

An Evaluation of the Performance of Multiple Passive Diffusion Devices for Indoor Air Sampling of VOCs

Joseph E. Odencrantz

Steven C. Thornley

Harry O'Neill

The United States Environmental Protection Agency is considering recommending longer-term sampling to achieve more accurate time-weighted-average detections for indoor air monitoring of volatile organic chemicals. The purpose of the research presented herein was to compare longer sampling times using passive diffusion samplers to the results from shorter-term testing periods using sorbent tubes and low-flow pumps (US EPA Method TO-17) at great frequency for trichloroethene (TCE) in indoor air. A controlled release of TCE in a large room allowed for over two-orders-of-magnitude daily concentration variability over the course of the two-week monitoring event. The daily concentration measurements by US EPA Method TO-17 and the passive diffusion samplers were performed in triplicate and had excellent reproducibility. The results of daily tests were averaged and compared with four passive diffusion devices exposed to indoor air for three, seven, ten, and fourteen days in accordance with ASTM D6196-02. A specific uptake rate for each of the passive devices at the four different time intervals and the statistical significance of the time-varying uptake rates were evaluated. The performance of each passive diffusion device was determined using a statistical performance criterion. The average concentration for all of the exposure periods could be reliably predicted using the established uptake rates for two of the four passive devices. © 2009 Wiley Periodicals, Inc.

INTRODUCTION

The use of sorbent tubes and other passive diffusion samplers for quantifying volatile organic compounds (VOCs) in ambient/indoor air and for vapor-intrusion assessment is common practice throughout Europe. Sorbent tubes with constant air flow and passive diffusion devices are likely to become mainstays of air sampling in the United States because of several issues associated with the use of canister techniques that are currently more widely used. Further, the use of sorbent technology is better suited for longer-duration sampling, larger molecular weight compounds, and isotopic analysis. The current standard 8- or 24-hour collection period used to sample indoor air for potential vapor-intrusion impacts may not adequately account for temporal variability and detect contamination best represented by longer-term sampling periods (several days to weeks or months) that provide for more accurate time-weighted-average detections.

For vapor-intrusion evaluations in the United States, the need for having tools to assess indoor air and ambient air environments for the two- to four-week period of time is critical for determining accurate time-weighted concentrations of VOCs.

There are numerous applications for passive diffusion devices to quantify VOCs. For instance, a study in Sweden reports the measurement of siloxanes using sorbent tubes for this large group of chemicals with molecular weights that vary from several hundred to thousands of grams per mole (Kaj et al., 2005). Statheropoulos et al. (2005) reports identifying over 150 compounds using a passive diffusion device to assess refuse waste bins to as large as 146.2 grams/mole ($C_{11}H_{14}$). The typical exposure time for passive diffusion devices for environmental assessment of indoor air environments is typically two to four weeks and for industrial hygiene evaluations four to eight hours (The Diffusive Monitor, 2001). Previous research has demonstrated the reliability of passive devices deployed for two weeks in indoor air environments when compared to active methods (Odenrantz et al., 2008). For vapor-intrusion evaluations in the United States, the need for having tools to assess indoor air and ambient air environments for the two- to four-week period of time is critical for determining accurate time-weighted concentrations of VOCs. Passive diffusion devices can also be used to characterize soil gas environments for sources, risk evaluation, remediation monitoring, spatial variability, and vapor-intrusion assessments (Odenrantz & O'Neill, 2009).

A controlled release of trichloroethene (TCE) in a large room was designed to challenge the various passive diffusion devices used in this study over a wide range of concentrations typically encountered in vapor-intrusion studies. The objective of the research described herein was to compare longer sampling times using passive diffusion samplers (American Society for Testing and Materials [ASTM], 2003; Health and Safety Executive, 1995; International Organization for Standardization, 2003) and to compare these results to shorter-term testing periods using sorbent tubes and low-flow pumps (US EPA Method TO-17) at great frequency for TCE in indoor air. An examination of the results of daily tests to the passive diffusion devices exposed to indoor air for three, seven, ten, and fourteen days revealed that all the passive devices were able to track the TCE to varying degrees of success. Passive uptake rates were calculated for each device at the different periods to determine the performance of each device using statistical evaluation tools.

