In cooperation with the New Hampshire Department of Environmental Services

USE OF PASSIVE DIFFUSION SAMPLERS FOR MONITORING VOLATILE ORGANIC COMPOUNDS IN GROUND WATER

Passive diffusion samplers have been tested at a number of sites where volatile organic compounds (VOC's) are the principal contaminants in ground water. Test results generally show good agreement between concentrations of VOC's in samples collected with diffusion samplers and concentrations in samples collected by purging the water from a well. Diffusion samplers offer several advantages over conventional and low-flow ground-water sampling procedures:

- ***Elimination of the need to purge a well before collecting a sample and to dispose of contaminated water.***
- ***Elimination of cross-contamination of samples associated with sampling with non-dedicated pumps or sample delivery tubes.***
- ***Reduction in sampling time by as much as 80 percent of that required for "purge type" sampling methods.***
- ***An increase in the frequency and spatial coverage of monitoring at a site because of the associated savings in time and money.***

The successful use of diffusion samplers depends on the following three primary factors: (1) understanding site conditions and contaminants of interest (defining sample objectives), (2) validating of results of diffusion samplers against more widely acknowledged sampling methods, and (3) applying diffusion samplers in the field.

INTRODUCTION

Methods for ground-water sampling continue to evolve. With the advent of low-flow and low-volume sampling methods (Pohlmann and others, 1994; and McFarlane, 1996), approaches have been developed that seek to minimize disturbance of the water column in the sampled well and the entrainment of large, locally mobile particulates suspended in the water sample. An extension of these low-flow sampling methods was passive (no purge) sampling, and specifically, the use of diffusion samplers (Vroblesky and Hyde, 1997). Diffusion samplers work on the principle of diffusion—chemical compounds dissolved in water move from areas of high concentration outside the sampler to the initially low concentration inside the sampler until equilibration is reached. These samplers are an effective tool for collecting samples for analysis of chlorinated and aromatic VOC's because these compounds can diffuse into the sampler. The primary advantage of using diffusion samplers is the cost savings associated with the reduced sampling time. Because purging of the water in the well is not required with diffusion sampling, sampling time can be reduced by 80 percent over methods that require purging of the well.

Two types of passive-diffusion samplers were used in previous studies—a water-vapor diffusion sampler, and a water-water diffusion sampler. Methods of construction and some applications of diffusion samplers are described by Vroblesky and Hyde (1997), Vroblesky and Robertson (1996), and Savoie and others (1999). The water-vapor diffusion sampler consists of a 40 milliliter (mL) glass vial enclosed in a water-free sealable polyethylene bag. Concentrations of contaminants in the vapor phase are not directly comparable to those in the water phase (Mullaney and others, 1999) because of a number of factors, including the physical and chemical properties of the VOC's and their interaction with the environment (the Henry's Law Constant can be used to help determine the tendency of a compound to partition between the water and vapor phases).

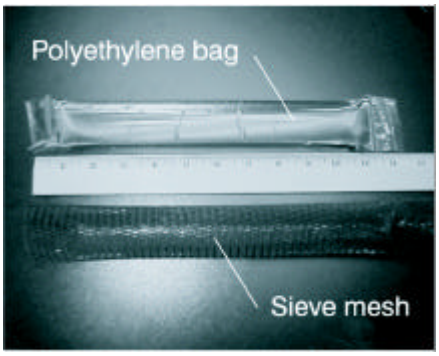

Figure 1. A diffusion bag and sieve mesh used to hold the bag inside a well.

Water-water diffusion samplers consist of deionized, contaminant-free water enclosed in polyethylene bags (fig. 1), which are suspended in the water column of a well in a mesh or slotted device next to the well screen opening to the aquifer. Contaminants in the well water, such as chlorinated and aromatic VOC's, are able to diffuse through the polyethylene bag into the previously contaminant-free water until the bag water and well water reach equilibrium.

Diffusion samplers can be used to increase the frequency of sampling and coverage of wells or locations to be sampled because of their time-saving benefits. Diffusion samplers are ideal for use in wells that are to be sampled repetitively, and diffusion sampling can be used to compliment or augment collection of samples by more traditional methods. Because of the speed of diffusion-sample retrieval compared to purge methods, concentrations measured during a sampling round may more closely approximate a snapshot in time than concentrations measured in samples collected by other methods.

