Technical note

Evaluation of the particle infiltration efficiency of three passive samplers and the PS-1 active air sampler

Milos Z. Markovica, Sebastian Prokopa, b, Ralf M. Staeblera, John Liggioa, Tom Harnera, *

a Environment Canada, Air Quality Processes Research Section, Toronto, Ontario, Canada
b Department of Biological Sciences, University of Toronto at Scarborough, Toronto, Ontario, Canada

HIGHLIGHTS

• The particle infiltration efficiencies (PIEs) of 4 common air samplers were evaluated.
• Online spectrophotometer was used to measure PIEs for ambient 250–4140 nm particles.
• GAPS, Lancaster, and Hi-Vol acquired representative ambient particle samples.
• A low PIE of 54 ± 8.0% was determined for the MONET passive sampler.

ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form 20 April 2015
Accepted 22 April 2015
Available online 28 April 2015

Keywords:
Air sampling
Passive samplers
Particle infiltration efficiency
Particle sampling
PUF disk sampler
Sampler evaluation

ABSTRACT

The particle infiltration efficiencies (PIE) of three passive and one active air samplers were evaluated under field conditions. A wide-range particle spectrometer operating in the 250–4140 nm range was used to acquire highly temporally resolved particle-number and size distributions for the different samplers compared to ambient air. Overall, three of the four evaluated samplers were able to acquire a representative sample of ambient particles with PIEs of 91.5 ± 13.7% for the GAPS Network sampler, 103 ± 15.5% for the Lancaster University sampler, and 89.6 ± 13.4% for a conventional PS-1 high-volume active air sampler (Hi-Vol). Significantly (p = 0.05) lower PIE of 54 ± 8.0% was acquired for the passive sampler used under the MONET program. These findings inform the comparability and use of passive and active samplers for measuring particle-associated priority chemicals in air.

1. Introduction

Passive air samplers are widely used for studying persistent organic pollutants (POPs) in air (Bogdal et al., 2013; Harner et al., 2006; Pozo et al., 2009). The appeal of the samplers is that they are inexpensive, do not require electricity and are small enough to be transported and deployed almost anywhere. These samplers consist of a sampling chamber and a sorbing medium. The most commonly used passive sampler for studies of POPs is a double-dome stainless steel shelter housing a polyurethane foam (PUF) disk (Harner et al., 2004; Jaward et al., 2004; Shoeib and Harner, 2002). The chamber protects the sampler from precipitation, sunlight and dampens the wind-effect on the sampling rate (Petrich et al., 2013; Thomas et al., 2006; Tuduri et al., 2006). Several regional- and global-scale air monitoring programs employ the PUF disk sampler using slightly different chamber configurations. These include the Global Atmospheric Passive Sampling (GAPS) Network (Bogdal et al., 2013; Pozo et al., 2009, 2006), the MOnitoring NETwork (MONET) operated in Europe and Africa by RECETOX, Masaryk University (Bohlin et al., 2014; Klánová et al., 2008), and various regional international studies using the Lancaster University sampler design (LANCS) (Jaward et al., 2004; Li et al., 2011). Increasingly, data from these programs are being combined into larger data sets for model application and validation and for risk assessment and risk management. Therefore, comparability among the different passive sampler designs and their comparability with conventional high-volume active air samplers are of key importance (UNEP, 2011).

While originally targeting mainly gas-phase compounds, PUF disk passive air samplers are increasingly being applied to assess...
mixed-phase or entirely particle-associated chemicals e.g. polycyclic aromatic compounds (Harner et al., 2013), polychlorinated dibenzodioxins and furans (PCDD/Fs) (Cortés et al., 2014) and high molecular weight, halogenated flame retardants (Bohlin et al., 2014). A compilation of field-based calibration studies of the PUF disk samplers has shown that sampling rates are typically in the range $4 \pm 2 \text{m}^3\text{day}^{-1}$ for both gas- and particle-phase compounds (Harner et al., 2014). However, discrepancies do exist and there is some debate regarding particle sampling efficiencies of the different passive sampler designs relative to typical high volume samplers (Bohlin et al., 2014; Klánová et al., 2008). It has been speculated that the double-dome sampling chamber may discriminate against larger particles (relative to an active high-volume sampler such as PS-1), and that the manner in which the sampler is attached (i.e. fixed vs hanging) may also play a role (Bohlin et al., 2014; Klánová et al., 2008). Degrendele et al. (2014) have shown that most of the chemical burden (e.g. PAHs, PCDD/Fs) of the particle-phase is associated with the smaller particles (<1 μm) due to their larger total surface area for sorption.