SAMPLING PROGRAM AND METHODS

Beacon Environmental Services, Inc. collected air samples using three sets of the same sample collection media/equipment. The TCE (≥ 99 percent pure) used for this study was obtained from Sigma-Aldrich, St. Louis, Missouri, and contained 40 ppm of diisopropylamine as stabilizer. A 10-mL aliquot of TCE was dispensed into a crimp-top, silicone rubber septum seal, 40 mL volatile organic analysis (VOA) vial. A 10-cm length by 0.0762 ID (cm) of PEEK tubing was used to create a diffusion pathway by piercing the silicone rubber septum and inserting the PEEK tubing. The diffusion device was constructed by Beacon and provided control of the TCE concentration that was in the room.

Three sample collection devices were designed to run simultaneously for 24 hours for the daily active samples and for three, seven, ten, and fourteen days for the various passive devices. The active method resulted in three tubes for quantification for each 24-hour period for 14 days. All samples were collected under strict chain-of-custody, and notes were taken daily. The pumping rate was approximately 20 mL/min, and GilAir pumps

(manufactured by Sensidyne LP, Clearwater, Florida) were used to draw indoor air for 24 hours through special sorbent-packed quarter-inch diameter stainless steel tubes (obtained from both Perkin Elmer LAS, Shelton, Connecticut, and Markes International Ltd, Wales, United Kingdom). The flow rates of the pumps were measured using a National Institute of Standards and Technology traceable flow meter at the beginning of the each sampling event and then again at the end of the each sampling event. The sorbent tubes were analyzed by US EPA Method TO-17 by Beacon at its laboratory in Bel Air, Maryland, using a thermal desorption system connected to a gas chromatograph/mass spectrometer (TD-GC/MS). The TD system allows for the recollection during analysis of the sample split onto a secondary, clean sorbent tube (if necessary).

There were four different passive devices used in the study. The first two were sorbent tubes consisting of quarter-inch diameter stainless steel tubes packed with custom adsorbents and the third and fourth the BeSure sampler (Beacon, Bel Air, Maryland) in axial and radial mode, respectively. A more complete description of the passive devices follows. All of the passive devices were deployed in triplicate and were exposed to indoor air for specific periods of time (three, seven, ten, or fourteen days) and then analyzed following ASTM D6196-03 by Beacon.

The experimental setup was designed to track the TCE concentrations in a large room to determine the performance of each of the deployed passive diffusion devices. Preliminary tests of the indoor air in the room revealed no TCE presence, with only low-level detections of midrange petroleum hydrocarbons. Exhibit 1 shows the overall study area layout. Note the location of the source of TCE with respect to the three sampling stations and the spatial distribution of the sampling devices at each of the sampling stations.

Exhibit 2 shows the overall layout of the room looking from Station A toward Station C. The three axial passive diffusion devices are above the stations, strung on a wire. The radial diffusion devices are next to the pump on the tabletop of each station hanging from the top of a stainless steel cup. The main distinction between an axial and radial sampling device is the radial sampler is exposed directly to the air/molecules to be sampled while the air/molecules must enter an opening for an axial sampling device.

Exhibit 3 is a photograph of Station A from above and shows the study arrangement of the active and passive devices. The inlets to the axial passive devices are orientated downward and are slightly less than two feet above the tabletop. The daily, active US EPA Method TO-17 device is located next to the stainless steel cup that holds the four sets of radial passive devices. Two BeSure axial samplers are depicted on the upper left side adjacent to seven passive diffusion tubes.