The diffusion-sampler method eliminates the need to dispose of potentially highly contaminated wastewaters produced by purge-type sampling methods. Cross contamination of samples is reduced by use of diffusion samplers because the contact with sampling equipment from multiple wells also is eliminated, unlike sampling conducted with non-dedicated pumps, tubing, or bailers.

EXAMPLES OF USE

Water-vapor diffusion samplers have been used successfully to collect samples for analysis of VOC's in areas where ground water nears the surface, like streams or lakebeds. Water-vapor diffusion samplers were used by Vroblesky and Roberston (1996) to collect time-series VOC data and to monitor changes in VOC concentrations in ground water discharging to surface-water bodies. Savoie and others (1999) used water-vapor diffusion samplers to delineate a VOC plume discharging to the Cochato River near the Baird and McGuire Superfund Site in Holbrook, Mass.

Previous studies using water-water diffusion samplers include those at several Air Force Bases—Hanscom Air Force Base in Massachusetts (Forest Lyford, U.S. Geological Survey, oral commun., 1999) and McClellan Air Force Base in California (Parsons Engineering Science, Inc., 1999). In both these studies, concentrations of VOC's detected in diffused water samples from unconsolidated and bedrock aquifer wells compared favorably to concentrations in water samples collected in accordance with low-flow, purging procedures (U.S. Environmental Protection Agency, 1996). Vroblesky and Hyde (1997) found that the concentrations of VOC's—primarily tetrachloroethylene (PCE), trichloroethylene (TCE), *cis*-1,2-dichloroethene (cis-1,2DCE), *trans*-1,2-dichloroethene (*trans*-1,2-DCE), 1,1-DCA, and vinyl chloride—in water-water diffusion samplers retrieved at five bedrock wells during one round of sampling were within 10 percent of results from samples retrieved by submersible and bladder pumps and bailers. Harte and others (in press) found that PCE, TCE, and *cis*-1,2DCE concentrations in water-water diffusion samples from wells tapping unconsolidated aquifers, had a strong positive linear correlation (root-mean square (R^2) of 0.94 or more) with concentrations measured in purged samples collected by low-flow procedures.

LIMITATIONS OF USE

Equilibration between the water-water diffusion sampler and well water is critical to ensuring that a representative sample is retrieved. The time to reach equilibrium can vary for each type of VOC and whether a water-water or water-vapor diffusion sample is being used. Harte and others (in press) found a poor natural log (Ln) correlation (R^2 of 0.15) between the length of time the water-water diffusion samplers were in the well (called deployment time), for deployment times exceeding 7 days, and the percent concentration differences of PCE between purged and diffusion samples. A graph of the comparison shows a wide variation in concentration differences of PCE relative to deployment time (fig. 2). Thus the effect of deployment time is not observable, possibly suggesting equilibrium was reached. The scatter of data points on the graph suggest differences are caused by factors other than the time required for equilibration.

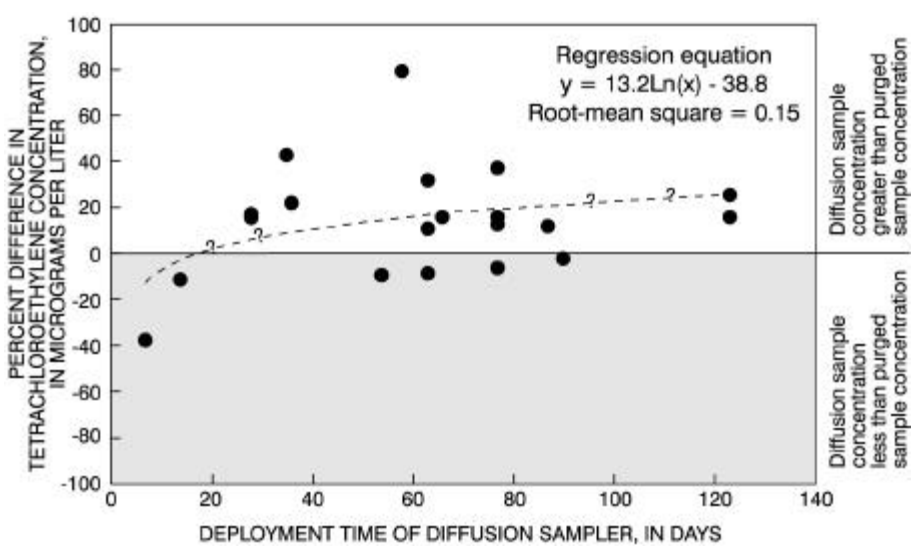

Figure 2. Comparison between deployment time of diffusion sampler and difference of measured concentrations of tetrachloroethylene from diffusion samples and purged samples.

