,2-DCA	Toluene
2-CVE	1,1-DCE	1,1,1-TCA
CF	<i>c</i> DCE	1,1,2-TCA
DBCM	<i>t</i> DCE	TCE
EDB	1,2-DCPA	1,2,3-TCPA
DBM	EB	Total xylenes

26 days in an aqueous mixture of target compounds having concentrations of approximately 200 $\mu\text{g}/\text{l}$. The samplers were simultaneously removed from the solution and allowed to stand in the open air at 21°C for various lengths of time prior to transferring the water to VOA vials. Recovered water was analyzed by a contract laboratory using EPA Method 8260b.

3. Results and discussion

The data from this investigation provide information on the equilibration times of PVD and PDB samplers, as well as the sensitivity of PDB samplers to a variety of VOCs. In addition, the data provide information regarding the stability of VOC concentrations in the diffusion samplers between the time of sampler recovery and the time that the PVD samplers are sealed and the PDB water is transferred to VOA vials. Finally, we examine the relationship between TCE concentrations obtained by using PVD samplers and concentrations obtained by using PDB samplers.

3.1. Equilibration time

Equilibration time for diffusion samplers under field conditions depends both on the time required by the diffusion sampler to equilibrate with ambient water and the time required for the environment disturbed by deployment of the sampler to return to ambient conditions. Laboratory tests provide information regarding the time required by the diffusion sampler to equilibrate with ambient water. Field data can be used to estimate the amount of time required for the contaminant concentrations in the well or sediment to restabilize following disturbances caused by sampler deployment.

Laboratory tests showed that both PVD and PDB samplers rapidly equilibrate to concentrations of VOCs in ambient water. In PVD samplers at 21°C, the time required for concentrations of the *c*DCE, benzene, TCE, toluene, EDB, and PCE to stabilize was approximately 24 h (Fig. 3). In PDB samplers at 21°C, concentrations for eight of the nine tested VOCs approximately matched the concentrations in the experiment test jar water after equilibrating for 48 h. A comparison of concentrations for five of the tested compounds (EDB, benzene, TCE, toluene, and PCE) in the PDB samplers is shown in Fig. 4. Naphth, *c*DCE, and total xylenes showed similar results but were not included in Fig. 4 for simplicity. The PDB-sampler MTBE concentrations did not match ambient water MTBE concentrations and will be discussed later in this paper. Recent tests by the General Electric Company also showed approximate equilibration of TCE and PCE concentra-

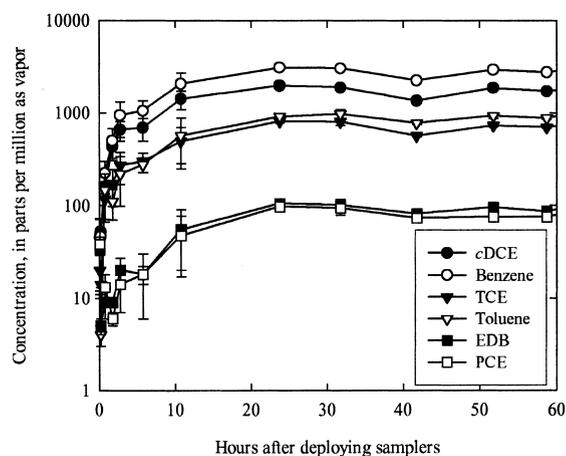


Fig. 3. Changes in concentrations of volatile organic compounds in vapor diffusion samplers following deployment of the samplers in water-filled jars under laboratory conditions. Error bars represent the standard deviation of duplicate or triplicate samples.

tions in PDB samplers by 48 h; however, their data suggest that some chlorinated compounds [1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,2-DCA), 1,1-dichloroethane (1,1-DCA), and vinyl chloride (VC)] may require between 96 and 168 h to equilibrate (T.M. Sivavec and S.S. Baghel, 2000, General Electric Company, written communication).

