

# Underground Tank Technology Update

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Comments and suggestions are welcome and may be directed to [John T. Quigley](mailto:John.T.Quigley@wisc.edu), Project Director, 432 N. Lake St., Madison, WI 53706. Tel 608/265-2083.

To comment on an article, or to suggest topics for *UTTU*, please e-mail [Pat Dutt](mailto:Pat.Dutt@wisc.edu) or call 607/272-3212.

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- sampling without purging, using a point source bailer in a well where groundwater is actively moving in the wellbore
- purging and sampling with bailers

For instance, field workers attached diffusion samplers to the bottom of a bladder pump, lowered the pump into a well and allowed it to sit for 34 days. Then workers used the bladder pump to pump three tubing and pump volumes of water from the well; purging the casing water was not necessary because approximately 53 gal/min of water was moving through the sampled interval. Workers used the bladder pump to collect a water sample for VOCs. Then they immediately recovered water samples from the diffusion samplers.

At another well (WQ-40B), diffusion samplers were placed adjacent to fractures and left to equilibrate for 49 days. Workers collected samples and lowered a submersible pump into the well. After purging three casing volumes of water, field workers used a submersible pump to collect water samples for VOCs. They removed the pump and replaced it with a bladder pump, and samples again were taken.

Following recovery of diffusion samplers, workers purged wells WQ-67, WQ-74QR and WQ-8 of three casing volumes of water using a bailer. "Water samples from the wells were obtained by lowering a point source bailer to the depth of the diffusion sampler. Upon recovery of the bailer, water samples were collected by slowly filling the sample-rinsed, glass 40-ml vials from a bottom-discharge bailer into the bottom of the vials. The vials were allowed to overflow several seconds and the samples were then preserved with three drops of hydrochloric acid. Sample bottles were capped with Teflon-lined bottle caps. If aeration of a sample was suspected or if bubbles were observed in a bottle, the sample was discarded and a new sample collected" (Vroblecky and Hyde, 1997).

Field workers collected duplicate samples from a single bailer at well PW-34C and obtained duplicate samples from a diffusion sampler at all sites.

**Results**

Water chemistry data showed a broad range in concentrations of CVOCs, <5 to >2,000 µg/L. Vroblecky and Hyde (1997) concluded: "In general, the CVOC concentrations in water obtained with the diffusion samplers prior to purging were similar to the CVOC concentrations in water obtained by purging and sampling with a submersible electric pump and to those obtained by purging with a bladder pump (see Table 1, Figures 1 and 2). Average concentrations of detected CVOCs in the diffusion samplers differed from the average concentrations of the respective CVOC obtained using the submersible electric pump by only 9.1 percent in water from one well and by 11.5 percent from the average concentrations of the respective CVOCs obtained by sampling with a bladder pump after purging with a submersible pump in [another well]."

Diffusion sampler and bladder pump (no purging) samples showed similar average CVOC concentrations, differing by about 11.5 percent. Differences between the 3-mil-thick and 4-mil-thick diffusion samplers were relatively minor.

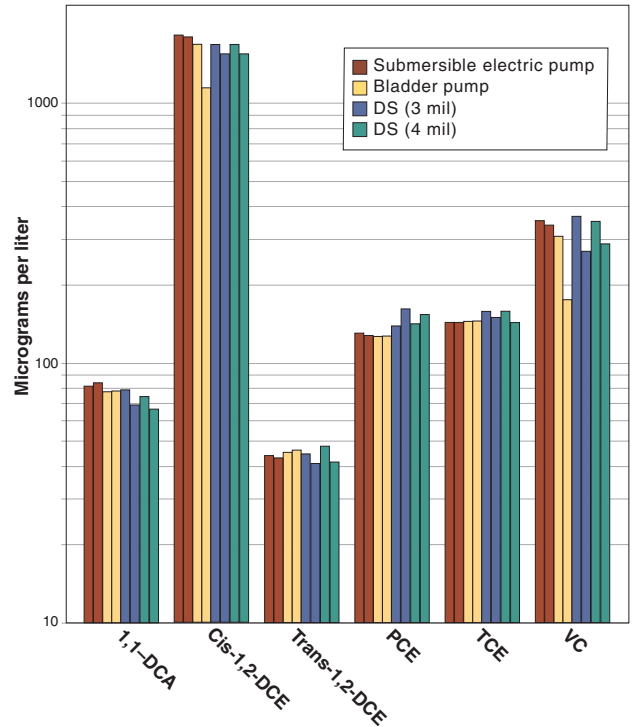


Figure 1. Data comparison: diffusion samplers (3-mil- and 4-mil-thick), bladder pump and submersible electric pump purging (Vroblecky and Hyde, 1997).