The four different passive devices were all deployed the first morning in triplicate for each of the four sampling durations, resulting in a total of 48 passive devices. The four types of passive collection devices (three axial and one radial) that were used in the study are summarized below:

1. TenaxGR/Carboxen Passive Diffusion Sampler-PT (Tenax GR, approximately 120 mg with a surface area of 24 m²/g and Carboxen-569, approximately 180 mg with a surface area of 485 m²/g)
2. Chromosorb 106 Passive Diffusion Sampler-PC (100 mg, with a surface area of 750 m²/gram)

The main distinction between an axial and radial sampling device is the radial sampler is exposed directly to the air/molecules to be sampled while the air/molecules must enter an opening for an axial sampling device.

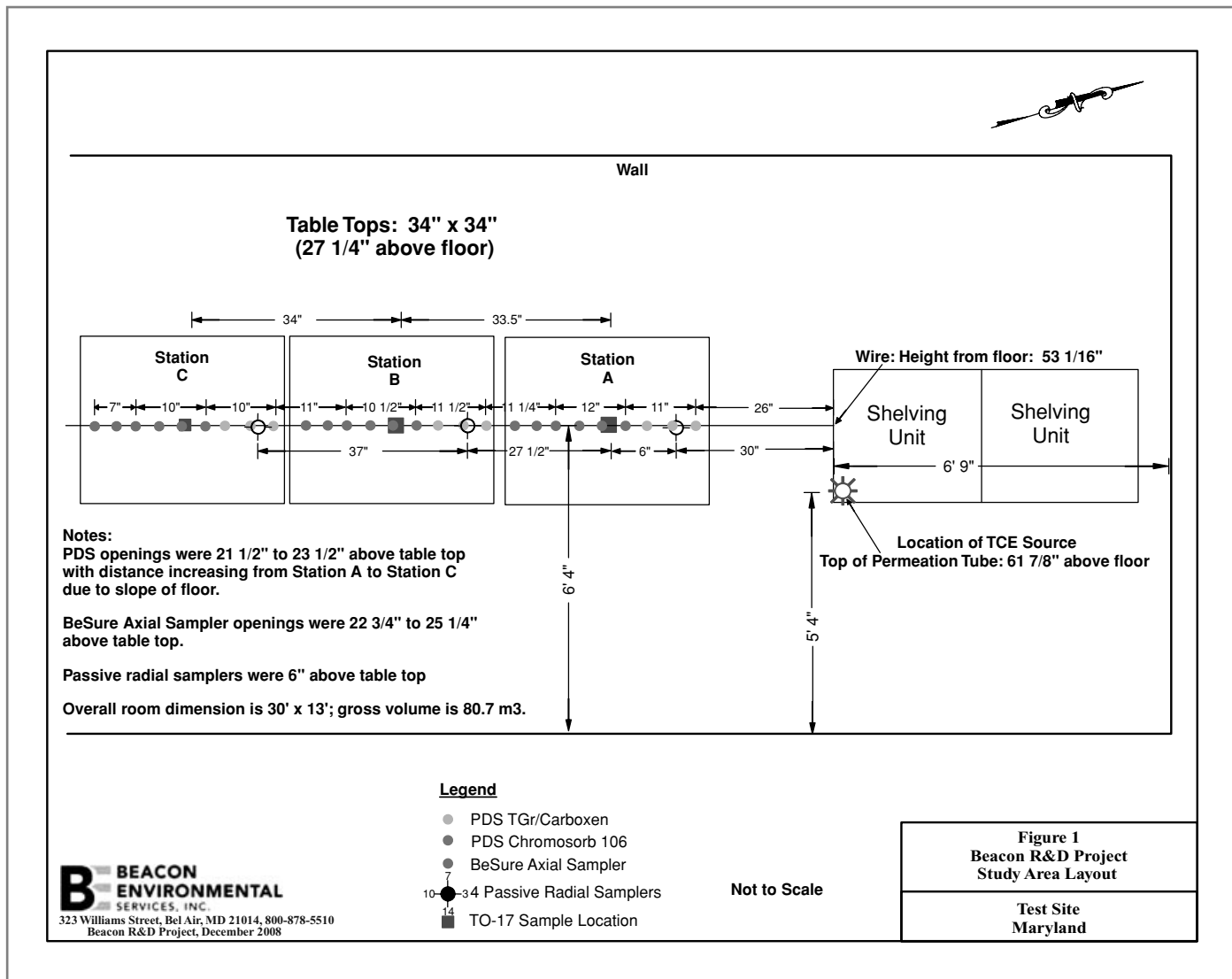


Exhibit 1. Passive diffusion device performance study layout

3. BeSure Axial Sampler-BA (see Clarke et al., 2008 for more detailed information)
4. BeSure Passive Radial Sampler-PR

At the end of each passive exposure period (three, seven, ten, and fourteen days), triplicates of each passive device were sealed and transported to Beacon’s laboratory for analysis. The testing began December 23, 2008, and was completed on January 6, 2009.

RESULTS/DISCUSSION