Field tests of PVD sampler equilibration times in various South Carolina streams showed differences in times required for the samplers to stabilize. The samplers stabilized within 12–24 h in a Coastal Plain stream where the aquifer sediments were sand with a relatively large hydraulic conductivity [21–65 foot/day (Nichols, 1993; Nichols et al., 1995; Phifer et al., 1995)] and where there was a strong upward hydraulic gradient (0.3 foot/foot; Fig. 5a). However, in the less permeable silty saprolite of a Piedmont stream, where the upward hydraulic gradient beneath the stream was only 0.02 foot/foot, the samplers had not stabilized after 65 h (Fig. 5b). The samplers in other environments stabilized at intermediate times (Fig. 5c,d). An explanation for the data is that the time required for the streambed sediment or the well water to recover from the disturbance caused by sampler installation varies as a function of the rate of water movement through the sediment. Thus, streambed sediments will recover more quickly in areas where the aquifer has a relatively large hydraulic conductivity and upward hydraulic gradient than in areas where the aquifer has a relatively low hydraulic conductivity and hydraulic gradient. However, an important concept to remember is that a typical use of PVD samplers in surface-water bottom sediment is to locate zones of discharging ground water contaminated with VOCs. For this use,

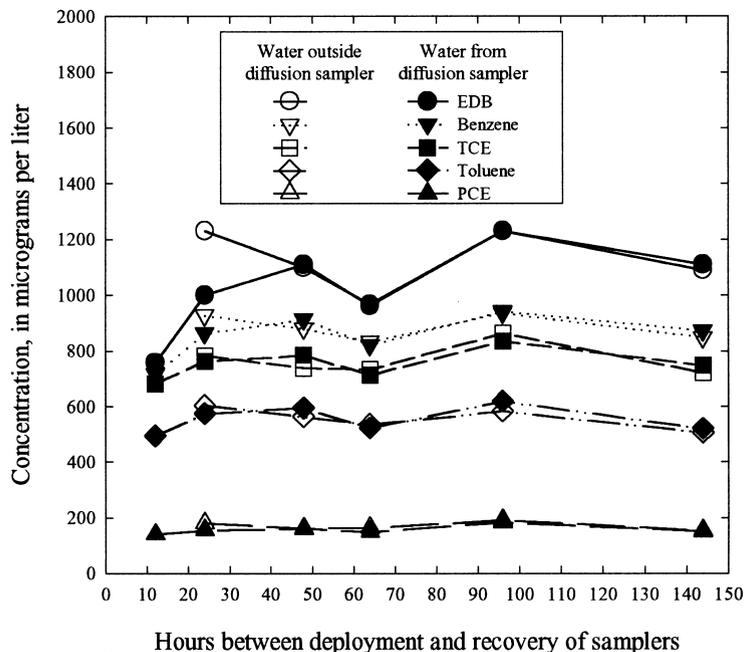


Fig. 4. Comparison of volatile organic compound concentrations in passive diffusion bag samplers to concentrations in water outside the passive diffusion bag samplers following sampler deployment in laboratory test jars.

merely the presence or absence of target VOCs in samplers can provide practical information. At all the tested locations, the PVD samplers achieved measurable concentrations of the target VOCs within 12 h or less (Fig. 5).

Further insight into equilibration times for PVD samplers in saturated sediment can be obtained by reviewing the literature regarding field tests of various types of dialysis samplers. Typically, these samplers differ from PVD samplers in that they contain water instead of vapor, typically are used to sample inorganic rather than organic constituents, and some utilize a different membrane type. However, the amount of sub-surface disturbance caused by sampler installation is similar for both types of samplers. In previous investigations, equilibration times of various dialysis samplers used to determine porewater concentrations of inorganic constituents include 3–20 days (Carignan, 1984), 100 h in unconsolidated clay and silt (Mayer, 1976), and 10 days using a 0.45- μm polysulfone membrane (Bottomly and Bayley, 1984). A variety of studies reported that 2 weeks or less was adequate for equilibration of these types of samplers in saturated sediment (Hesslein, 1976; Carignan et al., 1985; Davis and Galloway, 1993; Bertolin et al., 1995). Based on data presented in this and previous investigations, an equilibration time of 2 weeks in saturated sediment probably would be adequate for most investigations using PVD samplers in highly to moderately permeable sediments, such as sands or loose silts. Longer times may be required for

equilibration in low-permeability sediments, such as clay or tight silts.