Water-water diffusion sampling may not be an effective sampling method for all VOC's. Those compounds that have low-vapor pressures and(or) extremely high solubilities may not reach equilibrium between the water column and the contents of the sampler within a reasonable time frame (Paul Hare, General Electric Co., written commun., 1999). For example, acetone was observed not to reach equilibrium after 10 days, whereas most of the chlorinated solvents reached equilibrium within several days.

Well hydraulics, well construction features, and the natural circulation of water into the well from the aquifer should be considered when evaluating the probable effectiveness of water-water diffusion samplers in collecting representative ground-water samples. If the natural circulation in the well prevents an adequate exchange of water with the aquifer, then the water within the well will not be a reliable indicator of VOC concentrations in the aquifer. Wells with clogged openings and screens should be avoided for diffusion sampling. Stratification of the water within the well is also a consideration when using water-water diffusion samplers and comparing results to purged samples. Diffusion samples have a minimal effect on water circulation within a well and thus preserve any stratification of water, whereas purging can induce vertical mixing of the water.

Results of analyses of samples collected with diffusion samplers should be validated against analyses of samples collected by other sampling methods before diffusion sampling is applied in a

field-sampling program. Analyses of water-vapor diffusion samples cannot be directly compared to those of samples collected by other water sample methods, however, because of the difficulty of correlating vapor and water concentrations. In contrast, results of analyses of water-water diffusion samples can be validated by other water-sampling methods. Testing of diffusion samplers involves comparing results of VOC analyses of water collected from diffusion samplers with analyses of purged samples. The selection of "purged type" methods to validate diffusion results (specifically pumps), should be made on the basis of site conditions and testing objectives because pump performances in the collection of water samples for analyses of VOC's are not unique (Imbrigiotta and others, 1988).

Similarity in VOC concentrations between analyses of samples derived from diffusion samples with samples collected from standard low-flow methods suggest that diffusion samplers are adequate in sampling for VOC's. Differences in results, however, may also suggest an acceptable test if sampled water from the two methods are derived from different zones in the aquifer. Therefore, identification of differences may not constitute a rejection of the use of diffusion samplers in a sampling program. With this possibility, it may be difficult in some cases to determine the accuracy of diffusion sampling.

Water-water diffusion sampling is relatively untested for monitoring of water concentrations of VOC's less than 10 micrograms per liter (µg/L). At these trace levels, conventional or low-flow sampling methods should be used in addition to diffusion sampling.

STEPS IN USE OF DIFFUSION SAMPLER

A three-step process for using diffusion samplers includes (1) defining sampling objective(s), (2) validating sampler results, and (3) applying the use of the sampler in the field.

Defining Sampling Objectives

As with all sampling programs, the objectives in monitoring must be clearly defined and understood in order to evaluate the feasibility of using diffusion samplers at a site. Factors to consider include the types of chemicals to be monitored, number of sampling sites and frequency of sample collection, well hydraulics, and well construction.

Diffusion samplers are effective only for sampling VOC's, specifically chlorinated and aromatic compounds, because of the diffusive properties of these compounds. Water-quality indicators that are used to identify natural attenuation and biodegradation pathways of a contaminant plume (Wiedemeier and others, 1998) need to be sampled using purge sample methods.

Validating Sampler Results

Validation of water-water diffusion-sample results with established and accepted sample methods is necessary because of the potential variability in results. If results from diffusion samplers will be used to substitute results from another sampling method, some form of validation will be required. If results will be used in a reconnaissance mode, then detailed validation is optional.

