Comparison of Temporal Trends in VOCs as Measured with PDB Samplers and Low-Flow Sampling Methods

by Philip T. Harte

Abstract

The effectiveness of passive diffusion bag (pdb) samplers in the measurement of selected volatile organic compounds (VOCs) is dependent on a number of factors. At some sites and wells, pdb sampling methods provide an attractive alternative to other sampling methods. In this discussion, I provide two examples of comparisons of temporal trends in tetrachloroethylene (PCE) concentrations from passive and low-flow sampling methods. At the example field site, large changes in PCE concentrations occurred over the deployment period(s) of the pdb samplers, yet the concentrations from the pdb samples are similar to the low-flow samples and the overall trends are the same.

"The slopes of the temporal trends in concentrations were similar between the two methods."

Introduction

Several interesting questions have been raised as to the capability of passive sampling to accurately measure volatile organic compounds (VOCs) in ground water. The editorial, "Active Monitoring and Thoughtful Remediation," by Dr. Michael Barcelona in *Ground Water Monitoring and Remediation* (20, no. 2: 4) and subsequent discussions by Paul Hare and others and Dr. Barcelona's reply (*GWMR* 20, no. 4: 127–131) have been fascinating and thought provoking. In particular, questions raised by Dr. Barcelona regarding the need to further validate the use of pdb samplers against active sampling methods, and the need to evaluate the reliability of pdb samplers to provide accurate data on historical trends, can only serve to promote additional field validation efforts. The literature on field validation efforts continues to grow. Recently, the U.S. Geological Survey (USGS) published a user's guide and summary of selected field efforts (Vroblesky 2001a, 2001b).

The effectiveness of pdb samplers in the measurement of selected VOCs is dependent on a number of factors including the site hydrogeology, well construction, the ability of the VOC to diffuse through the samplers (typically a low-density polyethylene bag), the deployment time of the pdb samplers, and the rate of exchange of water between the well and aquifer under unstressed conditions at the sampled well. Some of these factors also affect samples taken using active sampling methods.

In this discussion, I provide two field examples of comparisons of temporal trends in VOC concentrations, specifically tetrachloroethylene (PCE), from passive and low-flow sampling methods. These examples provide additional evidence of the potential reliability of using passive sampling methods at some sites and wells to accurately measure appropriately sampled compounds.