In this work, we evaluate the ability of the different passive and active air samplers to acquire a representative ambient particle sample. This was accomplished by using an online particle spectrophotometer to measure the number concentration and size distributions of particles inside and outside of samplers, with high time resolution. The comparison of measured particle distributions will provide insight to the comparability of the passive and active samplers for measurements of particle-associated chemicals in air.

2. Methods

Three passive (GAPS network sampler (GAPS), Lancaster sampler (LANCS), and MOntoring NETwork (MONET) sampler) and one active PS-1 (Hi-Vol) offline samplers were evaluated at the Downsview field site (43.780°, -79.468°) located in the north part of the city of Toronto, Ontario, Canada, during November of 2014 (Fig. S1). The three passive samplers were installed onto a chain-linked fence ~1.5 m above ground, which is their standard sampling configuration (Fig. 1; see also Figs. S2 and S3). PUF disks were removed from the samplers to facilitate the characterization of the chambers, installation of the particle spectrometer sample inlet, and to prevent measurement bias from deposition of particles on PUF filters located inside of sampling domes just above the spectrometer sampling inlet (see below). One new hole was drilled in the middle of the bottom plate of each sampler to accommodate installation of a 2 inch long (0.25 inch OD) stainless steel tube through which the sampled air was extracted. Although all of the samplers contained several holes on the bottom plate, the new holes were drilled to ensure sampling from the middle of the sampler interior, where filters are located (when installed). The Hi-Vol sampler was placed onto a cart ~1 m above ground to provide sampling height similar to those of the three passive samplers (see Fig. S3). An existing hole on the side of the Hi-Vol was used to install sampling tubing to the interior ~6 inch from the sampling head that is located in the middle of the Hi-Vol’s sampling compartment. The Hi-Vol pump was turned on during the experiment, with a glass fiber filter installed in the sampling head generating a sampling rate of ~250 L min$^{-1}$. This is in the typical operating range for PS-1 samplers. The Miniature Wide Range Aerosol Spectrometer (Mini-WRAS, Model 1.371, Grimm Aerosol Technik GmbH & Co, Airing, Germany) was installed on a cart and placed directly below the three passive samplers and next to the Hi-Vol during sampling to minimize the length of sampling lines and potential particle losses from collisions with tubing walls. The inlet of the Mini-WRAS was connected to a Y-shaped fitting whose ends were each connected to a stainless steel ball valve. One of the valves was further connected to a stainless steel tee, from which connections were made to a HEPA filter (MODEL # 12144, Pall Life Sciences Corp., Port Washington, NY, USA) and the inside of a sampler. Similarly, the second valve was connected to a HEPA filter and the tubing leading to the area just outside of a sampler (generally < 12 inches away). Bypass HEPA filters were installed to split the total flow to the Mini-WRAS (~1.2 L min$^{-1}$) and reduce the sampling flow rate from a passive sampler to ~0.5 L min$^{-1}$ thus minimizing the impact on the “passivity” of the evaluated samplers. A compilation of field-based calibration studies of the passive samplers has shown that sampling rates for the PUF disk substrate are typically in the range $4 \pm 2 \text{m}^3\text{day}^{-1}$ (Harner et al., 2014). However, actual airflow rates through the chamber itself are more than an order of magnitude greater based on the previous assessments of inside versus outside wind speeds (Tuduri et al., 2006). Hence, the additional flow of 0.72 m$^3$ day$^{-1}$ due to Mini-WRAS sampling is expected to have a negligible impact on the particle infiltration efficiencies of the samplers. The HEPA filters were also used during the study for periodic “blank” measurements by the Mini-WRAS. The instrument
was calibrated by the manufacturer and certified three months prior to the study.