The time required for water in a well to equilibrate after a disturbance may be approximated by considering results of borehole-dilution studies used to estimate aquifer hydraulic conductivity. In borehole-dilution studies, a tracer is injected and mixed in an isolated section of well screen. Tracer concentrations and time then are measured until background levels are reached. Tracers typically include radioactive compounds (Halevy et al., 1967; Drost et al., 1968); fluoride salt (Grisak et al., 1977); chloride salt (Belanger, 1984); and de-ionized water (Pedler et al., 1992). The rate of tracer dilution is proportional to the ground-water velocity and is largely dependent on the hydraulic conductivity of the tested interval. In general, tracer dilution approximately follows a semi-logarithmic decay curve. According to measurements by Grisak et al. (1977), 90% of an injected tracer was diluted within 20 min in a well screen open to a gravel aquifer, and within 70 min in a well screen open to a sand aquifer. Aquifers comprising poorly permeable sediments may require 100–1000 h to recover 90% of the pre-disturbance conditions. A variety of investigations using PDB samplers in wells screened in overburden, bedrock, and sand aquifers have reported adequate equilibration within 14–17 days (O'Brien & Gere Engineers, Inc., 1997a,b; Blasland, Bouck, & Lee, Inc., 1998; Vroblesky et al., 1999). Therefore, the laboratory and field data and results of borehole dilution studies imply that

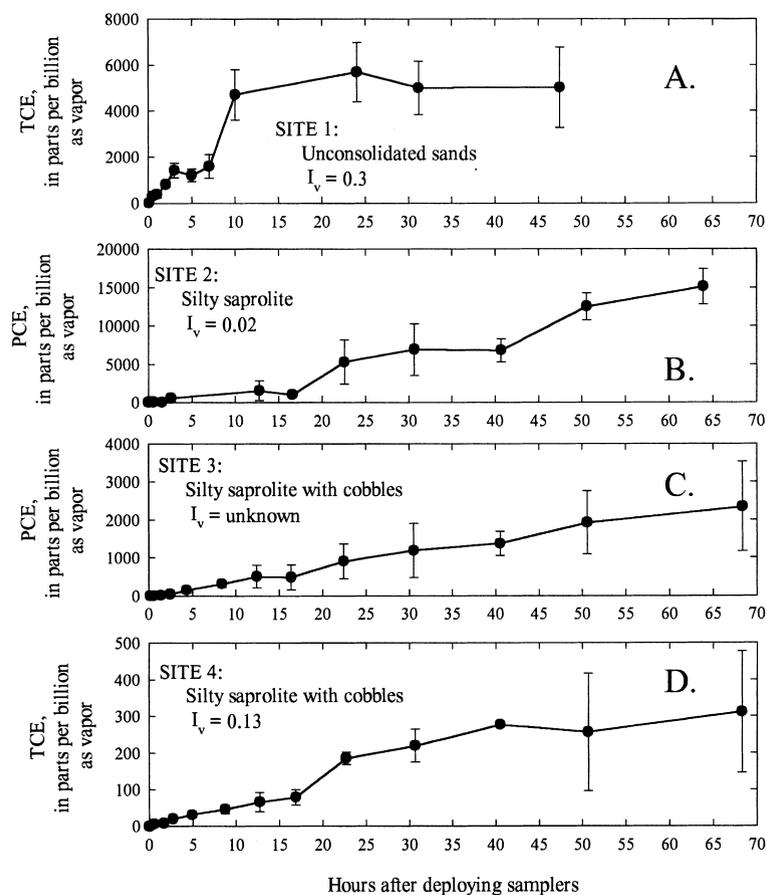


Fig. 5. Changes in trichloroethene (TCE) and tetrachloroethene (PCE) concentrations in vapor diffusion samplers from contaminated ground-water discharge zones of various sediment types and vertical hydraulic gradients (I_v). Error bars represent the standard deviation of duplicate or triplicate samples.

approximately 2 weeks of equilibration should be adequate for PDB samplers in most wells screened in sandy formations. As with the PVD samplers, longer times may be required for equilibration in low permeability sediments.