The examples given here are from two observation wells, one a

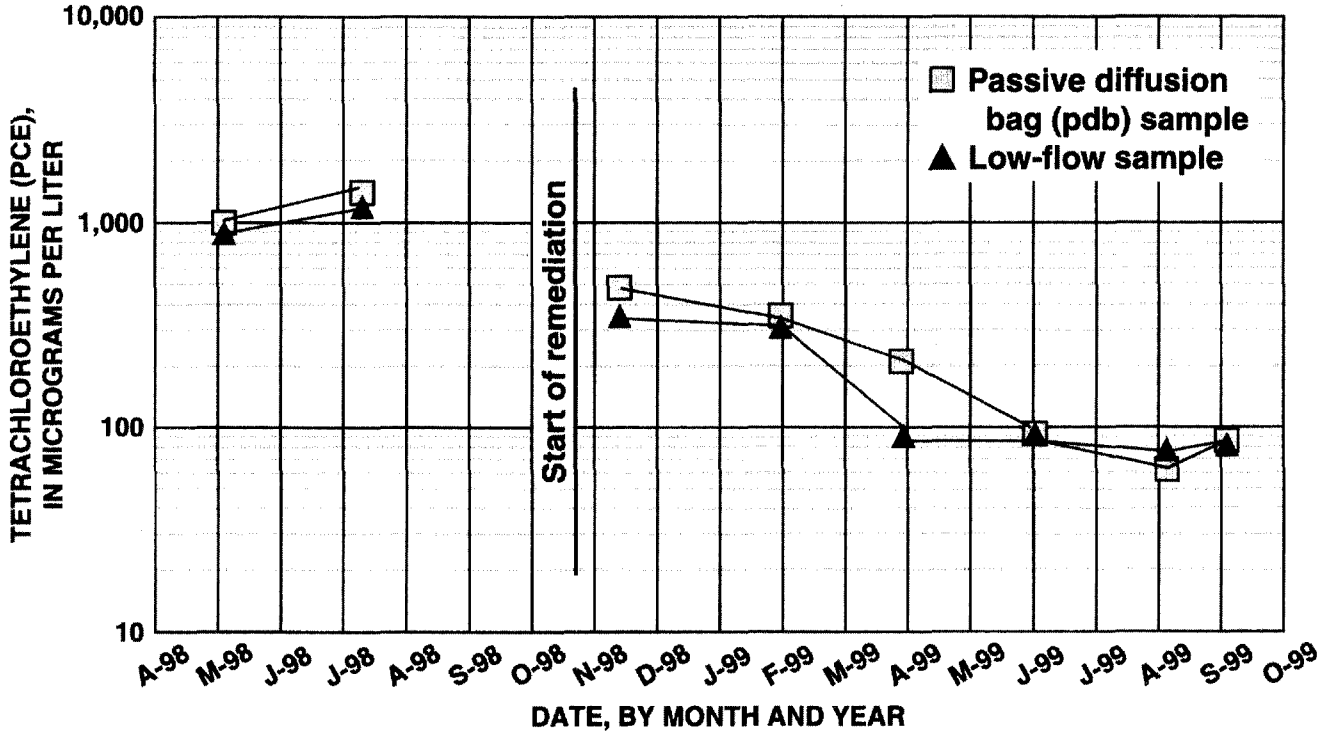

Figure 1. Trends in tetrachloroethylene (PCE) from passive diffusion bag and low-flow samples at well B95-15.

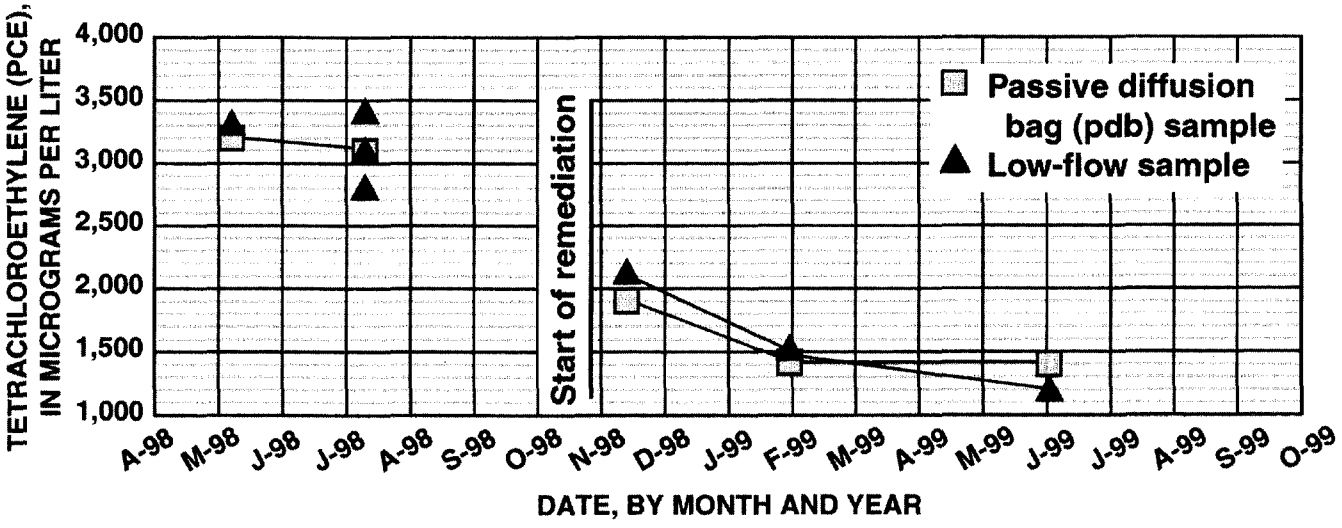

Figure 2. Trends in tetrachloroethylene (PCE) from passive diffusion bag and low-flow samples at well B95-13.