The performance study results consist of a presentation of the time history of the TCE release in the room and a detailed examination of the performance of the four passive diffusion devices. The time history of TCE was established by averaging the daily concentration from three triplicate samples (there were two days that only two data



Exhibit 2. Study layout showing the three stations, various passive diffusion devices and daily active measurement with pump (note the cords to the pumps and the tubes attached thereto)

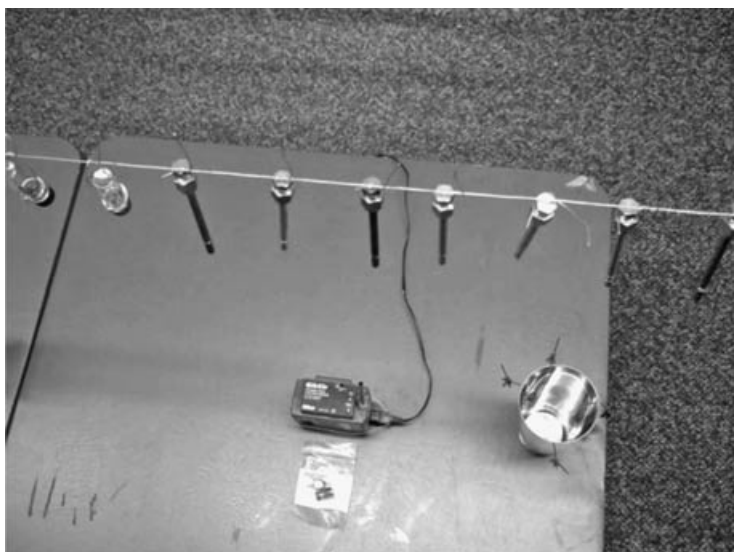


Exhibit 3. Overhead shot of sampling Station A. Note the active sampling pump with the cord and the passive devices both strung on the wire above the table and on the table itself right of the pump

points were used due to pump failure—days 9 and 11). There was minimal variability of TCE concentrations on a daily basis from the triplicate samples. Exhibit 4 is a plot of the daily average TCE concentration throughout the course of the experiment and shows there is a wide variability over the course of the sampling period. The first three days were an exponential growth (to Day 3), the next four days a flattening out followed by a quick drop (to Day 7), the next three days continuing a drop to very low levels (to Day 10), and the last four days another, much lower spike (to Day 14). Exhibit 5 is a semilogarithmic