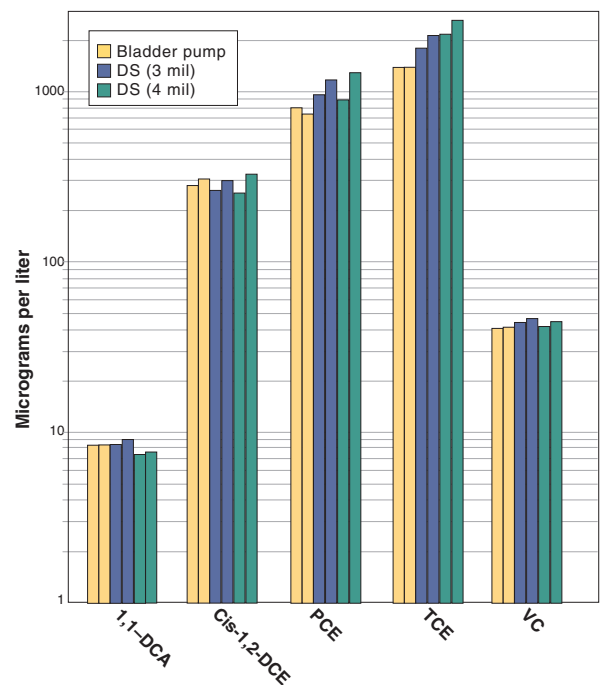


Figure 2. Data comparison: diffusion samplers (3-mil- and 4-mil-thick) and an in-place bladder pump (Vroblecky and Hyde, 1997).



Comparison of individual concentrations revealed that diffusion sample concentrations were often greater than pumped samples because "the discharge velocity of individual pulses from the bladder pump may have been high enough to allow VOC volatilization during sample collection. The higher concentrations of VOCs in the diffusion samples relative to the bladder pump imply that, in such a situation, samples obtained in the diffusion samplers may be *more* representative than those obtained using a bladder pump" (Vroblesky and Hyde, 1997). This was also true for samples obtained by purging and using a bladder pump or a submersible pump.

Researchers compared results of diffusion sampler and bailer methods at wells in both saprolite and fractured-rock wells (Table 2). Data indicated that "concentrations of CVOCs in vials filled from diffusion samplers closely matched the concentrations in water obtained from a point source bailer . . . [CVOC] concentrations from the diffusion samplers were within the range of concentrations detected in water from the bailer" (Vroblesky and Hyde, 1997).

A test that included inclusion of two 40-ml uncapped glass sampling vials within the membrane detected concentrations that were substantially lower than from either the bailer or regular diffusion methods. According to researchers (1997): "It is possible that the glass vials, although open at one end, slowed down diffusion into the vials sufficiently to cause lower concentrations inside the vials than outside the vials. Thus, incorporation of the 40-ml glass sampling vials into the diffusion samplers is not practical."

### Air bubble effect

Researchers installed two diffusion samplers in one well, a conventional sampler and a sampler with an air bubble that composed about one-third of the sample volume. After being in a well for 34 days, neither sample contained air bubbles. "Because volatile compounds can diffuse out of the polyethylene bags as well as into them, the trapped air apparently diffused out of the sampler, leaving only water. Of the two water samples recovered from the diffusion sampler to which an air bubble had been added, one sample closely matched the CVOC concentration in water obtained by using a point source bailer and by using the diffusion samplers with no air bubbles. The second sample from the diffusion sampler to which an air bubble had been added contained approximately half of the concentrations of PCE and TCE found in the first sample and in water samples from the point source bailer (Table 2). The variability in water collected from the same diffusion sampler implies that the lower concentrations in the second sample were caused by losses during transfer from the diffusion sampler to the sample bottle and not from losses within the diffusion sampler. The data imply that, although the presence of air bubbles in diffusion samplers should be avoided, their presence apparently has little influence on concentrations of CVOCs after sufficient equilibration time" (Vroblesky and Hyde, 1997).