An additional factor affecting the equilibration time of diffusion samplers is the water temperature. Theoretically, the equilibration time should be longer in cold environments than in warm environments. A previous investigation using dialysis samplers for major ions and nutrients showed that adequate equilibration times ranged from approximately 20 days in a cold (4–6°C) environment and approximately 15 days in a warm (20–25°C) environment (Carignan, 1984). Thus, polyethylene diffusion samplers also probably have a slightly longer equilibration time under cold conditions compared to warm conditions; however, such differences were not noted in the time frame of these experiments. Moreover, the data showed that even at a temperature of 8°C, there was less than 10% difference between concentrations in water from the diffusion

samplers and in water from outside the diffusion samplers after 7 days of equilibration in an aqueous mixture of VOCs [e.g. benzene, carbon tetrachloride (CT), chlorobenzene (CB), EDB, dichlorobenzene (DCB) isomers, ethyl benzene (EB), PCE, toluene, TCE, and others] (Fig. 6a). The average difference in VOC concentrations between ambient water and water within the PDB samplers was 11% (standard deviation of 12 $\mu\text{g}/\text{l}$) after 7 days and 3% (standard deviation of 4 $\mu\text{g}/\text{l}$) after 14 days (Fig. 6). Thus, differences in equilibration time due to temperature effects seem to be small for many VOCs after 7 days and for most tested compounds by 14 days.

3.2. Compound selectivity

Laboratory tests to determine the types of compounds for which PDB samplers are suitable were done by deploying PDB samplers in aqueous solutions of mixed VOCs across a broad range of concentrations.

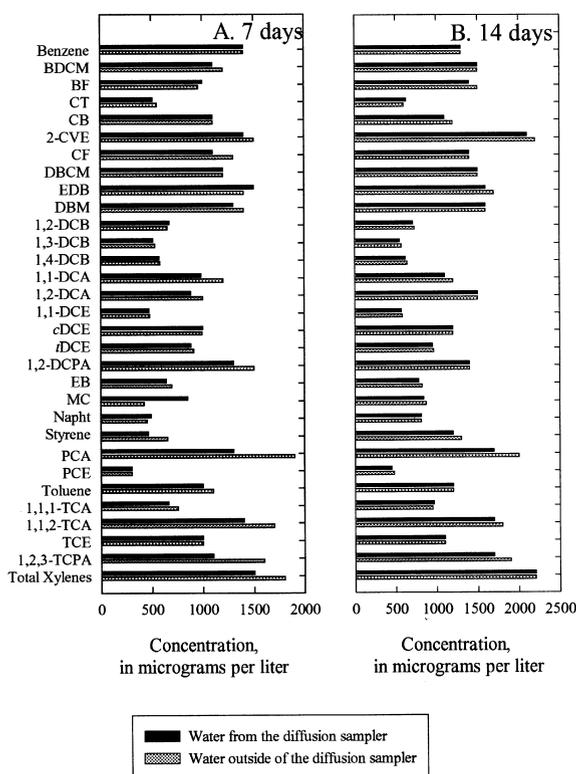


Fig. 6. Laboratory comparison of volatile organic compound concentrations in water from passive diffusion bag samplers to water outside the passive diffusion bag samplers at 8°C after equilibration times of (a) 7 days and (b) 14 days.

The PDB samplers produced VOC concentrations similar to VOC concentrations in ambient water for most tested compounds (Table 4). The Wilcoxon test statistic P (traditionally indicating a significant difference when $P < 0.05$) showed no statistical difference between non-zero concentrations in diffusion samplers and in ambient water for all but five of the 40 tested parameters. Three of the compounds [*trans*-1,3-dichloropropene (*t*DCPE), EB, and 1,1,2-trichloroethane (1,1,2-TCA)] and one mixture of compounds (total xylenes) showed average concentration differences of 11% or less between the diffusion sampler water and the ambient water (Table 4). When the poorest single match of the nine sample points for *t*DCPE and of the 15 sample points for EB were removed from the data set, the average differences between the concentrations in the diffusion sampler water and the ambient water were only 3% and 5%, respectively. Similarly, a comparison of several compounds of environmental interest shows that the diffusion samplers produce approximately representative concentrations even at concentrations between 5 and 50 µg/l (Fig. 7).