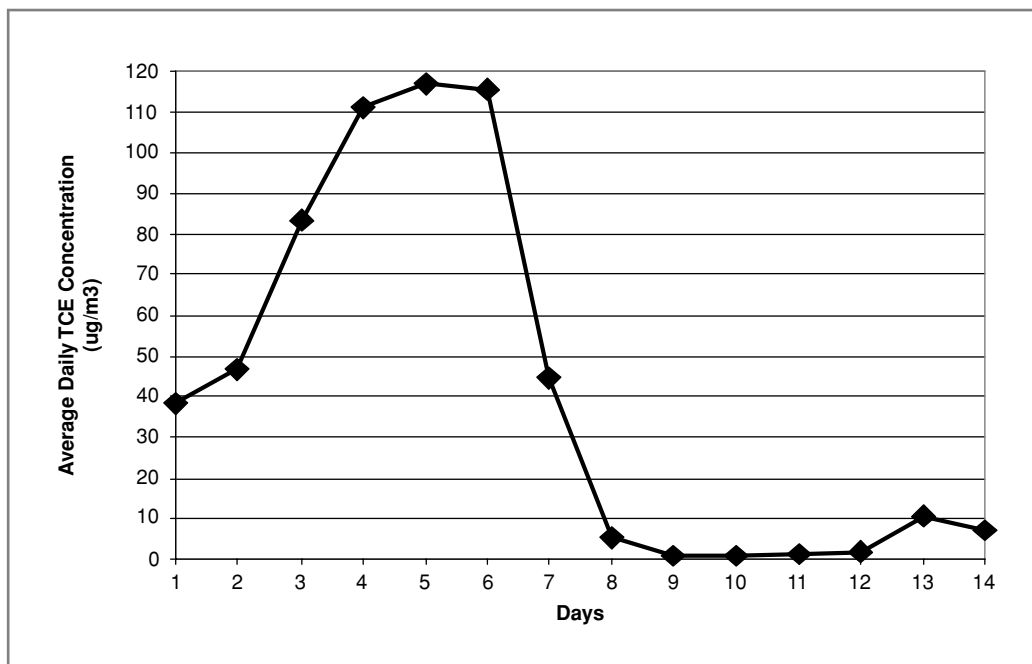


Exhibit 4. Linear plot of the indoor air TCE concentration history

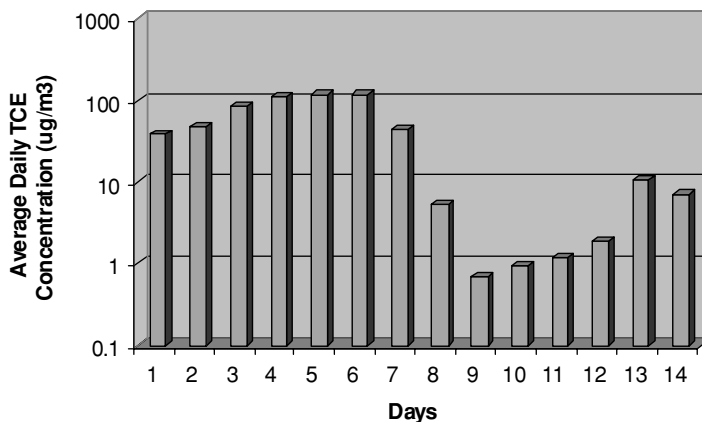


Exhibit 5. Semilogarithmic plot of the indoor air TCE concentration history

plot of the TCE concentration time history that allows a better examination of the lower-concentration dynamics.

A diffusive uptake rate is defined as the rate at which a diffusive sampler collects a particular gas or vapor from the atmosphere, expressed in nanograms per parts per million (volume/volume) per minute ($\text{ng.ppm}^{-1}(\text{V/V}) \text{min}^{-1}$), picograms per parts per billion (volume/volume) per minute ($\text{pg.ppb}^{-1}(\text{V/V}) \text{min}^{-1}$), or cubic centimeters per minute (cm^3/min) (ASTM, 2003). The different units of published uptake rates are rooted in the concentration being expressed either on a volume per volume basis or a mass per volume basis. An uptake rate allows for the determination of the average concentration as a function of exposure duration and the amount of mass of a particular compound sorbed

Exhibit 6. Summary of the uptake rates, standard deviation, and coefficient of variability

Type	Average Uptake Rate cm ³ /min	Standard Deviation cm ³ /min	Coefficient of Variation
PC	0.237	0.008	0.036
PT	0.148	0.044	0.300
BA	0.149	0.011	0.074
PR	2.024	0.543	0.268

onto the passive diffusion device in which an uptake rate was previously determined. Therefore, the establishment of an accurate uptake rate is key for determining a reliable average concentration for an exposure period. Many published uptake rates available in the literature were determined under controlled laboratory conditions, and the necessity for examining the variation in uptakes under a variety of real-world conditions is evident.