### Conclusions

From this study, Vroblesky and Hyde (1997) concluded:

- in some wells, groundwater flows through the open interval in a well with little interaction or mixing with water in the overlying well casing; here, water in the screened interval appears to be representative of the surrounding groundwater
- the polyethylene membrane of a passive diffusion sampler allows diffusion of the aquifer water's CVOCs into or back out of the deionized water
- after allowing equilibration in boreholes for a minimum of 11 days, researchers concluded that water from diffusion samplers had concentrations of CVOCs comparable to those obtained by
  - purging and sampling with a submersible electric pump
  - purging with a submersible electric pump and sampling with a bladder pump
  - sampling with an in-place bladder pump without purging
  - sampling without purging, using a point source bailer in a well where groundwater is actively moving in the wellbore
  - purging and sampling with a bailer
- for some constituents the average concentration was slightly higher in water obtained with the diffusion samplers than in water obtained with a submersible pump and with a bladder pump; this implies that the diffusion samplers may provide a more representative sample in some situations (Reviewer's comment: *This is true when purging is not done properly or not done at all. Diffusion samplers may also concentrate contaminants by sorption, creating a reservoir of high concentration.*)

### References

- Malott, V., "Passive Bag Diffusion Samplers," 2000, *Technical Sessions of the Technical Support Projection Meeting*, Washington D.C., April 25-28, 2000; <http://www.epa.gov/swertio1.search.htm>.
- Tunks, J. and P. Guest, "Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater," 2000, in *Risk, Regulatory, and Monitoring Considerations in Remediation of Chlorinated and Recalcitrant Compounds*, paper presented at The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 22-25, 2000; <http://www.batelle.org.bookstore>.
- Vroblesky, D. and W. T. Hyde, "Diffusion Samplers as an Inexpensive Approach to Monitoring VOCs in Ground Water," Summer 1997, *Ground Water Monitoring and Remediation*; <http://www.ngwa.org>.



## Diffusion sampler test in 15 observation wells

Vroblesky and Peters (2000) tested diffusion samplers at 15 observation wells at the Naval Station North Island, San Diego, California. Researchers compared data obtained from

- diffusion samplers
- low flow purging using bladder pumps
- low flow purging using peristaltic pumps

### The site

The Naval Air Station (NAS) North Island, used as an air station, harbor and training base, is about a mile west of San Diego Bay. Groundwater contaminants at this site included

- Stoddard solvent and mineral spirits, in refined petroleum product used as a thinning agent
- chlorinated aliphatic compounds (such as *cis*-1,2-dichloroethene)
- petroleum hydrocarbons
- JP-5 jet fuel

### Diffusion sampler description and deployment

The diffusion samplers used in this study were 2-inch-diameter, low-density polyethylene (LDPE) tubes heat-sealed at both ends and containing deionized water. The tubes were encased in an LDPE mesh that provided abrasion protection.

Researchers determined that, at most, the diffusion samplers and low-flow samplers contributed less than 5 µg/L VOCs to the samples. In addition, diffusion samplers submerged in buckets containing free-phase JP-5 and Stoddard solution did not show evidence of structural integrity loss during a two-month test period.

Field workers used plastic cable ties to attach diffusion samplers to bladder pump intakes. They also attached a Tygon tube to the sampler and extended it to land surface. "The tubing was secured by plastic ties to the diffusion sampler and to a weighted line at approximately 10-foot intervals." The tubing allowed collection of groundwater adjacent to each diffusion sampler by using low-flow methodology with a peristaltic pump.

Workers used PVC pipe with a removable rubber cap to install diffusion samplers in two wells that had LNAPL.

### Groundwater sample collection

The samplers remained in the wells for 65 to 71 days. According to Vroblesky and Peters (2000), "The wells were sampled at the time of sampler recovery using low-flow techniques. Low-flow sampling consisted of purging the well by means of a dedicated bladder pump or a peristaltic pump connected to the Tygon tubing that had been attached to each of the diffusion samplers prior to deployment." Purging continued until pH, water temperature and specific conductance stabilized; this usually took about 20 minutes and recovered 1 gallon of water.

Field workers used one of the following methods to retrieve diffusion samplers from wells:

- recovering the diffusion sampler from the well immediately following low-flow sampling by using a bladder pump from the depth at which the diffusion sampler had equilibrated
- using a peristaltic pump to sample (low-flow) groundwater adjacent to diffusion samplers, with dedicated Tygon tubing attached to each sampler
- using low-flow sampling with the shallowest depths and proceeding to the deepest depths
- using a dedicated bladder pump in some wells and a bladder pump attached to dedicated tubing in others
- using a peristaltic pump for low-flow sampling in two wells; diffusion samplers were recovered, and wells were immediately resampled by low-flow methodology using a bladder pump

Field workers also collected replicate samples from 10 percent of the sampling sites.