Although other tested compounds showed greater than 10% differences between concentrations in PDB sampler water and in ambient water, the concentrations of all but one compound (MTBE) were not statistically different enough to exclude the possibility that the differences were due to random variations in the data ($P > 0.05$). Of these compounds, four [bromomethane (BM); 1,2-DCA, *t*DCE, and methylene chloride (MC)] had average concentration differences ranging from 11 to 15%, and two (1,1-DCA and styrene) showed average concentrations differences of 17 and 22%, respectively (Table 4). When the poorest single match of the five sample points for styrene was removed from the data set, the average difference reduced to 13%. Use of diffusion samplers for these compounds should be limited to studies where the cited percent differences are within tolerance for the site-specific sampling goals.

Although PDB samplers seem to be capable of detecting the presence of MTBE in relatively high concentrations, the samplers are not reliable in quantifying concentrations. MTBE concentrations in diffusion sampler water were an average of 76% lower than in ambient water ($P = 0.001$, Table 4). A laboratory sampling of diffusion samplers over time showed that the MTBE concentration in the PDB sampler gradually approached ambient water, but was substantially below the concentration in the test jar water after 144 h of equilibration. A separate test showed that after 32 days of equilibration, the MTBE concentration in the diffusion sampler was only 64% of the concentration in the test jar water. The reason for the lack of suitability of diffusion samplers for MTBE was not determined, but may be related to the comparatively high solubility of MTBE (54 000 mg/l) relative to all of the other tested compounds (1.1–20 000 mg/l). It should be noted, however, that a field test of PVD samplers beneath a drainage ditch in an area of known MTBE discharge in Beaufort, South Carolina, showed that the samplers accumulated detectable concentrations of MTBE, indicating that they could be used to locate the MTBE discharge zone.

3.3. Sampler stability

A test to determine the amount of time that PDB samplers could be stored after recovery and prior to transferring the enclosed water to VOC vials showed no substantial loss in PCE, TCE, benzene, and toluene concentrations over the first 15 min following sampler recovery. Thereafter, the amount of VOC loss seemed to be compound dependent. PCE and benzene showed no substantial vapor loss over the first 60 min following sampler recovery; however, TCE and toluene concentrations in the samplers declined by approximately 20%

Table 4

Statistical comparisons of compound concentrations in water from passive diffusion bag samplers and from outside passive diffusion bag samplers in mixed solutions under laboratory conditions^a

Parameter	Percent difference between concentrations in water from diffusion samplers and from outside diffusion samplers				Concentration in water outside diffusion samplers in $\mu\text{g}/\text{l}$				Wilcoxon signed rank test <i>P</i> -statistic	Number of samples
	Max	Min	Avg	S.D.	Avg	Max	Min	S.D.		
Parameters with average percent differences of 10 or less										
Benzene	7	35	0	9	1400	16	523	529	0.974	24
BMDCM	5	16	0	5	1500	17	457	580	0.542	14
BF	6	16	1	4	1500	14	413	524	0.762	15
CB	2	9	0	3	1200	10	362	505	0.365	14
CT	7	42	0	10	600	8	190	232	0.67	15
CA	7	18	1	5	891	11	206	258	0.898	11
CF	9	41	0	13	1400	15	371	537	0.121	18
CM	5	18	0	6	420	14	111	138	0.578	7
2-CVE	6	7	4	1	2200	1500	1850	404	0.375	4
DBCM	5	18	0	5	1500	16	450	568	0.839	15
DBM	4	19	0	5	1700	16	481	643	0.82	13
1,2-DCB	2	5	0	1	730	6	213	294	0.463	15
1,3-DCB	2	4	0	1	570	6	226	248	0.193	11
1,4-DCB	2	4	0	1	640	5	184	258	0.296	15
DCDFM	4	8	3	2	176	30	56	59	0.844	6
1,1-DCE	6	18	1	5	590	15	215	210	0.934	15
<i>c</i> -DCE	7	50	0	11	1360	12	509	505	0.133	24
1,2-DCPA	6	28	0	8	1500	16	440	551	0.735	15
<i>c</i> -DCPE	7	44	1	14	182	11	64	60	0.164	9
EDB	7	49	0	11	1700	15	724	633	0.808	22
<i>t</i> -DCPE	7	40	0	13	213	11	68	69	0.008	9
EB	8	41	2	9	820	5	227	328	0.015	15
Napht	8	50	0	11	810	6	206	223	0.729	22
Toluene	7	29	0	7	1200	9	387	422	0.127	24
1,1,1-TCA	7	34	0	10	950	10	295	368	0.588	14
1,1,2-TCA	8	41	0	11	1900	17	581	748	0.015	15
TCE	5	25	0	6	1100	13	407	404	0.414	24
TCFM	4	17	0	5	280	10	78	81	0.652	10
1,2,3-TCPA	10	53	0	15	1900	20	589	745	0.078	15
PCA	10	51	0	14	2000	5	607	820	0.091	16
PCE	7	35	0	9	480	42	184	139	0.127	17
VC	4	15	0	4	362	10	81	102	0.083	11
Parameters with average percent differences of 11–15										
BM	15	30	3	9	405	13	111	122	0.57	9
1,2-DCA	11	40	0	15	1500	16	420	548	0.903	15
<i>t</i> -DCE	11	53	0	13	960	17	291	333	0.463	15
MC	13	51	0	14	870	19	271	293	0.146	14
Total xylenes	11	30	0	8	2300	17	529	768	0.006	20
Parameters with average percent differences greater than 15										
1,1-DCA	17	61	1	16	1200	17	427	496	0.277	15
MTBE*	76	98	36	22	3400	33	1640	1186	0.001	13
Styrene	22	57	8	22	1300	113	773	485	0.313	5