The calculated uptake rate for each device used in this study was established from the average of daily TO-17 values and the average mass from each of the passive diffusion devices at three, seven, ten, and fourteen days with the following relationship:

$$\text{Uptake Rate} = \text{Mass from Passive Device} \div \text{Average Concentration} * \text{Time}$$

$$\text{Units cm}^3/\text{min} = [\text{ng} \div (\mu\text{g}/\text{m}^3 * \text{min})] * 1,000$$

The uptake rates are fairly consistent over time even though the concentration variability on a daily basis was large. In order to evaluate the performance of each passive diffusion device, standard deviation and coefficient of variation (COV) were calculated from the established uptake rate at the four different exposure times for each device. The COV is defined as the standard deviation divided by the average uptake rate for each device.

The results of the performance study are presented in Exhibit 6. The TCE uptake rate for the PC configuration is approximately half of that reported in a previous laboratory study (ASTM D6196-03) for shorter-duration sampling and may be more representative of real-world conditions. The COV was lowest for the single sorbent tube (PC) and highest for the multiple sorbent tube (PT). The radial sorbent configuration (PR) had the highest uptake rate. The BeSure Axial Sampler (BA) uptake rate was nearly identical to PT (similar sorbent make-up); however, the BA coefficient of variation was four times lower. The average temperature throughout the performance evaluation period was 2.3°C, and the fluctuations in temperature accounted for less than 1 percent of the variability of the established uptake rates for each device.

The variability of the four calculated uptake rates for the three axial devices is shown in Exhibit 7. The plot clearly shows much more variability of the PT device (multiple sorbent tube) as compared to the multiple-sorbent BA device and the single-sorbent tube PC. A statistical guideline based on a COV of less than 0.10 allows reliable tracking of the magnitude and trends for all sampling periods (Bruno et al., 2008). The uptake rates for the PT and PR devices are deemed not reliable because the COVs were 0.300 and 0.258,