The procedures for validating results of analyses of diffusion samples with results of analyses of purged samples are fairly simple. The diffusion sampler is placed in the well for a deployment period that will allow for adequate equilibrium of the samples with well water, and then retrieved. Most studies (Paul Hare, written commun., 1999) use a deployment period of 2 weeks, but equilibrium of certain compounds may take less time. After retrieval, a purged sample is collected and results of analyses of both samples are compared. Harte and others (in press) found that although concentrations of VOC's changed during the deployment periods, the diffusion sampler concentrations were similar to the concentrations of purged samples at the time of retrieval indicating that the diffusion sampler provided a contemporaneous measurement of VOC. Therefore, the diffusion sample did not integrate concentrations over the deployment period and thus, simplified the comparison of results from the different sampling methods.

In most wells with short screens or short openings, a single diffusion sampler is deployed (normally at the midpoint of the screen or well opening) and checked against one purged sample (collected from the same depth interval). In wells with long screens or openings, depending on patterns of water-well circulation under unstressed and stressed conditions, multiple diffusion samplers could be deployed vertically, and results of analyses checked against a corresponding number of analyses from purged samples.

An example of the correlation of results of analyses of diffusion samples

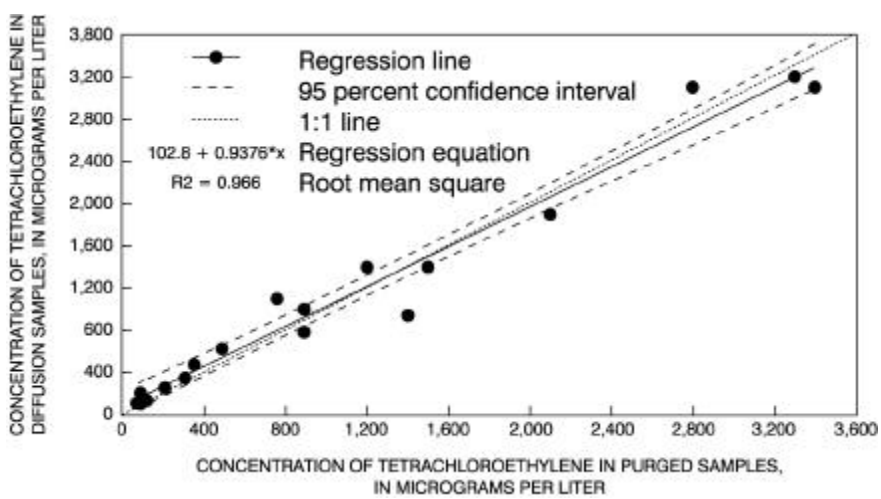

Figure 3. Results of laboratory analyses for tetrachloroethylene (PCE) in samples collected by diffusion and purge methods.

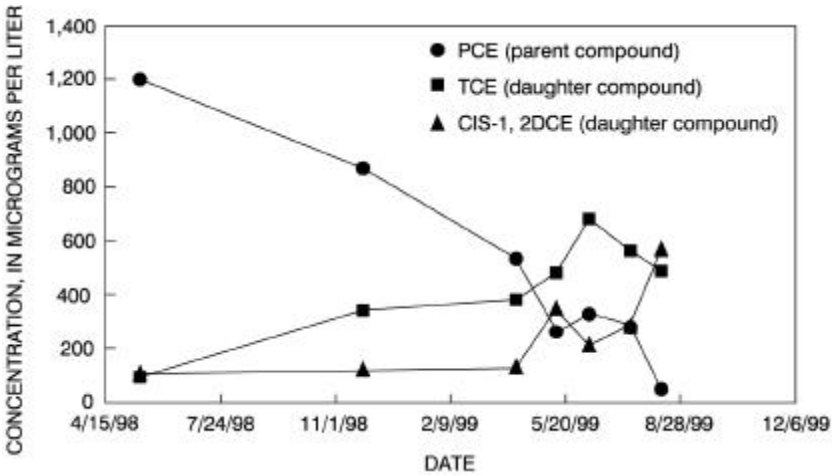

Figure 4. Example of monitoring for volatile organic compounds from diffusion samples.

with those of purged samples is shown in figure 3 for concentrations of PCE. The linear regression between concentrations from the analyses of the two sample methods produced a root-mean square of 0.966, indicating that diffusion samples and purged samples are strongly correlated when collected contemporaneously after a 1- to 8-week deployment period for the diffusion samples.