All tubing used in the experimental setup was made of stainless steel or conductive silicone to prevent particle losses from buildup of electrical charge during airflow. Particle number concentrations and size distributions, for particles with optical diameters in the 250 nm—4140 nm range, were acquired with the Mini-WRAS by alternating the sampling between channel 1 (Hi-Vol, inside of a sampler) and channel 2 (CH2, outside of a sampler/ambient atmosphere) by switching the two ball valves every 4 min. An airflow calibrator (Glibratror-2, Sensidyne LP, St. Petersburg, FL, USA) was used to measure the flows through both HEPA filters and each of the sampling lines leading to the inside and outside of a sampler. The measured flows were then used to correct the acquired number concentrations by accounting for the sample dilution caused by the use of the HEPA filters. Since the Mini-WRAS has a 1 min time resolution, the first measurement after each valve switch was removed (to eliminate sample transition biases) and the remaining three measurements were averaged. The number of acquired samples (N), each represented by the three measurement averages, inside and outside of each passive sampler, is given in Table 1. The agreement between the two data sets (from CH1 and CH2) for each sampler was evaluated using standard statistical parameters presented in Table 1. In this work, the particle infiltration efficiency (PIE) is defined as PIE = NMB - 100%, where NMB is normalized mean bias between particle number concentrations (measured across 17 size bins in 250—4140 nm optical size range) in ambient atmosphere and inside of each sampler undergoing evaluation. The overall uncertainty in the experimental method was calculated from uncertainties in airflow through the HEPA filter (~10%) each, uncertainty in airflow through the Mini-WRAS (5%), and spectrophotometer reproducibility (~3%) and found to be ~15%.

Supporting measurements of ambient wind speed, wind direction, and temperature were acquired with a 3D sonic anemometer (Model CSAT 3, Campbell Scientific Inc., Logan, Utah, USA). The instrument was co-located with the Mini-WRAS at ~1.25 m above ground (Fig. 1). The data were originally acquired with temporal resolution of 10 Hz and averaged to 1 min. One-minute averages were further averaged to the duration of each study and reported in Table S1.

3. Results and discussion

During the study, the measured particle number concentrations varied over 5 orders of magnitude and decreased exponentially with an increase in optical diameter as expected (Seinfeld and Pandis, 1996) (Fig. 2). The agreement between the particle number concentrations and size distributions measured inside and outside of the samplers was generally better for smaller (<2500 nm) particles except in the case of the MONET sampler where it was comparably poor for both fine and coarse particles. This could be a consequence of sampler design, or due to poor statistics (low abundance) for particles with larger (>2500 nm) diameters. The sampled number concentrations varied between the four offline samplers because they were evaluated on different sampling days (Nov. 5, 7, and 12) with different wind conditions. During all four studies, the wind direction was from the west-northwest, but wind speeds varied between 1.1 and 3.8 m s⁻¹ (Table S1). The particle population in air masses sampled during the study changed with time on the time scales that would not affect the measurement set-up and in particular the alternating nature of sampling (Fig. S4). A clear difference was observed between particle number concentrations measured inside and outside offline samplers over a sampling period of several hours.

The PS-1 Hi-Vol active air sampler performance evaluation produced a low normalized mean error (NME) of 10.4% (Table 1), suggesting that the sampler acquired representative ambient particle samples across all measured optical sizes that were within the experimental method uncertainty of ~15%. The particle number concentrations and size distributions measured inside of the Hi-Vol sampler, and in the ambient air (outside Hi-Vol) were highly correlated as indicated by the Pearson correlation coefficient of R² = 0.999. The linear regression analysis on the correlation plot of

![Fig. 2. Number size distribution of particles in the 250—4140 nm optical diameter range (in 17 size bins) inside and outside of the four commonly used offline samplers. The y-axis represents the number of particles measured per 1 L of sampled air on a logarithmic scale. The x-axis represents the averages of the optical size bins of measured particles on a logarithmic scale. The results for passive air samplers used by the GAPS Network (GAPS), Lancaster University (LANCS), and the Monitoring NETwork (MONET) program, and a conventional PS-1 high-volume (Hi-Vol) active air sampler are illustrated in blue, orange, red, and green respectively. The dashed lines represent the ambient particles measured outside and solid lines represent the ambient particles measured inside of the four offline samplers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
particle number concentrations and size distributions measured inside and outside of the sampler yielded a slope of \( m = 0.90 \). The particle infiltration efficiency for the Hi-Vol sample was calculated to be \( 89.6 \pm 13.4\% \).

For the GAPS passive sampler, the statistical evaluation of the data sets acquired inside and outside of the sampler led to a low NME of 8.84%. Such a low NME suggests that the GAPS sampler acquired number concentrations and size distributions of particles representative of the ambient levels. The Pearson correlation coefficient was \( R^2 = 0.999 \), suggesting that the correlation between the particle number concentrations and size distributions measured inside of the GAPS sampler and in the ambient air was high. The linear regression analysis produced a slope of 0.89, and the particle infiltration efficiency was calculated to be \( \text{PIE} = 91.5 \pm 13.7\% \).