### Results

For the most part, researchers found that data from diffusion samplers and low purge sampling were very similar. Researchers attributed differences between low-purge sampling and diffusion sampling to VOC degassing during peristaltic-pump sampling, which could produce samples that are artificially low in concentrations, or in-well mixing, which could produce lower or higher concentrations.

For instance, at one well interval, the diffusion sampler found higher TCE concentrations in water than the bladder pump samplers. This implies that the diffusion sampler sampled

Constituent	Diffusion sampler depth	Sampler concentration (µ/L)	Low-flow	Bladder pump concentration (µ/L)
Toluene	24.85-26.15	9	26	<5
Total xylenes	24.85-26.15	111-110	26	<5

Table 3. Toluene and total xylene concentration from diffusion samplers and low-flow bladder pump at well MW-13B (Vroblesky and Peters, 2000).

more discrete intervals. One sample of *cis*-1,2-dichloroethene from a diffusion sampler was 78 percent lower than the concentration from the bladder pump, which researchers attribute to "in-well mixing by low-flow sampling in a chemically stratified part of the screened interval." (*Reviewer's comment: This could happen with any well disturbance, e.g. putting in or taking out a pump or a bailer.*) Even over a distance as small as 3.4 ft, VOC concentrations can change dramatically.

VOC concentration data in another well, for example, showed that "the diffusion samplers collected point samples of groundwater whereas the bladder pump collected water either from a greater radius of influence or from water induced up the wellbore by low-flow sampling at shallower depths" (*Vroblecky and Peters, 2000*).

Researchers attributed higher concentrations of VOCs in diffusion samplers to sampling of more discrete intervals; however, at one well, "disturbing the well water by using the peristaltic pump and removing the diffusion samplers prior to sampling with the bladder pump may have induced mixing and affected the quality of the water sampled by the bladder pump" (*Vroblecky and Peters, 2000*). (*Reviewer's comment: This well water is water in a well, not necessarily in the aquifer.*)

In another well, both diffusion and low-flow sampling sequentially toward the center of a 25-ft screen indicated relatively uncontaminated waters. At one point, TCE concentrations were 47 to 84 percent lower (using low-flow sampling), indicating that low-flow sampling did not find the peak concentration that diffusion sampling did. Researchers believed that pumping may have mixed uncontaminated groundwater into the central part of the screen.

## Conclusions

Researchers concluded the following:

- in most observation wells, the vertical concentration gradients obtained using the diffusion sampler and low-flow sampler methods were similar
- most differences between the low-flow and diffusion sampling techniques could be attributed to:
  - VOC degassing during peristaltic-pump sampling
  - in-well mixing
- when workers used low-flow methods to purge multiple depths within a screened interval, there was a potential for each low-flow sampling event to disturb the equilibrated column
- diffusion sampling can provide a point sample and detect the zone of highest contaminant concentration
- low-flow sampling of multiple horizons within a single well screen can induce mixing
- at one well where the low-flow method detected contamination that the diffusion sampler apparently missed, previous sampling and follow-up sampling using low-flow methods showed no contamination, implying that the detections by low-flow sampling were false positives, possibly caused by cross-contamination

- bladder pumps and peristaltic pumps pose the same mixing potential, but the bladder pump has less potential for volatilization and probably gives a more representative sample
- other discrepancies, such as a low-flow method detecting contamination that a diffusion method missed, may be attributed to cross-contamination
- even in a 10-ft screen, substantial stratification of VOCs can exist; even a little mixing by low-flow pumping can obfuscate data from areas typified by sharp stratification (*Reviewer's comment: But when does this effect become significant?*)
- using diffusion samplers initially can delineate stratification; these samples, coupled with field gas chromatography, can give relatively inexpensive contaminant information

## Reference

Vroblecky, D.A. and B.C. Peters, "Diffusion Sampler Testing at Naval Air Station, North Island, San Diego County, CA, November 1999 to January 2000," *U.S.G.S. Water-Resources Investigation 00-4182*; for copies write U.S.G.S., Branch of Information Center, Box 25286, Denver, CO 80225-0286.