^aAvg, average; max, maximum; min, minimum; S.D., standard deviation; $\mu\text{g}/\text{l}$, micrograms per liter; *, four of the tests were done using MTBE as the sole volatile organic compound in solution.

over the same time interval. The data suggest that the samplers are relatively stable over a period of several minutes; however, it is highly advisable that the samples be transferred to VOA vials immediately upon recovery.

Concentrations of benzene, TCE, and toluene in uncapped PVD samplers at 21°C showed no substantial decrease over 60 to 90 min between sampler recovery and applying a seal to the sampling vials. These data suggest that VOC concentrations within the uncapped

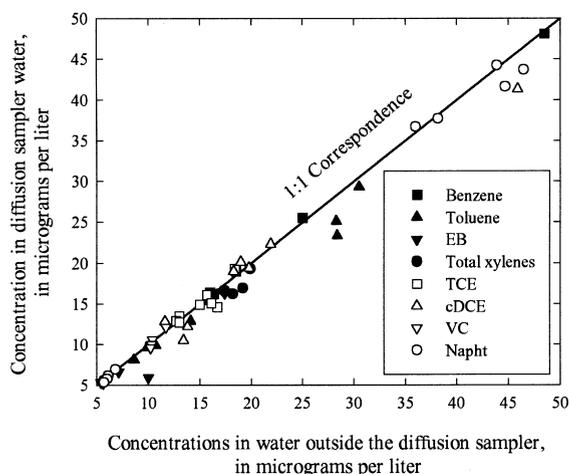


Fig. 7. Laboratory comparison of selected volatile organic compounds concentrations in water from passive diffusion bag samplers to water outside the passive diffusion bag samplers for values between 5 and 50 $\mu\text{g/l}$.

PVD samplers are relatively stable for at least 1 h at 21°C; however, results from the PDB tests indicate that the PVD samplers should be capped and sealed immediately upon recovery.

3.4. Comparison of VOCs in vapor and water samplers

A comparison of TCE concentrations shows a consistent relationship between concentrations obtained from PVD samplers and those from PDB samplers. Under laboratory conditions at 20°C and approximately 1 atm, the average concentration [ppb (vol/vol)] of TCE in the vapor samplers was approximately 86–88 times greater than the TCE concentration ($\mu\text{g/l}$) in solution. This is consistent with Henry's Law, which states that there is a linear relation between the partial pressure of a gas above a liquid and the mole fraction of the gas dissolved in the liquid. The equation is shown below:

$$H = \frac{C_g}{C_w}$$

where C_g and C_w are gaseous- and liquid-phase concentrations (mol/m^3), respectively, and H is the dimensionless Henry's constant. The ratio of TCE in the vapor samplers (mol/m^3) to TCE in the water samplers (mol/m^3) varied from 0.286 to 0.703 with an average value of 0.475 (standard deviation of 0.199 for nine samples). This ratio was similar to the value for H at 10°C (0.33) calculated as the average of eight experimental values summarized by Heron et al. (1998).