The NME for the LANCs sampler was also within the uncertainty of the experimental method, at 2.93%. The positive NMB of 2.88% suggested that across all measured optical diameters, the number concentrations of particles were higher inside of the LANCs sampler by 2.88% relative to the ambient levels as shown in Fig. 2. This trend appeared to be mostly driven by particles of larger sizes (>500 nm). The increased deposition of larger particles was previously observed at higher wind speeds due to the increase in turbulence from the interaction of wind with passive sampler housing (Ott and Peters, 2008; Wagner and Leith, 2001). Although increased turbulence could have contributed to the observed LANCs results due to high average wind speed of 3.8 ± 0.6 m s\(^{-1}\) (Table S1), we believe that the discrepancy in particle number concentrations observed in this study for larger particles was more likely to be driven by the method biases and low number of large particles available for the statistical evaluation. The Pearson correlation coefficient was high at \( R^2 = 0.999 \), suggesting that the particle number concentrations and size distributions sampled by the LANCs passive sampler were highly correlated to the ambient values. The linear regression analysis slope from the correlation plot was calculated to be \( m = 1.0 \), and the particle infiltration efficiency was calculated to be \( 103 \pm 15.5\% \).

The MONET sampler exhibited reduced particle infiltration compared to the GAPS and LANCs samplers with the NME of 46.4%. Consequently, the low particle infiltration efficiency of \( \text{PIE} = 53.6 \pm 8.04\% \) suggested that only about one half of the number of ambient particles in the 250–4140 nm optical size range were successfully transported inside of the sampler dome. The high Pearson correlation coefficient of \( R^2 = 0.999 \) suggested that the particle number concentrations inside and outside of the MONET sampler were highly correlated. Hence, the MONET sampler design may be the reason behind such low infiltration across all particle sizes.

This claim is further supported by the horizontal wind speed measured during the MONET sampler evaluation. The wind speed was 2.2 times higher than during the GAPS evaluation and 1.6 times lower than during the LANCs evaluation, when the particle number and size distribution measured inside the GAPS and LANCs sampler domes was highly representative of the ambient particle population. Although it can affect the performance of a passive air sampler, the wind speed range observed during the studies was not sufficient to explain the inability of the MONET sampler to acquire a representative particle samples for all sampled size bins from ambient air.

It is important to distinguish PIs that we have assessed for the various passive sampling chamber designs and the PS-1 sampler housing with ‘particle sampling’ that involves the deposition of particles onto the PUF disk substrate (or filtration on the glass fiber filter in the case of the PS-1 sampler). In this study, the particle number and size distributions for the passive sampling chambers were carried out with the PUF disks removed. This was done intentionally to minimize additional variables that would have been introduced by the different PUF disk types, dimensions and their orientation/position within each chamber. So the PIE determined here represents the first and critical step of ‘particle sampling’, namely the introduction of particles into the sampling chambers.

In summary, the results of the evaluation of the four common offline air samplers indicate that the Hi-Vol, GAPS and LANCS samplers are capable of acquiring a representative air sample for ambient particles in the 250–4140 nm size range within the uncertainty of our experimental method of ~15%, with the calculated PIs of 89.6 ± 13.4%, 91.5 ± 13.7%, and 103 ± 15.5%, respectively. Such high and comparable PIs confirm the application of these samplers for studies of particle-associated chemicals. The particle infiltration efficiency of the MONET passive sampler was determined to be low (\( \text{PIE} = 53.6 \pm 8.04\% \)) compared to the other passive samplers. The low PIE for the MONET sampler may be due to the large interior volume of the sampling chamber relative to its air exchange capacity (Fig. S2). Further research is needed to better understand the sampler characteristics that determine PIE and its variability under different meteorological conditions.

Acknowledgments

The authors thank Ky Su and Jasmin Schuster from Environment Canada’s Air Quality Processes Research Section for their help and support during the study. Partial funding for this study was provided by the Chemicals Management Plan, the Clean Air Regulatory Agenda, and the UNEP Secretariat for the Stockholm Convention on POPs. We also thank Lancaster University and RECETOX for providing sampling chambers for the study.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.04.051.