## Comparison of PVD and PDB diffusion samplers

This article summarizes the most recent laboratory and field data on two low-density polyethylene (LDPE) passive vapor-diffusion samplers (*Vroblecky and Campbell, 2001*):

- a sampler that contains an air-filled glass vial, enclosed in two layers of polyethylene, referred to as a passive vapor-diffusion (PVD) sampler
- a sampler that is a water-filled polyethylene bag sealed at both ends, known as a passive diffusion bag (PDB) sampler

The PVD samplers have been used to delineate VOC-contaminated groundwater discharge zones beneath surface-water bodies, whereas the PDB samplers have been useful for sampling VOCs in wells. A modified version of the PDB sampler has also been used to obtain aqueous concentrations of VOCs in groundwater/surface water interface.

This article will describe PVD and PDB sampler issues with respect to

- description and field procedure
- equilibration time
- types of VOCs that readily diffuse through the membranes
- amount of time that the samplers can be stored prior to sealing or transferring the water to sample vials



## Equilibration time

Under field conditions, diffusion sampler equilibration time is a function of

- time required by sampler to equilibrate with ambient water
- time required for the environment disturbed by deployment of the sampler to return to ambient conditions

Laboratory testing can give data for equilibration times with ambient water. Data indicated that equilibration time for benzene, toluene and EDB was 24 hours. (The same was not true for MTBE: the PDB-sampler MTBE concentrations did not match ambient water MTBE concentrations.)

Field data can be used to estimate the time required for contaminant concentrations in the well or sediment to restabilize following disturbances caused by sampler deployment. For instance, field testing of PDV samplers indicated the following:

- a 12 to 24-hour stabilization period in a stream with sand characterized by a high hydraulic conductivity and a strong upward hydraulic gradient
- a greater than 65-hour stabilization period for samplers in a silty saprolite
- intermediate stabilization times in other environments
- at all locations PVD samplers achieved measurable VOC concentrations within 12 hours

Researchers attributed differing stabilization times to “the time required for the streambed sediment or well water to recover from the disturbance caused by sampler installation, [which] 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 (if the streambed is connected to an 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” (Vroblecky and Campbell, 2001). The typical use of PVD samplers has been to locate zones of discharging groundwater contaminated with VOCs.

Using the findings of previous studies and this study, researchers designated two weeks as an adequate equilibration for PVD samplers in saturated, moderately permeable sediments, such as sands or loose silts. Longer times would be required for equilibration in clays or tight silts.

Borehole-dilution studies, where tracers are injected and their decay monitored, can give an estimate of the time required for water in a well to equilibrate after a disturbance.

Researchers have found that 90 percent of an injected tracer

- was diluted within 20 minutes in a well screen open to a gravel aquifer
- was diluted within 70 minutes in a well screen open to a sand aquifer
- took 100 to 1,000 hours or more to dilute in an aquifer with poorly permeable sediments

PDB field investigations showed equilibration times of 14 to 17 days, therefore, “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” (Vroblecky and Campbell, 2001). Equilibration would be expected to be relatively quick in either karst, sand or gravel environments (U.S. EPA, 1999).

Water temperature will also affect equilibration time: colder temperatures will translate into longer equilibration times.

## Compound selectivity: VOCs and MTBE

To determine compound selectivity, researchers deployed PDB samplers in aqueous solutions of mixed VOCs and analyzed water within the diffusion sampler and outside of the sampler. For the VOCs tested, there was less than 10 percent difference between concentration in the PDB and ambient water. This was not found to be true for MTBE. Researchers concluded: “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 76 percent lower than in ambient water” (Vroblecky and Campbell, 2001). Another test showed that even after 32 days, MTBE concentration in the PDB sampler was only 64 percent of that in the test jar. MTBE’s high solubility—54,000 mg/L—may be the reason for its lack of suitability for diffusion sampling. PVD samplers located beneath a drainage ditch, however, did successfully detect MTBE concentrations. (Reviewer’s comment: *Diffusion sampling is not suitable for MTBE and other compounds.*)

## VOC stability in sampler

Researchers investigated the time between opening the PDB and transferring sampled water to VOA vials. They found no loss of PCE, TCE, benzene or toluene over the first 15 minutes, but thereafter, VOC loss was compound specific. For instance:

- PCE and benzene showed no vapor loss over the first 60 minutes following sample recovery
- TCE and toluene concentrations in samplers declined by approximately 20 percent over the first 60 minutes
- benzene, TCE and toluene showed minimal loss over a 60 to 90-minute interval