4. Summary and conclusions

Equilibration time for polyethylene diffusion samplers under field conditions depends both on the time required by the diffusion sampler to equilibrate with ambient water and the time required for the environmental disturbance caused by sampler deployment to return to ambient conditions. Laboratory testing showed that the time required for concentrations of *c*DCE, benzene, TCE, toluene, EDB, and PCE to equilibrate in the vapor-filled PVD samplers was approximately 24 h at 21°C. Laboratory tests also showed that concentrations of EDB, benzene, TCE, toluene, PCE, Napht, *c*DCE, and total xylenes equilibrated in water-filled PDB samplers within approximately 48 h at 21°C. Some chlorinated solvents may require longer equilibration times.

In addition to the time required for organic compounds to diffuse through the diffusion sampler membrane, a second factor influencing equilibration times under field conditions is the time required for streambed sediments or well water to recover from the disturbance caused by sampler installation. Field tests using PVD samplers beneath streams showed that the samplers had stabilized within 12–24 h in permeable sediments having relatively large upward hydraulic gradients, but had not stabilized after 65 h in poorly permeable sediments having relatively low upward hydraulic gradients. The field tests also indicated that if the purpose of this type of sampling was to locate zones of discharging ground water contaminated with VOCs, then concentrations of target VOCs sufficient for that purpose had accumulated in the samplers at all tested sites within 12 h or less. Based on data from this study and previous investigations using dialysis samplers, an equilibrium period of approximately 2 weeks is probably adequate for most investigations using diffusion samplers in highly to moderately permeable sediment, such as sand or loose silts. Longer times may be required for equilibration in low permeability sediment, such as clay or tight silt.

The time required for water in a well to equilibrate after a disturbance was approximated using data from borehole dilution studies: equilibration time seemed to range from approximately 20 min in gravelly sediments to 1000 h or more in poorly permeable sediments. As a result, wells screened in poorly permeable aquifers, such as very fine loamy sand, clays, or poorly permeable fractured rock, may require a substantial time to equilibrate. The laboratory and field data from previous investigations showing adequate equilibration within 14–17 days, and results of borehole dilution studies, imply that approximately 2 weeks of equilibration should be adequate for PDB samplers in most wells screened in sandy formations.

Laboratory tests comparing VOC concentrations in

water from diffusion samplers to water contacting the diffusion samplers show that the samplers can be used for a broad variety of VOCs. For most of the tested compounds, the concentrations in water from within the PDB sampler closely matched those concentrations in water from outside the PDB samplers (average difference < 10 µg/l). Although four compounds [BM; 1,2-DCA; *trans*-1,2-dichloroethene (*t*DCE), and MC] showed average concentration differences from 11 to 15%, these differences were not statistically significant. Three tested compounds (1,1-DCA; MTBE; and styrene) showed average concentration differences greater than 15%. The differences for two of these compounds (1,1-DCA and styrene) were not statistically significant. The third compound, MTBE, showed a poor match between the diffusion sampler water and the ambient water, indicating that the diffusion samplers may be useful for detecting high concentrations of MTBE, but not useful for quantifying MTBE concentrations.

A test to determine the amount of time that PDB samplers could be stored prior to transferring the enclosed water to VOC vials showed no substantial loss in PCE, TCE, benzene, and toluene concentrations over the first 15 min following sampler recovery, but TCE and toluene concentrations declined thereafter. Laboratory data suggest that VOC concentrations within the PVD samplers are relatively stable for at least 1 h at 21°C; however, the loss of VOCs from water-filled PDB samplers strongly suggests that the PDB samples be transferred to VOA vials and the PVD samplers be capped and sealed immediately upon retrieval.

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