References

Bogdal, C., Scheringer, M., Abad, E., Abalos, M., Van Bavel, B., Hagberg, J., Fiedler, H., 2013. Worldwide distribution of persistent organic pollutants in air, including results of air monitoring by passive air sampling in five continents. TrAC Trend. Anal. Chem. 46, 150–161.

Böhlin, P., Audy, O., Szkiliková, L., Kukučka, P., Pribylová, P., Prokeš, R., Vojta, S., Klánová, J., 2014. Outdoor passive air monitoring of semi volatile organic compounds (SVOCs): a critical evaluation of performance and limitations of polyurethane foam (PUF) disks. Environ. Sci. Process Impacts 16, 433–444.

Cortés, J., González, C.M., Morales, L., Abalos, M., Abad, E., Aristizábal, B.H., 2014. PCDD/PCDF and dl-PCB in the ambient air of a tropical Andean city: passive and active sampling measurements near industrial and vehicular pollution sources. Sci. Total Environ. 491–492, 67–74.

Degrendele, C., Okonski, K., Melymuk, L., Landlová, L., Kukučka, P., Čupr, P., Klánová, J., 2014. Size specific distribution of the atmospheric particulate PCDD/Fs, dl-PCBs and PAHs on a seasonal scale: Implications for cancer risks from inhalation. Atmos. Environ. 98, 410–416.

Harner, T., Bartlow, M., Holoubek, I., Klánová, J., Wania, F., Gioia, R., Moeckel, C., Sweetman, A.J., Jones, K.C., 2006. Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue. Environ. Pollut. 144, 361–364.

Harner, T., Mitrovic, M., Abhersen, L., Schuster, J., 2014. Characterization of PUF disk passive air samplers for new priority chemicals: a review. Organohalogen Compd. 76, 11–29.

Harner, T., Shoebib, M., Diamond, M., Stern, G., Rosenberg, B., 2004. Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. Environ. Sci. Technol. 38, 4474–4483.

Harner, T., Su, K., Genualdi, S., Karpowicz, J., Abhersen, L., Mihele, C., Schuster, J., Charland, J.-F., Narayan, J., 2013. Calibration and application of PUF disk passive air samplers for tracking polycyclic aromatic compounds (PAcs). Atmos. Environ. 75, 123–128.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., 2004. Passive air
sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. Environ. Sci. Technol. 38, 34–41.

Klánová, J., Eupr, P., Růžoutek, J., Harner, T., 2008. Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. Environ. Sci. Technol. 42, 550–555.

Li, X., Li, Y., Zhang, Q., Wang, P., Yang, H., Jiang, G., Wei, F., 2011. Evaluation of atmospheric sources of PCDD/Fs, PCBs and PBDEs around a steel industrial complex in northeast China using passive air samplers. Chemosphere 84, 957–963.

Ott, D.K., Peters, T.M., 2008. A shelter to protect a passive sampler for coarse particulate matter, PM10 – 2.5. Aerosol Sci. Technol. 42, 299–305.

Petrich, N.T., Spak, S.N., Carmichael, G.R., Hu, D., Martinez, A., Hornbuckle, K.C., 2013. Simulating and explaining passive air sampling rates for semivolatile compounds on polyurethane foam passive samplers. Environ. Sci. Technol. 47, 8591–8598.

Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS Study. Environ. Sci. Technol. 43, 796–803.

Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. Environ. Sci. Technol. 40, 4867–4873.

Seinfeld, J.H., Pandis, S.N., 1996. Atmospheric Chemistry and Physics. John Wiley & Sons, New York.

Shoeib, M., Harner, T., 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. Environ. Sci. Technol. 36, 4142–4151.

Thomas, J., Holsen, T.M., Dhaniyala, S., 2006. Computational fluid dynamic modeling of two passive samplers. Environ. Pollut. 144, 384–392.

Tuduri, L., Harner, T., Hung, H., 2006. Polyurethane foam (PUF) disks passive air samplers: wind effect on sampling rates. Environ. Pollut. 144, 377–383.

UNEP, 2011. Draft Revised Guidance on the Global Monitoring Plan for Persistent Organic Pollutants. Document UNEP/POPS/COP.5/INF/27; accessible at www.pops.int.

Wagner, J., Leith, D., 2001. Passive aerosol sampler. Part I: principle of operation. Aerosol Sci. Technol. 34, 186–192.