## Conclusions

Vroblecky and Campbell (2001) based the following conclusions on laboratory and field testing of PVD and PDB samplers of VOCs:

- equilibration time depends on both the time required for equilibration with the ambient water in the sampler and time required for environmental disturbance to stop after sample deployment
- time required for *c*-DCE, benzene, TCE, toluene, EDB and PCE to equilibrate in vapor-filled PVD samplers (in the laboratory) was 24 hours at 21°C



- PVC rod accommodates as many as 12 sampling cells (pre-drilled cylindrical hole spacing is 12.7 cm)
- a string of up to five rods can be connected together for sampling over long-screened well intervals

When the sampler device is ready, field workers lower it into the well. A stainless steel weight attached to the bottom of the deepest PVC rod ensures that the samplers are positioned at the correct depth. A rope at the top of the casing is used to secure the sampling device.

The U.S. Geological Survey sampler has the following characteristics:

- a low-density polyethylene tubing consisting of 45-cm-long section of 5.08-cm-diameter, 40-mil polyethylene tubing
- tubing heat-sealed on both ends
- the sampler is filled with 300 ml of deionized distilled water (a longer, 7.62-cm-diameter tubing that holds 500 ml of water is available)

Field workers place the sampler in a flex-guard polyethylene mesh tubing for abrasion protection, then lower the weighted sample to the desired depth. For this field test, workers placed samplers end-to-end in three wells to obtain vertical contamination profiles.

### Conventional well sampling and micropurging comparison

Because the diffusion samplers needed to be left in the wells for 14 days, a 14-day lag period occurred between the two sets of data. Upon retrieving the diffusion samplers, field workers also performed conventional well sampling and/or micropurging (low-flow purge-and-sample). This data was used to normalize the data from the diffusion samplers.

### Comparison of results

Tunks and Guest (2000) used statistical analysis (analysis of variance or ANOVA) to determine variability arising from the four methods used. They found no statistically significant differences among the four data sets. *(Reviewer’s comment: Variances may have been set so high that chances of finding*

*significant differences were very small.)* They did find some interesting differences in terms of cost and use of the samplers/sampling methods (Table 4).

Cost estimates for each sampling method, per sample, are:

- USGS, \$65
- DMLS™, \$555
- micropurge, \$308
- conventional, \$444

Expenses include labor, equipment, and disposal/management of investigation-derived waste. These numbers reflect costs for this field study only, although some of the costs involve one-time expenses. Labor and material costs vary depending on scope of the event: with more samples taken, cost per sample would decrease, assuming some materials are reusable.

### Conclusions

Researchers conclude that of the two diffusion samplers, the USGS sampler is more cost-effective. Diffusion samplers, however, are not applicable for all situations; in particular, they cannot give quantifiable concentrations of MTBE and other compounds or ions that do not diffuse through polyethylene. Diffusion sampling techniques could be used in natural attenuation monitoring; however, sampling of other ions such as Fe<sup>2+</sup> or oxygen would require use of other sampling methods.

In terms of future work, researchers advocate performing a similar analysis in various hydrogeologic settings (low-permeability vs. high-permeability aquifers) and creating a larger database by increasing the number of wells and samples taken.

### Reference

Tunks, J. and P. Guest, "Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater," 2000, in *Risk, Regulatory, and Monitoring Considerations in Remediation of Chlorinated and Recalcitrant Compounds*, The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 22-25, 2000; <http://www.battelle.org/bookstore>.

Criteria	USGS	DMLS™	Micropurge	Conventional
Ease of use	Excellent	Fair	Poor	Fair
Generation of IDW (investigation-derived waste, in liters)	<1	<1	100	500
Cost to provide dedicated equipment in each well	Low	High	Low	High
Decontamination required if dedicated equipment is not used	Minimal	High	Moderate	Moderate
Immediacy of sample availability	Slow	Slow	Rapid	Rapid
Can analytes other than VOCs be monitored?	No	No	Yes	Yes
Can vertical distribution of contaminants be evaluated?	Yes	Yes	Partial	No
Suitable for monitoring natural attenuation?	No	No	Yes	Partial

Table 4. Comparison of USGS, DMLS™, micropurge and conventional sampling devices/methods (Tunks and Guest, 2000).





## Limitations of diffusion samplers

This article is based on excerpts from Michael Barcelona's articles published in *Ground Water Monitoring and Remediation* (Barcelona, Fall and Spring 2000).