Applying Samplers to the Field Program

Large reconnaissance and repetitive sampling programs at sites with relatively high concentrations of VOC's (greater than 50 µg/L) may benefit from the use of diffusion samplers. Repetitive and high-frequency sampling may allow for identification of short-term chemical transport effects. An example of detailed time series data of VOC's in a bedrock well is shown in figure 4. Results of analyses of samples collected by water-water diffusion samplers show a decrease in the primary VOC (PCE) but increases in secondary or daughter products of PCE (TCE, and *cis*-1,2DCE), which occur during the process called reductive dehalogenation (Chapelle, 1993). The high-frequency times-series data collected by this method allowed for the quantification of degradation activity in the bedrock aquifer system.

—By Philip T. Harte, Michael J. Brayton, and Wayne Ives[1]

REFERENCES

Chapelle, F.H., 1993, Ground-water microbiology and geochemistry: New York, John Wiley and Sons, Inc., 424 p.

Harte, P.T., Brayton, M.J., Ives, Wayne, Perkins, Sharon, Brown, Jr., Carroll, and Willey, R.E., in press, Testing and application of diffusion samplers to identify temporal trends in volatile organic compounds: U.S. Geological Survey Open-File Report 00-196.

Imbrigiotta, T.E., Gibs, Jacob, Fusillo, T.V., Kish, G.R., and Hochreiter, J.J., 1988, Field evaluation of seven sampling devices for purgeable organic compounds in ground water *in* Ground-Water Contamination: Field Methods, Collins, A.G., and Johnson, A.J., eds.: Philadelphia, American Society for Testing and Materials, ASTM STP 963, p. 258-273.

McFarlane, I.D., 1996, Low-flow groundwater sampling for manufactured gas plant sites, *in* Hydrology and Hydrogeology of Urban and Urbanizing Areas, April 1996, Annual meeting, Boston, Mass.: American Institute of Hydrology, p. GWQI23-GWQI24.

Mullaney, J.R., Mondazzi, R.A., and Stone, J.R., 1999, Hydrogeology and water quality of the Nutmeg Valley Area, Wolcott and Waterbury, Connecticut: U.S. Geological Survey Water-Resources Investigations Report 99-4081, 90 p.

Parsons Engineering Science, Inc., 1999, Technical report for the evaluation of groundwater diffusion samplers: Denver Air Force Center for Environmental Excellence Technology Transfer Division, chap. 7, 4 appendices.

Pohlmann, K.F., Icopini, G.A., McArthur, R.D., Rosal, C.G., 1994, Evaluation of sampling and field-filtration methods for the analysis of trace metals in ground water: U.S. Environmental Protection Agency 600/R-94/119, 79 p.

Rathburn, R.E., 1998, Transport, behavior, and fate of volatile organic compounds in streams: U.S. Geological Survey Professional Paper 1589, 151 p.

Savoie, J.G., Lyford, F.P., and Clifford, Scott, 1999, Potential for advection of volatile organic compounds in ground water to the Cochato River, Baird and McGuire Superfund Site, Holbrook, Mass., March and April 1998: U.S. Geological Survey Water-Resources Investigations Report 98-4257, 19 p.

U.S. Environmental Protection Agency, 1996, Low stress (low flow) purging and sampling procedure for the collection of ground-water samples from monitoring wells: Region 1, Standard Operating Procedures no. GW0001, rev. 2, p. 13.

Vroblesky, D.A., Hyde, W.T., 1997, Diffusion samplers as an inexpensive approach to monitoring VOC's in ground water: Ground Water Monitoring and Remediation, Summer 1997, p. 177-184.

Vroblesky, D.A., Robertson, J.F., 1996, Temporal changes in VOC discharge to surface water from a fractured rock aquifer during well installation and operation, Greenville, South Carolina: Ground Water Monitoring and Remediation, Summer 1996, p. 196-201.

Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Gordon, E.K., Hass, P.E., Miller, R.N., Hansen, J.E., and Chapelle, F.H., 1998, Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water: U.S. Environmental Protection Agency, 600/R-99/128, 272 p.

For more information, please contact:

District Chief
U.S. Geological Survey
361 Commerce Way
Pembroke, NH 03275
(603) 226-7807 Phone
(603) 226-7894 FAX
or e-mail: dc_nh@usgs.gov

Visit the USGS web site at URL:

http://nh.water.usgs.gov or **http://www.usgs.gov**

[1]New Hampshire Department of Environmental Services