5-foot screened well (B95-13) and the other a 10-foot screened well (B95-15), which are set in a highly permeable aquifer at a remedial site primarily contaminated with PCE (Harte et al. 2001). The characteristics of the aquifer and wells at the site allow good natural flushing of water between the well and aquifer. These wells and others at the site show negligible drawdown after the removal of several well-bore volumes of water, which indicates a good hydraulic connection between the well screen and the permeable aquifer. Furthermore, PCE has a relatively rapid equilibration rate (less than 48 hours) between the water inside the pdb and water in the well (Vroblesky and Campbell 2001). With these conditions at the site, the use of pdb samplers is favorable for the collection of VOCs from wells.

Results

At the field site, large changes in PCE concentrations (order of magnitude change) occurred over the deployment period(s) of the pdb samplers. Plots of PCE concentrations from the two wells, as measured by pdb samplers and low-flow sampling, however, showed strong agreement between the two methods (Figures 1 and 2). Figure 1 shows results from well B95-15 on a log-concentration scale for eight paired samples. Figure 2 shows results from well B95-13 on a linear-concentration scale for five paired samples. The overall pattern of decline from the two types of samples is similar. The pdb

samplers captured the large variations in PCE concentrations before and after the start of remedial activities. PCE concentrations at well B95-15 (Figure 1) varied by one order of magnitude, whereas concentrations at well B95-13 (Figure 2) varied by one-third order of magnitude. In both wells, trends in PCE concentrations from pdb samplers matched the trends in the low-flow samples. Note that the pdb was deployed immediately after the preceding samples, yet the PCE concentration of the pdb sample is similar to the PCE concentration of the low-flow sample taken on the same day that the pdb sampler was retrieved. For example, the pdb sampler retrieved in July 1998 was installed in the well immediately after the retrieval and collection of the preceding samples in May 1998 (Figures 1 and 2).

At well B95-15 (Figure 1), PCE concentrations from pdb samples exceeded that of low-flow samples in six out of the eight paired samples (Figure 1). Differences in concentrations ranged from 0 to 200 micrograms per liter (µg/L) or 0 to 60 relative-percent difference (RPD). In three of the eight paired samples, differences in concentrations exceeded the maximum RPD of 11 that was obtained from field duplicate samples. Therefore, it is likely that in these three paired samples, there are some tangible differences in the results that are not associated with background noise such as lab and sample error. The maximum RPD of 60 occurred in April 1999, which is the only paired sample with a pdb sampler retrieval time that was more than eight hours different from that of the low-flow sample. This concentration difference suggests that some short-term changes in concentration at the well may have occurred. Excluding the April 1999 paired sample, the RPD for the remaining seven paired samples ranged from 0 to 22. Although concentrations differ (but were not statistically different), the trends in concentrations are similar between the two methods. The absolute change in concentration from the maximum (July 1998) to the minimum (August 1999) is 183% for the pdb samples and 176% for the low-flow samples.

At well B95-13 (Figure 2), PCE concentrations from pdb samples were lower than concentrations in low-flow samples in three of the five paired samples. Differences in concentrations ranged from 0 to 300 µg/L or 0 to 10.5 RPD. All differences were less than the maximum RPD of 11 between field duplicates. In July 1998, three low-flow samples were collected at different pump rates. The high concentrations of these samples are associated with the high pump rates. The concentration from the pdb retrieved on July 1998 is between the concentrations from the low-flow samples on that same date. The sensitivity of PCE concentrations to variations in pump rates suggests there is chemical heterogeneity in concentrations over the screen length. Although there are differences in concentrations, the trends are similar between results from the two methods. The absolute change in concentration from the maximum (July 1998) to the minimum (June 1999) is 75% for the pdb samples and 95% for the low-flow samples (using the highest concentration from July 1998 as the initial low-flow concentration).

Conclusion

The analysis of temporal trends in PCE concentration determined by the two sample methods indicates that pdb samplers adequately sample the large variation in PCE concentrations at the site. The slopes of the temporal trends in concentrations were similar between the two methods, and the pdb sample concentration generally reflected the instantaneous concentration sampled by the low-flow method. Therefore, the pdb samplers provide an appropriate sampling method for PCE at these wells.

As Dr. Barcelona pointed out, one or two wells do not make the case for widespread application of pdb samplers at all sites. Application of pdb samplers in some circumstances, however, is appropriate for assessing temporal and spatial variations in VOC concentrations and, therefore, should be considered as a useful tool in a hydrogeologist's toolbox.

References

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Biographical Sketch

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