Barcelona stresses that successful monitoring programs are contingent on "consistent, high-quality sampling and analytical data. The dependence on quality data becomes even greater in monitoring efforts for risk-cost based corrective action or monitored natural attenuation studies."

"It would seem then that the perceptive consultant, regulator or analyst would recognize the importance of high-quality, consistent data sets and evaluate performance actively. I fear that we may be losing our bearings in this regard through limited data validation programs that allow adoption of so-called 'passive sampling methods'" (Barcelona, Spring 2000).

"Validation rarely extends to the field methods and practices of sampling, where far greater errors may enter data sets. In the best case, field blanks, field standards and spiked samples allow us to identify transport-related errors. In the worst case, an ill-proven or careless sampling effort results in the collection of grossly biased data" (Barcelona, Fall 2000). This is in reference to passive diffusion sampling, which he defines as "sampling groundwater without purging the well or sampling point." The underlying assumption is that there is always flow sufficient in the screen (or point) to maintain formation water quality in the screened interval. "The use of passive diffusion 'methods' requires sustained leaps of faith that are not technically defensible. . . I hold that without confirmed sustained flow through the screened interval, application of the diffusion bag samplers is ill-advised. . . Whether or not the diffusion samplers only reflect the most recent conditions really depends on comparable diffusion rates into and out of the bags (i.e., approaching steady-state conditions). They provide no supporting data for back-diffusion, which would allow one to estimate what the samples represent" (Barcelona, Spring 2000).

"This assumption [of sustained flow] is not born out by the literature, which is full of examples of water quality variations in minutes (i.e., for volatile organics) to hours (i.e., major ions, pH, O<sub>2</sub>) in short-screened, unpumped monitoring wells. This does not take into account the problems of mass averaging and mixing in long-screened wells (i.e., less than 5 feet). How is it, then, that one entertains the use of polyethylene "diffusive" samplers in well screens? Water level and gradient changes may occur, influencing flow during the so-called "sampling" period. Therefore, the "time" of sampling and sample origin remain indeterminate" (Fall, 2000).

Barcelona admits that diffusion samplers offer some advantages, such as waste minimization. However, because MTBE, semi-volatiles and ions cannot be measured, he

relegates this technique to the novelty category. "It seems to me that sampling methods should not determine the purposes for monitoring particularly when monitored natural attenuation and geochemical determinations have been advanced in the industry" (Fall, 2000).

Another objection to diffusive sampling concerns well disturbance. "Dedicated sampling devices used in a consistent protocol without a doubt cause less disturbance of in-well conditions than deploying a string of bags. The emplacement method itself flushes the well at least partially" (Barcelona, Fall 2000).

As for the value of multiple vertical well samples: [These] "samples in long-screened wells have merit in research studies or field trials of in-situ remediation technologies. The added cost of multiple analyses is difficult to justify as opposed to easily replicated discrete samples. Their interpretation of multiple samples for practical monitoring purposes should be justified by the proponents of the method. Analytical costs are the driver and multiple samples seem to work at cross-purposes with practical goals" (Fall, 2000).

As for studies of diffusion samplers, some of which are described in this issue of UTTU: "I can only fairly judge the potential applicability of new methods based on peer-reviewed studies, which are rigorously designed and executed. The more recent references provided by the commentaries do not meet this criterion" (Fall, 2000).

Gustavson and Harkin (2000) agree at least partially with Barcelona. They point out that although semipermeable membrane devices do have advantages over other sampling techniques, their use is limited because the devices

- measure only truly dissolved compounds
- give only integrated long-term trends of contaminant concentrations and sample episodic events

### References

Barcelona, M.J., "Active Monitoring and Thoughtful Remediation," Editorial, *Ground Water Monitoring and Remediation*, Spring 2000; <http://www.ngwa.org>.

Barcelona, M.J., "Active Monitoring and Thoughtful Remediation," Discussion, *Ground Water Monitoring and Remediation*, Fall, 2000; <http://www.ngwa.org/>.

Gustavson, K.E. and J.M. Harkin, "Comparison of Sampling Techniques and Evaluation of Semipermeable Membrane Devices (SPMDs) for Monitoring Polynuclear Aromatic Hydrocarbons (PAHs) in Groundwater," 2000, *Environmental Science & Technology*, Vol. 34, No. 20; <http://www.pubs.acs.org>.

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