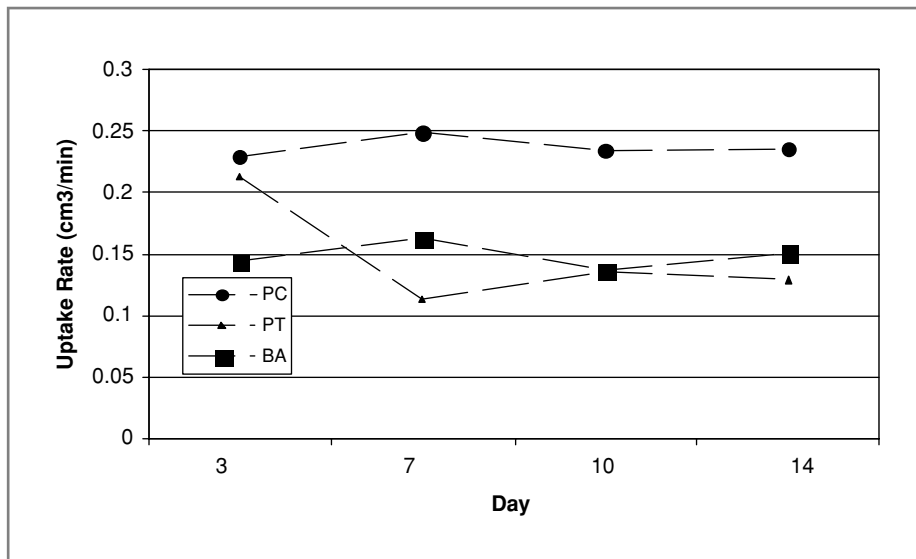


Exhibit 7. Time-varying, calculated uptake rates for the three axial devices

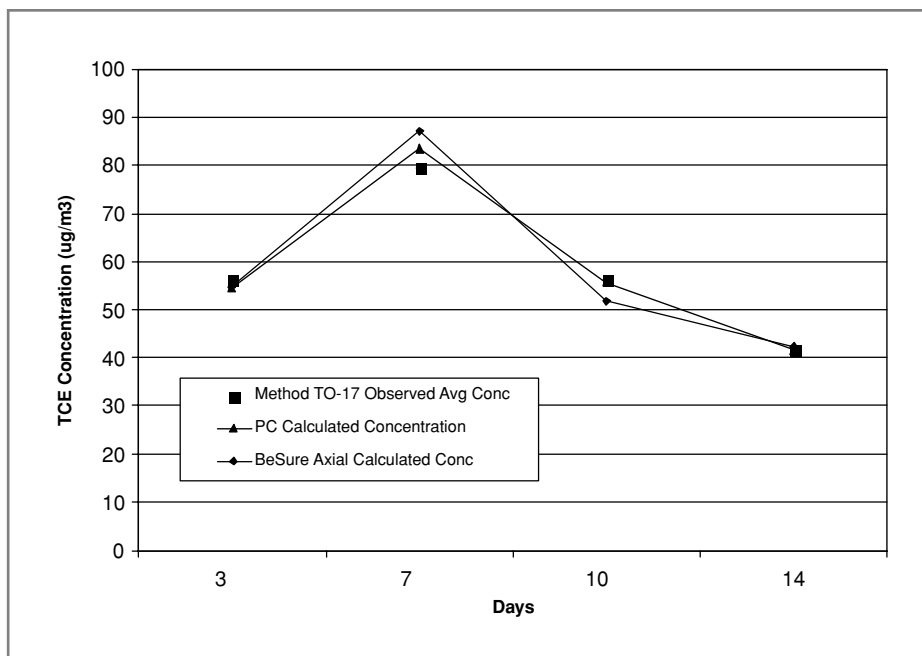


Exhibit 8. Projected concentration of TCE from the mass collected on the PC and BA passive devices compared to the measured average concentrations

respectively. However, the PC and BA passive diffusion device uptake rates are deemed reliable at COVs of 0.036 and 0.074, respectively.

In order to illustrate the reliability of the two passive diffusion devices that passed the performance study criterion, the calculated uptake rate, the average mass of TCE on each device, and the time the device was left in the room were used to calculate the time-weighted TCE concentration in the room. Exhibit 8 shows the observed average concentration for each of the four times plotted along with the calculated time-weighted

TCE concentration in the room for the PC and BA passive diffusion devices. The established uptake rates from the study described herein can be used reliably to provide an accurate concentration for three, seven, ten, and fourteen days. The results of the performance study demonstrate the passive PC (tube with Chromosorb 106) and BA (BeSure axial sampler) devices are a simple and cost-effective tool for characterizing VOC time-weighted concentration without the need for a pump.

CONCLUSIONS

The following is a summary of the research completed in the performance study and is not presented in any particular order of importance.

- A controlled release of TCE in an indoor air environment allowed for over two-orders-of-magnitude daily concentration variability over the course of the two-week monitoring event.
- The daily concentration measurements by US EPA Method TO-17 and the passive diffusion samplers were deployed in triplicate and had excellent reproducibility.
- The COV of the uptake rate was lowest for the single-sorbent tube (PC) and highest for the multiple-sorbent tube (PT). The radial sorbent configuration (PR) had the highest uptake rate. The BeSure Axial Sampler (BA) uptake rate was nearly identical to PT (similar sorbent make-up); however, the BA COV was four times lower at 0.074.
- The TCE uptake rate for the PC configuration is approximately half of that reported in a previous laboratory study (ASTM D6196-03) for shorter-duration sampling and may be more representative of real-world conditions.
- The performance of all the passive diffusion devices was analyzed in this study for large fluctuations of TCE concentrations. The average concentration for all of the exposure periods could be reliably predicted using the established uptake rates for the PC and BA devices and with no pump/active air flow/vacuum. The PT and PR devices' COVs were above 0.10 and did not produce reliable concentration estimates.
- The results of the performance study demonstrate the passive PC (tube with Chromosorb 106) and BA (BeSure axial sampler) devices are a simple and cost-effective tool for characterizing VOC time-weighted concentration without the need for a pump.

ACKNOWLEDGMENTS

We would like to thank Lee Marotta of PerkinElmer LAS, Shelton, Connecticut, for providing numerous tubes, caps, and associated materials for use in this study. We would also like to thank Elizabeth Woolfenden of Markes International Limited, Wales, United Kingdom, for supplying an abundance of useful reference material.

REFERENCES

- American Society for Testing and Materials (ASTM). (2003). Standard practice for selection of sorbents, sampling, and thermal desorption analysis procedures for volatile organic compounds in air. ASTM D6196-03. West Conshohocken, PA: ASTM International.

- Bruno, P., Caselli, M., de Gennaro, G., Iacobellis, S., & Tutino, M. (2008). Monitoring of volatile organic compounds in non-residential indoor environments. *Indoor Air*, 18, 250–256.
- Clarke, J. N., Goodwin, D., O'Neill, H., & Odencrantz, J. E. (2008). Application of passive soil gas technology to determine the source and extent of a PCE groundwater plume in an urban environment. *Remediation*, 18(4), 55–62.
- Health and Safety Executive. (1995). Methods for the determination of hazardous substances, Volatile organic compounds in air: Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography (MDHS80). Health and Safety Laboratory. Merseyside, UK: Author.
- International Organization for Standardization. (2003). Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography—Part 2: Diffusive sampling. ISO 16017-2. Geneva, Switzerland: Author.
- Kaj, L., Andersson, J., Cousins, A. P., Remberger, M., Brorstrom-Lunden, E., & Cato, I. I. (2005). Monitoring of volatile organic compounds in non-residential indoor environments—Subreport 4. Siloxanes. Stockholm: Swedish Environmental Research Institute.
- Odencrantz, J. E., & O'Neill, H. (2009). Passive to active tie-in for soil gas surveys: Improved technique for source-area, spatial variability, remediation-monitoring, and vapor-intrusion assessment. *Remediation*, 19(2), 71–83.
- Odencrantz, J. E., Steinmacher, S. J., O'Neill, H., Case, J. D., & Johnson, P. C. (2008). Residential vapor intrusion evaluation: Long-duration passive sampling vs. short-duration active sampling. *Remediation*, 18(4), 49–54.
- Statheropoulos, M., Agapiou, A., & Pallis, G. (2005). A study of volatile organic compounds evolved in urban waste disposal bins. *Atmospheric Environment*, 39, 4639–4645.
- The Diffusive Monitor. (2001, July). Retrieved July 9, 2009, from <http://www.hsl.gov.uk/pdfs/diffusive-monitor/issue12.pdf>

Joseph E. Odencrantz, PhD, P.E., is technical director and Western Region manager for Beacon Environmental Services (www.beacon-usa.com). He obtained his MS and PhD in civil and environmental engineering from the University of Illinois at Urbana-Champaign and his BS in civil engineering from the University of Maine at Orono. He has published extensively on fate and transport of organics, water supply, biodegradation processes, risk assessment, water reuse, regulatory policy, and treatment systems. Dr. Odencrantz has served internationally as a private consultant and expert in several countries.

Steven C. Thornley is laboratory director of Beacon Environmental Services. He received his BS in chemistry from Lock Haven University in Pennsylvania in 1992 and immediately began his career in the field of analytical chemistry. His growing concern over the abundance of solvent usage in environmental laboratories led to a pursuit of developing thermal desorption injection techniques in 1995. He has developed analytical methods for the Army Corps of Engineers and numerous private clients to target a broad range of compounds both organic and inorganic without the use of extraction solvents.

Harry O'Neill is the president of Beacon Environmental Services and has managed soil gas investigations for 18 years for the DOD, DOE, and commercial markets. He continues to be on the forefront of passive and active sorbent technologies at the national and international level and has implemented the technologies at thousands of sites. He received his BA from Loyola College in Maryland.
